Perturbed angular correlation study of the magnetic phase transitions in the rare-earth cobalt Laves phases $RCo_2$

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The order and other properties of the magnetic phase transitions in the rare-earth ($R$)-cobalt Laves phases $RCo_2$ 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 RCo$_2$ 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 $\delta \approx (1 - T/T_C)^{\epsilon}$ with $\epsilon = -1.0(1)$.

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I. INTRODUCTION

The magnetic hyperfine field $B_{hf}$ 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 $RCo_2$ ($R$=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 $RCo_2$ 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 at the rare earths. Among the $R_xM_y$, the Laves phases $RCo_2$ 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 Schmitt4).

The interest in the $RCo_2$ 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 $B$ is discussed in terms of a Landau expansion of the free energy in powers of the magnetization $M$

$$F(M) = \frac{1}{2} a_1(T)M^2 + \frac{1}{4} a_3(T)M^4 + \frac{1}{6} a_5(T)M^6 \ldots - M \cdot B.$$ (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 fluctuations8 at higher temperatures.

It was soon realized that the band structure of YCo$_2$—with the same $C15$ lattice as $RCo_2$—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 magnetism came from the observation of spontaneous magnetic order of the $d$-electron system in the related $RCo_2$ compounds. The substitution of nonmagnetic Y by magnetic rare earth atoms leads to $3d$-$4f$ intersublattice ex-
change and the corresponding molecular field \( B_{\text{mol}} = \lambda_{fd} M_R \), where \( M_R \) is the \( R \) sublattice magnetization and \( \lambda_{fd} \) 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 sub-system 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 \( R = \text{Gd}, \text{Tb} \) (\( T_C \approx 392 \) K and 231 K, respectively) exhibit second-order transitions (SOT’s), those with \( R = \text{Dy}, \text{Ho}, \text{Er} \) (\( T_C \approx 138, 98, \) and 40 K, respectively) first-order transitions (FOT’s).

This change of order has been shown by Bloch et al.\(^5\) Shimizu,\(^7,16\) and Inoue and Shimizu\(^7,18\) to be related to the sign of the \( M^4 \) term in Eq. (1). Metamagnetic FOT’s in a paramagnetic compound \( (a_1>0,a_2>0,a_3<0) \) 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

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

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.\(^5\) 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 \( R = \text{Sm}, \text{Nd}, \text{and Pr} \) 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$_2$ (\( T_C \approx 97.9 \) K) and PrCo$_2$ (\( T_C \approx 39.9 \) 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.\(^5\) and Inoue and Shimizu\(^18\) is therefore considered to apply to the heavy RCo$_2$ only. Crystal field effects\(^5\) and the volume dependence of the expansion coefficients of the free energy\(^7\) 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 \( ^{111}\text{Cd} \) in RCo$_2$ comes from the Co sublattice. The measurement of the temperature dependence of the magnetic 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 \( ^{111}\text{Cd} \) (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 \( ^{111}\text{In}/^{111}\text{Cd} \) in
RCO$_2$ occupies the rare-earth site, while, e.g., in RAl$_2$ the same probe resides on the Al site.

II. EXPERIMENTAL DETAILS

A. Sample preparation and equipment

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. 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 $^{111}$In/$^{111}$Cd by diffusion (800°C, 12 h) of carrier-free $^{111}$In into the host lattices. PAC measurements were carried out with a standard four-detector BaF$_2$ setup in the temperature range 10 K < $T$ < 400 K. Temperatures $T$ < 290 K were obtained with a closed-cycle He refrigerator. The samples (diameter < 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 $\Delta T$ ≈ 0.1 K. For the case of GdCo$_2$ temperatures $T$ > 290 K were produced with an especially designed PAC furnace with a temperature stability $\Delta T$ ≈ 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 $\gamma$ rays of a $\gamma$-$\gamma$ 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).

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

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

The frequencies $\omega_n$ 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 $\omega_M = 2\pi \nu_M = g \mu_B B / h$ ($g$ represents the nuclear $g$ factor, $\mu_B$ the nuclear magneton).

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

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

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 $\delta$ on the angular correlation can be approximated by

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

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

$$G_{kk}(t) = \sum_i f_i G_{kk}^i(t). \quad (6)$$

$f_i$ (with $\Sigma f_i = 1$) is the relative intensity of the $i$th fraction.

III. MEASUREMENTS AND RESULTS

A. RCo$_2$ ($R=$ Gd, Tb, Sm)—compounds with second-order transitions

Figure 1 shows a series of PAC spectra of $^{111}$Cd:TbCo$_2$ 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 $\delta \approx 0.01$. The precession frequency $\nu_M$ 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 $T/T_C = 0.97$, 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 $\nu_M$ can be determined accurately to $\nu_M(T) \approx 0.2 \nu_M(0)$. After the disappearance of the magnetic oscillations, the PAC pattern consists of an initial,
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 $f_{\text{para}}$ describing probes in the paramagnetic phase, the other one with intensity $(1-f_{\text{para}})$ describing probes in the ferrimagnetic phase. The perturbation factor in the paramagnetic phase is $G_{\text{para}}^p(t)\approx 1$.

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 $\omega_f$ characterizes the strength of the fluctuating interaction and $\tau$ its correlation time. 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 $\nu_M$, the relative width $\delta$ 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 $\delta$ 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 $\delta\times(1-T/T_C)^{\varepsilon}$ 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 ($\delta$...
At $T/T_C > 0.97$, the spectra of both compounds show a critical increase of the relative linewidth $\delta$ 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 $\nu_M$ 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 $\nu_M(T) > 0.1 \nu_M(0)$, while in the case of TbCo$_2$ and SmCo$_2$, one has $\nu_M(T) > 0.2 \nu_M(0)$.

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

### B. $R$Co$_2$ ($R$ = 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 $R$Co$_2$ 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 SOTs, at $T<T_C$ ($T_C=137.6$ K for DyCo$_2$, see Sec. IV A) one observes the periodic modulation characteristic for the ferrimagnetic phase and at $T>T_C$ the — almost — un perturbed 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 SOTs — the coexistence of the ferrimagnetic and the paramagnetic phase in a small temperature interval and as at SOTs, 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

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**FIG. 2.** The relative width $\delta$ 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 $\delta \approx (1 - T/T_C)^{\varepsilon}$ with $\varepsilon = 1.0(1)$ to the data of TbCo$_2$.

**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 $\nu_M$ 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.
compounds. The continuous slight increase of the relative linewidth $\delta$ to temperatures $T > T_C$ 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)
component, but—as in DyCo₂—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 RCo₂ (R= Dy, Ho, Er, Nd, Pr) are shown in Fig. 9 as a function of temperature. Figure 9 also contains the paramagnetic fractions of RCo₂ with SOT’s (R= Gd, Tb, Sm).

No pronounced hysteresis was detected at the FOT’s of RCo₂. 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.

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 RCo₂ (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 during the measurement and/or a sample inhomogeneity producing a spread in the order temperature TC. 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 Γ₆ of the temperature distribution: ΔT≈Γ₆. In our experiments we have carefully monitored the sample temperature and established that Γ₆≤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 TC distribution I(Tₖ; Tₐ) (with Tₖ as most frequent order temperature). Depending on the underlying mechanism, both a symmetric or an asymmetric distribution I(Tₖ; Tₐ) is conceivable. The main features of the Tₖ distribution can be inferred from the resulting temperature dependence of the paramagnetic fraction

\[ f_{\text{para}}(T) = \int_0^T I(Tₖ; Tₐ) dTₖ. \]

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 Tₖ distribution with \( I(Tₖ−ΔTₖ)<I(Tₖ+ΔTₖ) \). For the numerical analysis of the measured trends of \( f_{\text{para}}(T) \) shown in Fig. 9 we have
TABLE I. The parameters $T_C$, $\Gamma_L$, $\Gamma_R$ of an asymmetric Lorentzian distribution of the order temperature in $RCo_2$ 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 $T_C$.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$T_C$(K)</th>
<th>$\Gamma_L$(K)</th>
<th>$\Gamma_R$(K)</th>
<th>$\Gamma_C$(K)</th>
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<tbody>
<tr>
<td>GdCo$_2$</td>
<td>392.0(2)</td>
<td>0.85(15)</td>
<td>0.9(2)</td>
<td>0.9(2)</td>
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<td>TbCo$_2$</td>
<td>231.4(1)</td>
<td>0.30(5)</td>
<td>2.2(4)</td>
<td>1.4(2)</td>
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<td>DyCo$_2$</td>
<td>137.6(1)</td>
<td>0.50(5)</td>
<td>2.9(2)</td>
<td>1.7(1)</td>
</tr>
<tr>
<td>HoCo$_2$</td>
<td>78.2(1)</td>
<td>0.6(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ErCo$_2$</td>
<td>34.1(1)</td>
<td>0.5(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SmCo$_2$</td>
<td>206.4(1)</td>
<td>0.2(1)</td>
<td>3.1(5)</td>
<td>1.7(3)</td>
</tr>
<tr>
<td>NdCo$_2$</td>
<td>97.9(1)</td>
<td>0.2(1)</td>
<td>3.8(4)</td>
<td>2.0(2)</td>
</tr>
<tr>
<td>PrCo$_2$</td>
<td>39.9(1)</td>
<td>0.5(1)</td>
<td>2.1(3)</td>
<td>1.3(2)</td>
</tr>
</tbody>
</table>

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 $T_C$, $\Gamma_L$, $\Gamma_R$, and $\Gamma_C=(\Gamma_L+\Gamma_R)/2$ obtained by least-squares fits of Eq. (7) to the data $f_{para}(T)$ 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 $f_{para}(T)$ 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 $RCo_2$. The critical behavior of the static magnetic hyperfine field $B_M$ and the corresponding magnetic hyperfine frequency $\nu_M$ close to a SOT with transition temperature $T_C$ can be expressed by the power law\footnote{E. W. Fischer, Phys. Rev. Lett. 47, 1728 (1981).}

$$\nu_M(T) = \nu_M(0)(1-T/T_C)^\beta.$$  

Assuming that the critical exponent $\beta$ 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 $T_C$, 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 $\Gamma_S$ and of the Curie temperature $I(T';T_C)$ with width $\Gamma_C$ 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 $\Gamma_C$ and $T_C$, one obtains for a SOT with $\nu_M(T)$ given by Eq. (8) and constant sample temperature $T$

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

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

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

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 $\beta$: \footnote{E. W. Fischer and D. S. Raab, J. Magn. Magn. Mater. 24, 87 (1981).}

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

If an asymmetric $T_C$ distribution with $\Gamma_L \neq \Gamma_R$ is assumed, $\Gamma_C$ 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 $\Gamma_S$ and the most frequent temperature $T$, one obtain the same relation as Eq. (11) with $\Gamma_S$ instead of $\Gamma_C$.

In Fig. 10 we have plotted the relative linewidth $\delta$ 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 $\ln \beta \Gamma_C/T_C$ 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 $\beta \Gamma_C/T_C$ caused by the instability of the sample temperature—estimated from $\Gamma_S \approx 0.1$ K, $T_C \approx 250$ K, and $\beta \approx 0.32$ to be $\beta \Gamma_S/T_C = 1.3 \times 10^{-4}$—is at least one order of magnitude smaller than the experimental values of $\beta \Gamma_C/T_C \approx 1-3 \times 10^{-5}$ derived from the experimental data in Fig. 10 so that the critical increase of the relative
linewidth towards the order temperature can be understood almost entirely as the result of a \( T_C \) distribution.

The widths \( \Gamma_C \) 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 \( G_{22}^{\text{theor}}(t) = \sum_r \Delta I(\nu_M) G_{22}(t, \nu_M) \) with the asymmetric frequency distribution \( I(\nu_M) \) [Eq. (9)] resulting from a \( T_C \) distribution (symmetric or asymmetric) for given sets of parameters \( \Gamma_C, \beta, T_C, T \). 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 (\( \Gamma_C/T_C \ll 0.01, t = 1 - T/T_C > 10^{-3} \)) the output parameters of the analysis (\( \Gamma_C, \beta \) and the slope \( b \) of the relation \( \ln b = a + b \ln(1 - T/T_C) \)) may differ as much as 10 percent from the assumed input parameters of the \( T_C \) distribution.

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 \( \nu_M \) 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 \( \nu_M \) 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 \( \Gamma_C \) of this distribution will require further systematic studies. The value of \( \Gamma_C \) 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 \( \Gamma_C \).

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 $v_M(T) \geq 0.2 \, v_M(0)$ which corresponds to a lower limit of the reduced temperature of $t = (1 - T/T_C) \geq 5 \times 10^{-3}$. The frequency limit in the case of GdCo$_2$ is a factor of 2 lower [$v_M(T) \geq 0.1 \, v_M(0)$] because the absolute width $\Gamma_C$ 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, $\Gamma_C/T_C$ (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 $t = (1 - T/T_C) \geq 10^{-3}$. 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. 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. A theory accounting for all these effects has not yet been established. In Fig. 4 we compare the experimental trend of $v_M(T)$ 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 $v_M(0)$ 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 $5 \times 10^{-2} \leq t \leq 10^{-3}$ the data are well described by $\ln v_M \approx \beta \ln t$. The values of the corresponding critical exponent $\beta$ 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 $\beta$ values in terms of the theories of static critical phenomena is not very meaningful.

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

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 ($1 - T/T_C$).

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 $RCo_2$ 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 $RCo_2$ have been reported by Ross and Crangle. 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 $RCo_2$ ($R=\text{Dy, Ho, Er}$) 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$^{43}$ 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 $RCo_2$ with FOT's ($R=\text{Dy, Ho, Er}$) was missing in the case of NdCo$_2$ (as in TbCo$_2$ where the transition is of second order) which is taken frequently 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 $RCo_2$ is accompanied by anisotropic distortions of the cubic C15 unit cell.$^{45}$ For the light $RCo_2$ 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 $RCo_2$ 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 $RCo_2$ ($R=\text{Gd, Tb, Sm}$) with SOT's.

The magnetic hyperfine field of $^{57}$Fe in NdCo$_2$ and Ho Co$_2$ 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 $RCo_2$ ($R=\text{Dy, Ho, Er, Nd and Pr}$) and frequency jump $\nu_M(T_C)$ at the FOT. Frequencies are in MHz.

<table>
<thead>
<tr>
<th>$RCo_2$</th>
<th>$T_C$ (K)</th>
<th>$\nu_M(0)$</th>
<th>$\nu_M(T_C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DyCo$_2$</td>
<td>137.6</td>
<td>42.72</td>
<td>29.5</td>
</tr>
<tr>
<td>HoCo$_2$</td>
<td>78.2</td>
<td>41.22</td>
<td>37.3</td>
</tr>
<tr>
<td>ErCo$_2$</td>
<td>34.1</td>
<td>40.20</td>
<td>39.3</td>
</tr>
<tr>
<td>NdCo$_2$</td>
<td>97.9</td>
<td>37.30</td>
<td>21.0</td>
</tr>
<tr>
<td>PrCo$_2$</td>
<td>39.9</td>
<td>29.44</td>
<td>26.3</td>
</tr>
</tbody>
</table>

The change of order in the heavy $RCo_2$ has been explained by Bloch et al.$^{5}$ 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 $RCo_2$ 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 $\nu_M(0)$ (extrapolated from 9 K) of the $RCo_2$ 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 $RCo_2$. 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 $RCo_2$ is mainly determined by the Co moment. In the case of the FOT compounds $RCo_2$ ($R=\text{Dy, Ho, Er}$,

FIG. 12. The discontinuous jump of the magnetic hyperfine frequency $\nu_M(T_C)$ of $^{111}$Cd at the FOT's of $RCo_2$, 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 $RCo_2$. 014409-11
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, at one $M=0$, the other one at $M=M_S \neq 0$. 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 $\text{RCO}_2$ the transition is driven by the $3d$-$4f$ exchange interaction and occurs—as explained by Cyrot and Lavagna—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 in terms of the Landau coefficients $a_1$:  

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

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. Assuming that for $\text{RCO}_2$ 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 $\text{RCO}_2$ 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 $\text{RCO}_2$ suggest a smaller magnitude of $a_3(0)$ in the light $\text{RCO}_2$, which might be a consequence of the larger lattice parameters and a stronger crystal field interaction.

1. Frauenfelder, H. and R. M. Steffen, in