The order of the magnetic phase transitions in RCo$_2$ (R = rare earth) intermetallic compounds

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Abstract.   It has been found experimentally that the order of the magnetic phase transitions in RCo$_2$ compounds (R standing for rare-earth metals) at T_c changes from second order for the light-rare-earth series up to TbCo$_2$ to first order for the heavier-rare-earth compounds DyCo$_2$, HoCo$_2$ and ErCo$_2$. On the basis of results of fixed-spin-moment band-structure calculations for the isostructural compound YCo$_2$ at different lattice constants, we propose an explanation for this behaviour. In contrast to the widely accepted Inoue–Shimizu theory for this class of compounds, our explanation also includes Pr, Nd which were thought to behave differently due to the influence of crystal-field effects. We show that an itinerant-electron metamagnetic transition in these compounds can occur only over a certain range of lattice constants and that the possibility of a first-order phase transition is connected to features of the electronic structure rather than to the magnitude of the transition temperature as conjectured earlier. The influence of the latter is only important if the transition takes place at elevated temperatures, where effects of spin fluctuations can suppress a first-order transition.

1. Introduction

At the beginning of the 1960s Wohlfarth and Rhodes [1] introduced the concept of itinerant-electron metamagnetism (IEM). From the very beginning YCo$_2$ (and also fcc Pd) was considered as a promising candidate for showing this phenomenon. YCo$_2$ is a strongly enhanced Pauli paramagnet and shows a pronounced maximum in the temperature dependence of the susceptibility $\chi(T)$ (for a recent investigation see [2]). Both the strongly enhanced susceptibility and the maximum in $\chi(T)$ indicate the possibility of an itinerant metamagnetic transition at a certain critical field [1]. After many years of experimental work undertaken by various groups in order to determine the critical field for YCo$_2$, Goto and co-workers [3] finally succeeded in measuring the IEM in YCo$_2$ (and LuCo$_2$) at a field of about 70 T. However, even before this direct experimental confirmation of the existence of an IEM in YCo$_2$ the IEM concept was successfully used to explain the magnetic properties of RCo$_2$ compounds, where R is a magnetic rare earth. While YCo$_2$ is a paramagnet, the cobalt sublattice becomes magnetic in the presence of magnetic rare earths substituted for Y in the cubic Laves phase structure RCo$_2$. On the basis of these results it became widely accepted that the molecular field created by the localized 4f moments causes the metamagnetic transition from paramagnetic to a magnetically ordered state of the cobalt sublattice [4].

Bloch and Lemaire [6] were the first to employ the so-called s–d model to describe the paramagnetic behaviour of the susceptibility of various RCo$_2$ compounds where localized

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moments of rare earths coexist with itinerant 3d moments of cobalt. Bloch *et al* [7] used this model to explain the mechanism of the magnetic phase transitions in RCo_2; in particular they explained why the order of the transition changes from second order for light-rare-earth compounds (including $TbCo_2$) to first order for (Dy, Ho, Er)Co_2. Inoue and Shimizu [8] later proposed a more refined version of this theory for the phase transition in RCo_2 (see below, section 1.3). Nevertheless, the explanation proposed in the latter two papers has an important restriction since it cannot be applied to $PrCo_2$, $NdCo_2$ and $SmCo_2$. This shortcoming was noticed by the authors [7, 8] and was attributed to the influence of crystal-field effects which should play a major role in these compounds. However, one should note that crystal-field effects play a role not only for the compounds with Pr, Nd and Sm but also, for example, in the case of $ErCo_2$ as neutron diffraction experiments show [9].

In the present paper we propose a different kind of explanation for the change of the order of the magnetic transition in RCo_2 over the full rare-earth series. To this end we give in the following subsections of this introduction a brief summary of the important experimental facts and the ideas which form the current background for their explanation. For a more detailed review of the present state of theory and experiment for RCo_2 compounds we refer the reader to the chapters written by Duc and Goto [4] and more recently by Duc and Brommer [5].

1.1. Itinerant-electron metamagnetism and properties of YCo_2

The theory of itinerant magnetism is usually formulated on the basis of an expansion of the magnetic free energy in a power series in the magnetization. This expansion follows from the fact that, by definition, in itinerant magnetic systems the band splitting is much smaller than the bandwidth and thus the free energy $F(M, T)$ can be written as [10]

$$F(M, T) = \frac{a_1(T)}{2}M^2 + \frac{a_3(T)}{4}M^4 + \frac{a_5(T)}{6}M^6 + \cdots - MH_x \qquad (1.1)$$

where M is the magnetization per unit volume and H_x is an external field. In the Stoner theory of itinerant magnetism the coefficients $a_i(T)$ are given by the density of states and its derivatives at the Fermi level. The first coefficient $a_1(T)$ determines the inverse of the exchange-enhanced susceptibility and represents the famous Stoner criterion for the appearance of ferromagnetism in the case $a_1(T) < 0$. In our analysis in section 2 we obtain the values of these coefficients at $T = 0$ directly from the results of fixed-spin-moment [11] (FSM) band-structure calculations. For the general expressions of the canonical theory (including also the s–d model which will be used below) we refer the reader to the review of Shimizu [10] on itinerant-electron magnetism.

The different magnetic states can now be described using the coefficients $a_i(T)$. Following the original Rhodes–Wohlfarth [1] formulation of itinerant metamagnetism one finds that the system always has an energy minimum at the non-magnetic state whenever $a_1 > 0$. If now $a_3(T)$ is negative, the system will show a first-order phase transition into a magnetic state with finite magnetic moment at some critical value of the external field H_x. The condition $a_3 < 0$ follows from the expansion of the free energy up to fourth order in the magnetization. Such a condition was also used by Bloch *et al* [7] and Inoue and Shimizu [8] for the explanation of the order of the phase transition in RCo_2 for the heavy rare earths R = Gd–Er.

For our purposes we will require a more stringent condition for the IEM as introduced by Shimizu [12]. He considered an expansion (equation (1.1)) of the free energy up to sixth order in the magnetization. In this case the first-order transition from the low-moment (or non-magnetic) state to the high-moment state (metamagnetic phase transition—MMPT) becomes

possible at a critical external field if the factor $a_1 a_5 / a_3^2$ satisfies the following relation:

$$\frac{3}{16} < \frac{a_1 a_5}{a_3^2} < \frac{9}{20} \qquad \text{for } a_3 < 0. \qquad (1.2)$$

If $a_1 a_5 / a_3^2 > 9/20$ the system is a simple paramagnet; if $a_1 a_5 / a_3^2 < 3/16$ the system has a stable magnetic minimum of the free energy at zero external field. The latter relation can be considered as a generalized Stoner criterion for the appearance of ferromagnetism in itinerant systems.

Given that $a_3 < 0$ it can be shown that the temperature dependence of the susceptibility $\chi(T)$ shows a maximum at a finite temperature (a detailed discussion of this behaviour is given in references [1] and [10]). Such a behaviour of $\chi(T)$ was found in YCo$_2$ [13] which exhibits a broad maximum at about 250 K. Many efforts have been made to predict the magnitude of the critical field of an IEM transition for this compound. Cyrot and Lavagna [14] calculated the electronic structure of non-magnetic YCo$_2$ using a tight-binding Hartree–Fock approach. To determine the critical field they applied a rigid-band model to the density of states and obtained $H_c = 100$ T. Shimizu [10] used experimental observations for the Curie temperatures of RCo$_2$ and got $H_c = 142$ T. Mohn and Schwarz [15] performed an *ab initio* FSM band-structure calculation and found a value similar to the latter one, namely $H_c = 144$ T. Before the experimental determination of the magnitude of the actual critical field for YCo$_2$ by Goto *et al* [3] who found roughly $H_c = 70$ T, Shimizu had concluded [12] that the actual knowledge obtained so far was not sufficient for one to predict the value of H_c with any degree of certainty. Nevertheless, Yamada and Shimizu [17] and Yamada [18], using a spin-fluctuation theory with freely varying parameters, fitted a value around 70 T.

The important results of the application of spin-fluctuation theory to the metamagnetic transition in YCo$_2$ led to the conclusion that spin-fluctuation effects at finite temperature can exclude the possibility of a first-order metamagnetic transition [15, 18]. This proposition has been confirmed experimentally for YCo$_2$ where the first-order transition becomes smeared out and is no longer observed at temperatures above 100 K [3]. From these results it becomes obvious that effects of spin fluctuations have to be taken into account when the phase transitions in GdCo$_2$ and TbCo$_2$ are discussed because of their comparably high transition temperatures.

1.2. Exchange interactions and magnetism in RCo$_2$ compounds

In RCo$_2$ compounds the local 4f moments of the rare earths coexist with the spontaneous Co magnetic moment. The moment on the cobalt sites ranges from 0.8 to 1.0 μ_B over the RCo$_2$ series [4] and is described as being induced by the molecular field exerted by the localized 4f moments. This latter conjecture is supported by the large number of measurements of induced moments of Co in Laves phase compounds of the type $(Y_{1-x}R_x)Co_2$. As a hypothesis it was assumed in these experiments that changing the concentration x tunes the molecular field acting on the Co sublattice [3, 19]. The critical concentration x for the onset of 3d magnetism has been determined for R = Er, Ho, Dy, Tb and Gd. Interpretations of these results have been based essentially on the assumption that the MMPT in RCo$_2$ occurs at a molecular field that is the same as the critical field (70 T) observed for YCo$_2$.

From these experiments the resulting mean-field exchange constants of the R–Co and R–R interactions have been determined. The values of R–Co exchange constants are found to be nearly constant for R = Gd–Er [19] which is in agreement with the determination of these values based on the expression given for the Curie temperature within the s–d model [6]. Surprisingly such data for R = Pr, Nd and Sm are not available in the literature, although it would be interesting to compare the magnitudes of the mean-field exchange constants

calculated from the values of the critical concentrations x for the cases of the light and heavy rare earths in the same way as was done in the above case in reference [19]. However, applications of the s–d model for Pr, Nd and Sm give higher values for the R–Co exchange constant which are again close to each other (see table 1 in [21]). The latter observation supports our conclusion that the mechanism of the formation of the Co moments should be different in the cases of $(Pr, Sm, Nd)Co_2$ and $(Tb–Er)Co_2$.

All RCo_2 compounds investigated form intermetallic compounds and crystallize in the C15-type cubic Laves phase structure ($MgCu_2$). The values of the ordering temperature, the values of the lattice constants and also the orders of the magnetic phase transitions for the RCo_2 compounds are collected from the literature [22] and are given in table 1.

Table 1. The ordering temperatures T_c, orders of the phase transition at T_c and lattice constants for RCo_2.

	T_c (K)	Order of PT	Lattice constant (Å)
$PrCo_2$	34	II	7.309
$NdCo_2$	98	II	7.298
$SmCo_2$	204	II	7.263
$GdCo_2$	398	II	7.258
$TbCo_2$	230	II	7.206
$DyCo_2$	135	I	7.188
$HoCo_2$	89	I	7.166
$ErCo_2$	30	I	7.154
$TmCo_2$	~ 4	II	7.135
YCo_2	—	MMPT	7.215

It should be noted that there are some discrepancies in the literature concerning the values of the ordering temperatures and lattice constants depending on the purity of the samples etc, which, however, do not exceed a few K and 0.005 Å, respectively [22]. In our investigation we rely on the lattice constants reported by Burzo [23]. Among the rare-earth compounds, $DyCo_2$, $HoCo_2$ and $ErCo_2$ show a first-order phase transition while all the others have a second-order one. The order can easily be seen from measurements of the resistivity [24] or the thermal expansion coefficient [25]. The ordering temperatures are found to be approximately proportional to the de Gennes factors of the rare earths [26].

Before going into the details of the s–d model one should also mention the attempt of Duc *et al* [27] who proposed that the mechanism responsible for the first-order transition is connected with the volume discontinuity at the transition point. In this approach, the order of the transition is assumed to result from the interplay between the magnetic and elastic energy. However, the inclusion of the elastic energy into the theory again does not explain why in the case of R = Dy, Ho, Er the transition is first order while it is second order otherwise, because the volume discontinuity itself in the former cases seems to be a consequence of the discontinuous phase transition rather than being a reason for it.

1.3. The order of the transition in RCo_2 according to Inoue–Shimizu theory

In order to describe the system in which itinerant electrons interact with localized magnetic moments, the so-called s–d model introduced by Vonsovskij [28] is widely used. For example, this model is an important tool in the theory of the Kondo effect [29] and the theory of transition metal alloys [30]. Bloch and Lemaire [6] fitted the high-temperature behaviour of the susceptibility of RCo_2 (for R = Tb–Er) using molecular-field expressions of the s–d model and later Stewart [31] extended this work to R = Sm, Pr, Nd.

The application of the s–d model to provide an explanation of the order of the phase transitions in RCo_2 is based on following assumptions [7]:

 (a) the structure of the 3d band is the same for all compounds RCo_2 (including YCo_2);
 (b) the molecular-field approximation is applied; rare-earth-ion moments have their free-ion values M_f and are coupled to the cobalt spin M_d via a term $I_{R-Co}M_f \cdot M_d$.

We use the symbols I_{R-Co} and I_{R-R} for molecular-field constants of the interactions between R–Co and R–R moments respectively, in such a way that M_f and M_d denote average moments per atom. For the original definitions of the molecular-field constants I see the relevant papers [6,7]. A thorough discussion of the physical origin of the magnetic interactions in RCo_2 can be found in [26, 31, 32].

Under these assumptions the free energy of the system is written as [10, 12]

$$F = F_d + F_f - I_{R-Co}M_f \cdot M_d \tag{1.3}$$

where F_d is magnetic free energy of the itinerant d subsystem as expressed by equation (1.1) and F_f is free energy of the localized 4f moments in an effective field $I_{R-Co}M_d + I_{R-R}M_f$, so the corresponding free energy reads

$$F_f = -k_B T \ln \left\{ \sinh \left[x \frac{(2J + 1)}{2J} \right] \Big/ \sinh \left[x \frac{1}{2J} \right] \right\} \tag{1.4}$$

with

$$x = g_J \mu_B J (I_{R-Co}M_d + I_{R-R}M_f)/(k_B T).$$

J is the total angular momentum quantum number of the free R ions and g_J is the respective Landé factor. Assuming that M is a suitable order parameter (see below) the expansion of the free energy (equation (1.3)) can be written as

$$F(M, T) = \frac{c_1(T)}{2} M^2 + \frac{c_3(T)}{4} M^4 + \frac{c_5(T)}{6} M^6 + \cdots . \tag{1.5}$$

Originally Bloch *et al* [7] expanded the total free energy (equation (1.3)) in a power series in $M = M_d$ and showed that the coefficient of M_d^4 can change sign from negative to positive with increasing temperature. To this end it is necessary for the susceptibility to have a maximum followed by a flat region such as has been found experimentally for YCo_2 (see section 1.1). The negativity of the coefficient c_3 at low temperature gives rise to the possibility of the first-order phase transition in RCo_2 in this temperature region following the Rhodes–Wohlfarth formulation of the MMPT. At higher temperature, starting from at around 200 K, the coefficient c_3 of M_d^4 becomes positive which permits a second-order transition only. Similar arguments were applied by Inoue and Shimizu [8] but using an expansion of the free energy (see equation (1.3)) in a power series in the total magnetization $M = M_d + M_f$ since they assumed that the proper thermodynamic variable of an s–d system (in the case given, a d–f system) is neither M_d nor M_f, but the total moment M.

In both cases, regardless of whether the magnetic moment M_d or the total moment $M = M_d + M_f$ is used as the order parameter, the coefficient c_3 in the expansion of the free energy in equation (1.5) consists of two contributions. One of them is proportional to a_3 (from the expansion of F_d (equation (1.1))) and the other one arises from the localized moments of the f electrons via the expansion of F_f and always has a positive sign. Using arguments from Stoner theory and the experimental susceptibility curve, Bloch *et al* [7] derived that in the case of YCo_2 the coefficient a_3 changes with temperature as $a_3(T) = a_3(0)[1 - (T/250 \text{ K})^2]$ with $a_3(0) < 0$. Taking the temperature dependence of $a_3(T)$ and adding the always positive contribution from the localized part means that c_3 has to change sign from negative to positive at a certain value of T less than 250 K.

From table 1 it can be seen that $ErCo_2$, $HoCo_2$, $DyCo_2$ do indeed have first-order transitions at low temperatures and $TbCo_2$, $GdCo_2$ have second-order ones at $T \gtrsim 200$ K. It is also seen that $PrCo_2$, $NdCo_2$ and $TmCo_2$ show second-order transitions although their transition temperatures are much less than 200 K (see figure 1). To account for this discrepancy Bloch *et al* [7] blamed this inconsistency of their theory on influences of crystal-field effects, which should be even larger for the light rare earths. In their work they devised a way in which crystal-field effects can be incorporated in their model, but they also point out the inevitable difficulties that arise since crystal-field effects are not large enough to be effective at very low transition temperatures.
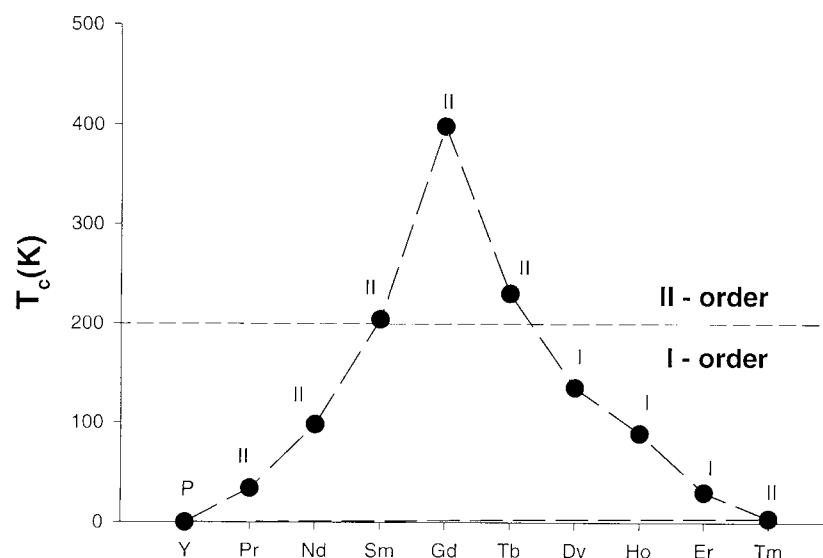

Figure 1. The ordering temperature and order of the phase transition in RCo_2 compounds. The dotted line is the critical temperature in the Inoue–Shimizu theory (see the text).

2. Magnetic properties of the d subsystem in RCo_2

In this section we show that there is a reason for the absence of the first-order phase transition in these compounds other than the crystal-field effects mentioned earlier. Taking RFe_2 as an example, Cyrot and Lavagna [14] clearly showed that if the d band of the transition metal is ferromagnetic at $T = 0$ K in RM_2 compounds, the transition to the magnetically ordered state is always of second order. If the magnetization curve of the d subsystem is s-shaped like for YCo_2 (equation (1.2) is satisfied), then, in order to decide whether a first-order transition is possible, the Inoue–Shimizu theory or Cyrot and Lavagna [14] arguments should be applied. Both of them lead to the same conclusions. We will show below that for YCo_2 at a lattice constant equal to those for light rare earths there is a stable magnetic minimum of the total-energy curve at $T = 0$ K. This means that the magnetic transitions in the light-rare-earth compounds RCo_2 should be treated in a similar way to those for RFe_2 rather than as for heavy-rare-earth RCo_2 compounds.

A further explanation will be essentially based on the following very simplified summary of the previous paragraph:

- The possibility of first-order phase transitions in RCo_2 compounds within the s–d model rests on the metastable magnetic properties of the d band of Co. If in the d subsystem the conditions for the IEM are not fulfilled at $T = 0$ K, the transition to the paramagnetic state is always of second order.

Moreover it has been shown that spin-fluctuation effects [15, 18] can also exclude the possibility of a first-order phase transition at elevated temperatures.

We base our investigation on the *ab initio* fixed-spin-moment calculations for YCo_2 at different lattice constants as performed by Mohn and Schwarz [15]. At fixed unit-cell volumes the total energy versus magnetic moment has been calculated within density functional theory using the augmented-spherical-wave method (ASW) [16]. The resulting total energies have been fitted to a polynomial as a function of the magnetization and the unit-cell volume. In table 2 we give the values of the calculated coefficients of the free-energy expansion as defined by equation (1.1).

Table 2. The calculated coefficients of the expansion (1.1) for YCo_2 at various lattice constants and $T = 0$. The resulting energies and magnetic moments are given in Ryd/atom and μ_B/atom respectively. An IEM is found when the condition $0.1875 < a_1 a_5 / a_3^2 < 0.45$ is fulfilled.

Lattice constant (Å)	a_1 (Ryd/μ_B^2)	a_3 (Ryd/μ_B^4)	a_5 (Ryd/μ_B^6)	$a_1 a_5 / a_3^2$
7.309 (PrCo₂)	0.0018085	−0.081794	0.21318	0.05763
7.298 (NdCo₂)	0.0023236	−0.081701	0.21242	0.07394
7.263 (SmCo₂)	0.0040114	−0.081519	0.21007	0.12681
7.258 (GdCo₂)	0.0042579	−0.081505	0.20974	0.13444
7.206 (TbCo₂)	0.0068830	−0.081446	0.20635	0.21412
7.188 (DyCo₂)	0.0078120	−0.081442	0.20519	0.24167
7.166 (HoCo₂)	0.0089568	−0.081428	0.20376	0.27525
7.154 (ErCo₂)	0.0095842	−0.081411	0.20298	0.29352
7.135 (TmCo₂)	0.0105804	−0.081364	0.20173	0.32241
7.215 (YCo₂)	0.0064218	−0.081449	0.20694	0.20032

Hathaway and Cullen [33] have utilized Mohn–Schwarz [15] results in order to estimate the values of the itinerant Co moments in the RCo_2 series and in $Y_{1-x}Gd_xCo_2$ alloys and they found good agreement with experiment. They demonstrated that FSM calculations for YCo_2 at lattice constants corresponding to those for RCo_2 yield a proper description of the magnetic moment values of the 3d subsystem in RCo_2 compounds. Nordström *et al* [32] have performed spin-polarized *ab initio* calculations for $GdCo_2$ where the 4f electrons were treated realistically and found a strong dependence of the values of the Co moments on the size of the lattice constants rather than a dependence on the state of the 4f shell of Gd. These results show that the magnetism in the Co subsystem is strongly governed by the unit-cell volume.

The calculated dependencies of the total energy versus magnetization in YCo_2 for lattice constants taken from table 1 are presented in figure 2. Regardless of the fact that for all lattice constants which correspond to light R = Pr–Gd the conventional Stoner criterion is not satisfied, there exists a stable magnetic minimum, meaning that the Co subsystem should be magnetic at $T = 0$ K even if no molecular field from the R ions is present. Starting from the case where the lattice constant is equal to the experimental one for YCo_2 and for the whole heavy RCo_2 series, the non-magnetic minimum is stable but magnetic states can be induced by an 'external field' which acts on the Co subsystem. Strictly speaking, the conditions formulated in equation (1.2) for itinerant-electron metamagnetism in the Co subsystem are fulfilled only in the case of RCo_2 for heavy R = Tb–Tm but not for the light ones, R = Pr–Gd. In the latter cases the d subband is magnetically split by the Stoner exchange interaction and the phase
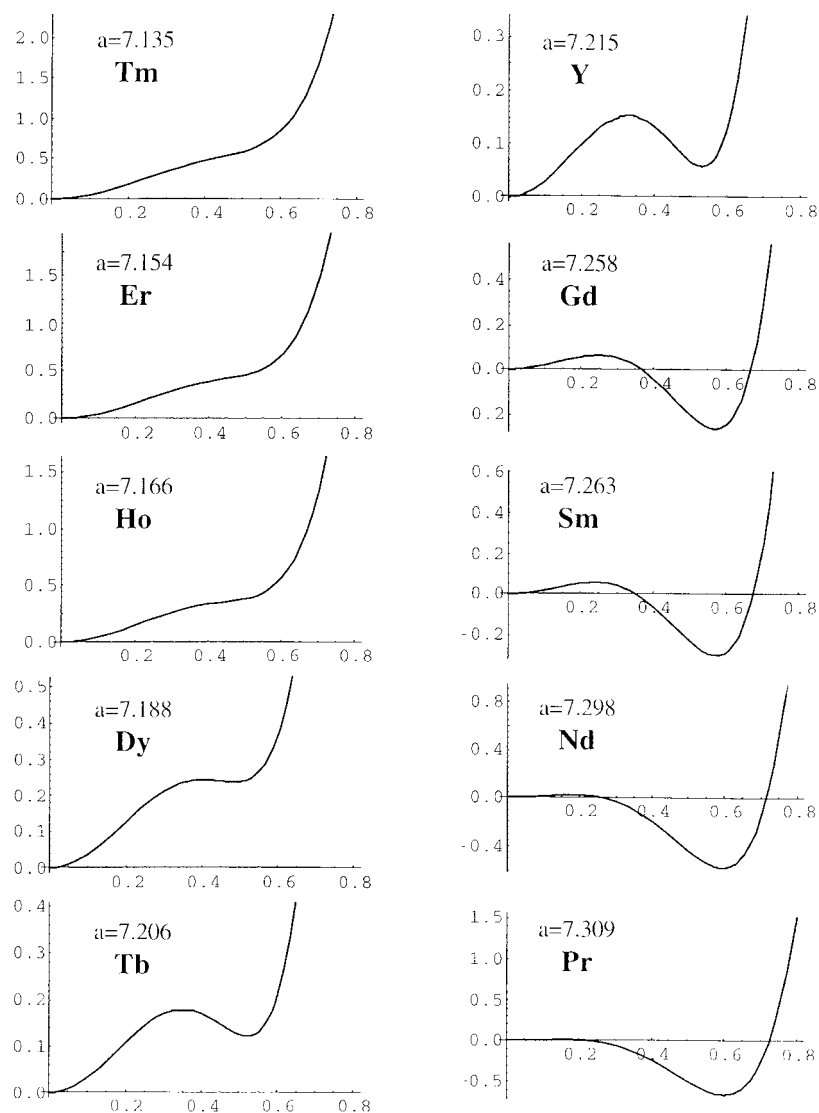
Figure 2. Total energy (in mRyd) versus magnetic moment per unit cell (in Bohr magnetons) of YCo_2 obtained from FSM calculation at different lattice constants. The lattice constants chosen correspond to those given for the RCo_2 compounds in table 1.

transition to the magnetically ordered state is continuous. In the former case the splitting of the d band is induced by the rare-earth-ion molecular field and the transition to the magnetically ordered state is of first order.

From our investigation we can formulate upper and lower limits for the lattice constant a_0 for which the conditions (equation (1.2)) for the IEM are satisfied: $7.05 \text{ Å} < a_0 < 7.22 \text{ Å}$. If $a_0 > 7.22 \text{ Å}$ the Co atoms in YCo_2 carry a magnetic moment; if $a_0 < 7.05 \text{ Å}$ YCo_2 is simply non-magnetic. It is satisfying to note that $LuCo_2$ with a completely filled f shell again shows an IEM [3] like YCo_2. This behaviour is to be expected, since the lattice constant of $LuCo_2$ (7.12 Å) lies well within the calculated range for the IEM given above.

From the results presented in figure 2 we conclude that the assumption of a rigid structure of the Co band (see section 1.3) throughout the RCo_2 series is not at all valid. The changes in the lattice constant drastically change the mechanism of the Co-moment formation at the ordering temperature between the heavy- and light-rare-earth-containing compounds. These changes (see figure 2) explain why in the light RCo_2 the magnetic phase transition is second order although the ordering temperature is low: a first-order phase transition in the light-rare-earth compounds $PrCo_2$, $NdCo_2$ and $SmCo_2$ is impossible because the IEM conditions are not fulfilled for the d subsystem and the Co atoms carry a magnetic moment caused by spontaneous polarization due to the exchange interaction within the Co d band. The second-order transition in these compounds is thus a consequence of the internal properties of the d subsystem rather than being caused by crystal-field effects on the rare-earth atom (see section 1.3).

We summarize our discussion in figure 3, where the dependence of the order of the phase transition on the lattice constant is presented. For the light rare earths with their large lattice constants, the Co subsystem is always spontaneously magnetic which leads to the observed second-order phase transition at T_c as expected for a ferromagnet. Below a critical lattice constant the IEM condition for the Co subsystem is met, so its magnetic ordering is induced by the 'external' field produced by the f shell of the rare earth. This change of the mechanism of magnetic ordering in the Co subsystem inevitably leads to the observed change of the order of the magnetic phase transition at T_c. From figure 2 it follows that in the case of $GdCo_2$ the first-order transition is impossible, but in the case of $TbCo_2$ the IEM condition for the d band is satisfied, so this compound should fall in the first-order class. However, due to the large ordering temperature of 230 K, collective excitations (spin fluctuations) can be expected to readily suppress the possibility of an IEM [15, 18] at this temperature, so $TbCo_2$ falls again into the second-order class. At low temperatures the metamagnetic character of the d subsystem in $TbCo_2$ has been confirmed experimentally by Levitin *et al* [34] and Franse *et al* [35]. They
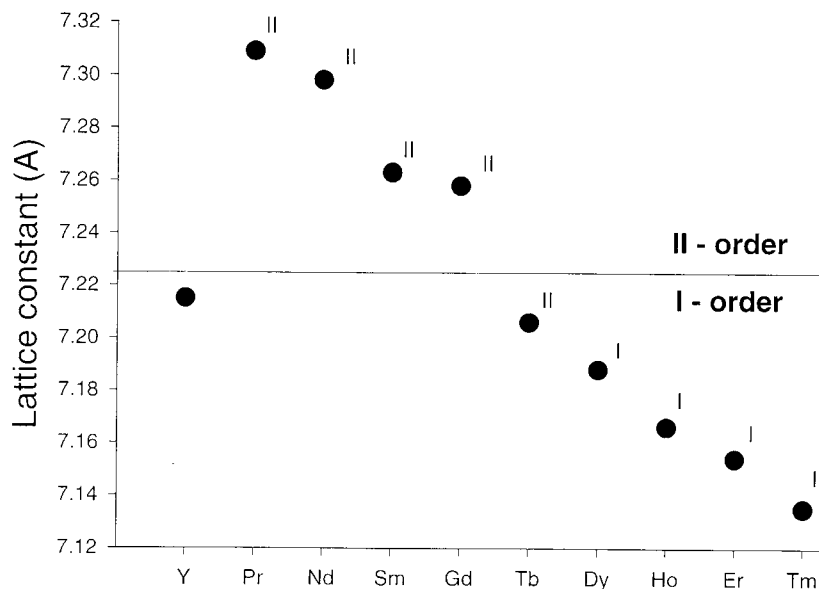

Figure 3. The value of the lattice constant and order of the phase transition in RCo_2 compounds. The full line represents the estimated critical value above which the condition for the MMPT (equation (1.2)) is no longer satisfied in the Co d band.

found that if the transition temperature is reduced by substitution of Tb for Y in $Tb_{1-x}Y_xCo_2$ compounds, the character of the phase transition can be changed from second towards first order. This is in contrast to the case for $Gd_{1-x}Y_xCo_2$, where such a change in the order of the transition has not been found [36]. This different behaviour is not surprising if one looks at figure 2: in contrast to the case for $TbCo_2$, for $GdCo_2$ the condition for the first-order transition is not satisfied at any temperature. For Y-rich $Gd_{1-x}Y_xCo_2$ the condition (equation (1.2)) will of course become satisfied for some large value of x; however, for such a low concentration of Gd the magnitude of the resulting molecular field of the local 4f moments is already insufficient to induce magnetism in the cobalt d subsystem.

The importance of the lattice constant dependence of the magnetic properties of the d subband was also noticed by Duc *et al* [20] when they analysed experimental data on (Nd, Dy)Co_2 and (Nd, Pr)Co_2 compounds. In order to explain the change in the order of the transition when substituting Dy or Pr for Nd, they introduced a critical lattice constant of 7.275 Å for which the coefficient $a_3(0)$ should change its sign. It should be noted that this value is not only larger than our estimate ($\sim$7.22 Å) but also does not allow one to explain the behaviour of $Gd_{1-x}Y_xCo_2$ and $Tb_{1-x}Y_xCo_2$ as discussed in the previous section.

Finally we have to give an explanation for the reappearance of the second-order phase transition in $TmCo_2$ (figure 3). Although it appears from its lattice constant that an IEM should be possible, experiment finds a normal second-order transition at a Curie temperature of only 4 K. The explanation for this unique behaviour lies in the shape of the $E(M)$ curve which becomes comparable to that for usual paramagnetic behaviour (see figure 2), so the molecular field produced by the 4f ions is too weak to cause the IEM necessary for a first-order transition.

3. Summary

Depending on the value of the lattice constant there are two different physical situations possible in RCo_2: (i) the lattice constant is larger than a certain critical value—in this case the d band of Co is magnetic without an application of an external field; (ii) the lattice constant is smaller than the critical value—in this case the d subsystem of Co is non-magnetic but an IEM transition to a magnetic state can be induced by an external field (the molecular field of the 4f ions).

What makes the Co sublattice a special case in these compounds is the fact that they do not form a simple itinerant magnetic system, but they exhibit a metamagnetic behaviour. In the case of an ordinary paramagnet it is obvious that on increasing the lattice constant the d band of Co becomes narrowed and at some critical value of the unit-cell volume magnetism should appear. Not obvious is the fact that, as we show in section 2, the critical value of the lattice constant is found in the middle of the RCo_2 series. Only this behaviour explains why in the light RCo_2 the transition to the magnetically ordered state is of second order and not of first order as would follow from the Inoue–Shimizu theory.

During recent years the properties of the RCo_2 compounds and their pseudo-ternary analogues have been investigated intensively, applying high pressures and fields (see e.g. [37], [38]). These experiments again showed that the magnetism of the d subsystem strongly depends on the volume of the unit cell. It has been demonstrated that at above a certain magnitude of the pressure the magnetism of the cobalt sublattice disappears for the cases of $ErCo_2$ and $HoCo_2$ (see [38]).

Over the last two decades more attention was paid to the heavy RCo_2 compounds than to the light ones. In particular, highly interesting experiments were performed recently in connection with the change of the order of the phase transition under high pressure [37] and alloying via substitutions for R or for Co (see [4]).

In those cases where the transition temperature is high, the arguments of Inoue–Shimizu theory or a spin-fluctuation analysis along the lines proposed by Yamada [18] often describe the observed trends correctly. In the cases with low transition temperatures (light RCo$_2$) the volume dependence of the magnetic ordering in the d sublattice plays the dominant role in the determination of the order of the phase transition. In view of this, high-pressure experiments on PrCo$_2$ and NdCo$_2$ are highly desirable—where the influence of finite-temperature effects on the structure of the d band is of minor importance at the ordering temperature, with the result that effects of the lattice contraction on the order of the phase transition should be clearly seen.

Acknowledgments

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