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# Magnetic states and magnetic transitions in RCo<sub>2</sub> Laves phases

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## Abstract

Magnetic states and the order of the magnetic transitions in RCo<sub>2</sub> cubic Laves phases with R = Gd–Tm have been studied by a first-principle density functional theory (DFT) calculation using a linear muffin tin orbital (LMTO) method. The total energy,  $E_t$ , and magnetic moments are calculated as a function of lattice constant,  $a$ . For R = Dy, Ho and Er,  $E_t(a)$  shows two minima at a smaller and a larger lattice volume, corresponding to a low and a high spin state of Co, respectively. Further, the fixed spin moment calculations indicate that the magnetic moment dependence of the total energy,  $E_t(M)$ , also exhibits two minima, corresponding to a low and a high spin state of Co at the calculated equilibrium lattice constant, respectively, for R = Dy, Ho and Er. The double minimum features of  $E_t(a)$  and  $E_t(M)$  are responsible for the first-order magnetic transition at  $T_C$  in RCo<sub>2</sub> with R = Dy, Ho and Er. On the other hand, for R = Gd and Tb, both  $E_t(a)$  and  $E_t(M)$  show a single minimum at a stable high spin state of Co. For TmCo<sub>2</sub>,  $E_t(a)$  shows a single minimum at a stable low spin state of Co, while the corresponding  $E_t(M)$  also has two minima corresponding to a low and a high spin state of Co. The results are also discussed using the Landau–Ginzburg theory by analysing the Landau expansion coefficients derived from the fixed spin-moment calculation results. The calculated lattice constant and magnetic moments are in good agreement with the experimental results and successfully explain the change in the order of the magnetic transition.

## 1. Introduction

The cubic Laves phases RCo<sub>2</sub> (where R = rare earth elements) have long been studied for their interesting magnetic properties, which arise from the coexistence and interaction of

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the magnetic moments of the highly localized 4f electrons of the rare earth elements and of the itinerant 3d electrons of the transition elements [1, 2]. In RCo<sub>2</sub> compounds, the Co 3d band states are ‘nearly magnetic’ and at the borderline of the onset of 3d magnetism. YCo<sub>2</sub> and LuCo<sub>2</sub> are nonmagnetic and the application of an external field of about 100 T can induce a discontinuous splitting of the majority and minority 3d subbands and result in the formation of a Co magnetic moment, i.e. an itinerant electron metamagnetic (IEM) transition [3]. A similar metamagnetic transition can be induced by the exchange field,  $H_{fd}^{Co}$ , due to the ferromagnetically ordered 4f magnetic moments in RCo<sub>2</sub> with R = Dy, Ho and Er at  $T_C$  and the magnetic phase transition is of the first-order type. The magnetic ordering of the Co sublattice can be eliminated by replacing Er by Y for  $x \geq 0.43$  in Er<sub>1-x</sub>Y<sub>x</sub>Co<sub>2</sub> or by exerting a pressure of  $P \geq 30$  kbar [4, 5]. On the other hand, SmCo<sub>2</sub>, GdCo<sub>2</sub> and TbCo<sub>2</sub> with larger lattice constants display second-order magnetic transition at  $T_C$  and their Co moments persist above  $T_C$ . In TmCo<sub>2</sub>, the molecular field does not exceed the critical value necessary to induce long-range magnetic order in the Co d-electron subsystem, in contrast to the other heavy RCo<sub>2</sub> compounds [6]. The results indicate that the magnetism of the Co sublattice strongly depends on the type of rare earth element and the lattice constant.

Recently, much more attention has been paid to RCo<sub>2</sub>-based alloys with R = Dy, Ho and Er, which show a large magnetocaloric effect (MCE) [7–9]. The large magnetocaloric effect is ascribed to the strong first-order magnetic transition at  $T_C$  and the field-induced itinerant electronic metamagnetic transition above  $T_C$ .

The order of the magnetic transitions in RCo<sub>2</sub> was first studied theoretically by Wohlfarth and Rhodes [10], Bloch *et al* [11] and Shimizu *et al* [12, 15] using the phenomenological Landau expansion of the free energy in powers of the magnetization,  $M$ :

$$F(M, T) = \frac{a_1(T)}{2}M^2 + \frac{a_3(T)}{4}M^4 + \frac{a_5(T)}{6}M^6 - \mu_0 H M. \quad (1)$$

The Landau coefficients  $a_i(T)$  could take either positive or negative values, depending on the density of states and their derivatives near the Fermi level. The first coefficient  $a_1(T)$  represents the Stoner criterion for the appearance of ferromagnetic order as  $a_1(T) < 0$ . In the case of  $\mu_0 H = 0$ ,  $a_1 > 0$ ,  $a_3 < 0$ ,  $a_5 > 0$  and  $a_1 a_5 / a_3^2 < 1/4$ , the magnetic free energy  $F(M)$  shows two minima at  $M = 0$  and a finite value of  $M = M_0$ . If the values for the two minima are very similar near  $T_C$ , a discontinuous change in  $M$  is expected at the ferromagnetic-to-paramagnetic transition, i.e. a first-order magnetic transition (FOMT) occurs at around  $T_C$ .

With increasing temperature,  $a_3$  will increase from negative to positive values. The temperature dependence of  $a_3$  is expressed in equation (2):

$$a_3(T) = a_3(0)[1 - (T/T_3)^2]; \quad a_3(0) < 0. \quad (2)$$

For RCo<sub>2</sub> with  $T_C < T_3$ , a FOMT will occur at  $T_C$ . Bloch *et al* [11] estimated  $T_3 = 250$  K from the temperature dependence of the paramagnetic susceptibility of YCo<sub>2</sub>. Inoue and Shimizu [15] got  $T_3 = 150$  K, according to the order of the magnetic transition and  $T_C$  for DyCo<sub>2</sub> and Gd<sub>1-x</sub>Y<sub>x</sub>Co<sub>2</sub> Laves phases. The model predicts that the magnetic transitions for R = Pr, Nd, Dy, Ho, and Er are of first order, while for R = Sm, Gd, and Tb the transitions are of second order.

However, the temperature dependence of spin fluctuation is much stronger than that of the Landau expansion coefficients. Spin fluctuation plays a more important role at finite temperature in itinerant electronic magnets. Yamada [13, 14] discussed the itinerant electron metamagnetism at finite temperature based on the Landau–Ginzburg theory by including the effect of the spin fluctuations. The magnetic free energy at zero external field is expressed in equation (3):

$$F(M, T) = \frac{A_1(T)}{2}M^2 + \frac{A_3(T)}{4}M^4 + \frac{A_5(T)}{6}M^6 \quad (3)$$

where

$$A_1(T) = a_1 + \frac{5}{3}a_3\xi(T)^2 + \frac{35}{9}a_5\xi(T)^4; \quad A_3(T) = a_3 + \frac{14}{3}a_5\xi(T)^2; \quad A_5(T) = a_5.$$

$\xi(T)^2$  is the mean square amplitude of spin fluctuation, which is a monotonically increasing function of  $T$ . The temperature dependence of the Landau coefficients  $a_1$ ,  $a_3$  and  $a_5$  is weak and could be neglected. Assuming that the zero-point spin fluctuation,  $\xi(0)^2$  is also ignored in the case of  $a_1 > 0$ ,  $a_3 < 0$ ,  $a_5 > 0$  and  $3/16 < a_1a_5/a_3^2 < 9/20$ , the paramagnetic state is stable at  $H = 0$  but the ferromagnetic state is formed at high magnetic field. As  $5/28 < a_1a_5/a_3^2 < 3/16$ , the ferromagnetic state is stable at low temperature and a first-order magnetic transition is expected at  $T_C$ . For  $a_1a_5/a_3^2 < 5/28$ , a second-order magnetic transition occurs.

The band structure calculations for the cubic RCo<sub>2</sub> with R = Gd–Yb were performed by Nordstrom *et al* [16], where the 4f electrons are treated as core states. The authors show that two self-consistent moments—with saturated and unsaturated Co moments—were obtained for R = Dy–Yb. Khmelevskiy *et al* [17] performed fixed spin-moment band structure calculations for the isostructural compound YCo<sub>2</sub> with the same lattice constants of RCo<sub>2</sub>. The effect of 4f-spin density on the splitting of 3d bands is ignored in the calculation. They ascribe the different order of the magnetic transitions to the different lattice constant of RCo<sub>2</sub> compounds. The authors show that the magnetic transitions of RCo<sub>2</sub> at  $T_C$  are of first order for R = Tb, Dy, Ho, Er, and Tm, while the magnetic transitions are of second order for R = Pr, Nd, Sm, and Gd. Diviš *et al* [18] calculated the electronic structure of RCo<sub>2</sub> with R = Y, Nd, Ho, and Er. The results indicate that the crucial factor driving the stability of the magnetism in RCo<sub>2</sub> is the induced spin splitting of the rare earth 5d states by the R 4f and Co 3d states.

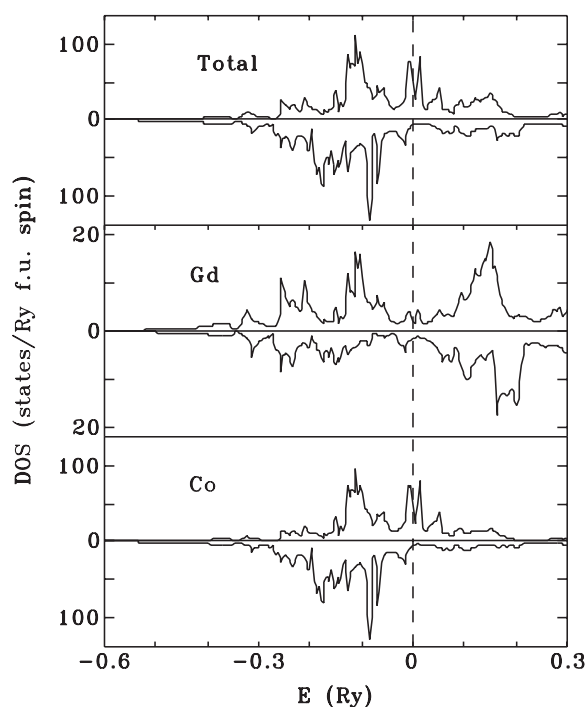
In order to clarify the nature of the magnetic ordering transitions in RCo<sub>2</sub> Laves phases, we have performed a first-principle density functional theory calculation using the linear muffin tin orbital method in these compounds. The calculations indicate that the total energy,  $E_t(a)$ , as a function of lattice constant, shows a double minimum feature for RCo<sub>2</sub> with R = Dy, Ho, and Er, which is responsible for the first-order magnetic transition at  $T_C$ .

## 2. Crystallographic aspects and computational details

The structure of RCo<sub>2</sub> is the cubic MgCu<sub>2</sub> type with the space group  $Fd\bar{3}m$ . The rare earth and Co atoms are positioned at (0, 0, 0) and (0.625, 0.625, 0.625), respectively. The small anisotropic lattice distortions are observed in some RCo<sub>2</sub> Laves phases at low temperature [19]. In the present calculations, all the compounds are treated as having the cubic MgCu<sub>2</sub>-type structure.

We performed first-principles electronic structure calculations in the framework of density functional theory (DFT) [20, 21]. The standard approximation to the DFT-like local spin density approximation (LSDA) or generalized gradient approximation (GGA) fails to describe the on-site Coulomb interaction and correlation between highly localized electrons such as 4f electrons in rare earth (RE) and RE-based compounds. One simple method is that the localized 4f orbitals are not contained in the valence basis set but are treated as part of the atomic-like core [22]. More complex methods include a LDA +  $U$  approach [23–25], a self-interaction corrected (SIC) LSDA scheme [22], and a dynamic mean field theory [26].

In our electronic structure calculations, we apply the linear muffin-tin orbital method (LMTO) with the atomic sphere approximation (ASA) using the Stuttgart LMTO-ASA 4.7 package [27–29]. Exchange and correlation effects are treated with LSDA parameterization given by von Barth and Hedin [30]. All relativistic effects are included, except the spin-orbit interaction, and the Kohn–Sham equations are used to obtain a self-consistent solution. The



**Figure 1.** Spin-projected total and partial density of states (DOS) for  $\text{GdCo}_2$  calculated at the experimental lattice constant ( $a = 7.258 \text{ \AA}$ ). The Fermi level is at  $E = 0$ .

4f states are treated as fractional core electrons and each rare earth atom has three electrons entering its valence bands. The number of 4f electrons is fixed to an integer, as in the infinite- $U$  limit of the Hubbard model, and the 4f moments are described by the well-known Russell–Saunders coupling. The approximation conforms to the fact that rare earth element often displays a  $\text{R}^{3+}$  state in RE-based compounds.

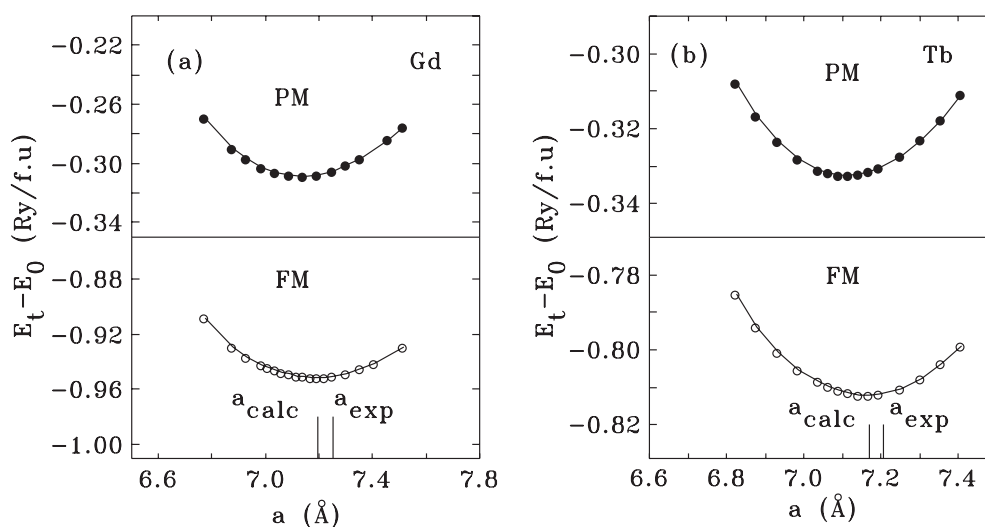
The self-consistent calculations are performed at 145 inequivalent  $k$ -points in the irreducible  $1/48$  Brillouin zone. The tetrahedron method of Brillouin zone integration is used for the calculation of the density of states (DOS).

The fixed spin-moment calculations have been performed in order to explore the possible stable and/or metastable magnetic states. In this scheme, the difference between the number of the spin up and spin down electrons are fixed during the self-consistent field calculation. As is well known, the magnetic moment of R is anti-parallel to that of Co in heavy rare earth  $\text{RCO}_2$  Laves phases. In the fixed moment calculations, the increase in the Co magnetic moment means a decrease in the moment per formula unit,  $M_{\text{f.u.}}$ .

### 3. Result and discussion

#### 3.1. Magnetic states in $\text{GdCo}_2$ and $\text{TbCo}_2$

Figure 1 shows the spin-projected total and partial density of states (DOS) for  $\text{GdCo}_2$  calculated at the experimental lattice constant. The vertical line indicates the position of the Fermi level. As stated above, 4f states are treated as core electrons. The 3d–5d hybridization dominates the band structure feature. There are no remarkable gaps in the total DOS curves. The s-states are



**Figure 2.** Variation in the total energies as a function of lattice constant for RCo<sub>2</sub>: (a) R = Gd,  $E_0 = -28\,095.5$  Ryd; and (b) R = Tb,  $E_0 = -28\,970.5$  Ryd. PM and FM denote the nonmagnetic and magnetic states, respectively.  $a_{\text{calc}}$  and  $a_{\text{exp}}$  are the calculated and experimental lattice constants, respectively.

at about  $-0.28$  Ryd, while the d-state peaks of Co and Gd atoms and p-state peaks of Co are at about  $-0.1$  Ryd. Comparing the local DOS of Gd and Co, it is clear that the DOS of Co contributes mostly to the total DOS near the Fermi level.

Figure 2 displays the total energy of GdCo<sub>2</sub> and TbCo<sub>2</sub> as a function of lattice constant under paramagnetic (PM) and magnetic (FM) states. As expected, the PM total energy is clearly higher than that of the FM state. The ground state is magnetically ordered. The lattice constant dependence of total energy,  $E_t(a)$ , shows a single minimum for R = Gd and Tb. The calculated equilibrium lattice constant,  $a_{\text{calc}}$ , is underestimated by about 1% in comparison with the experimental value,  $a_{\text{exp}}$ , due to the LSDA treatment of the exchange–correlation.

The calculated magnetic moments for GdCo<sub>2</sub> and TbCo<sub>2</sub> are shown in figure 3. As the lattice constant,  $a$ , is less than a critical value  $a_{\text{crit}}$ , the Co moment increases slowly with increasing  $a$ . However, when  $a$  is increased above  $a_{\text{crit}}$ , the Co magnetic moment jumps from about  $0.2$  to  $1.0 \mu_B$ . For  $a > a_{\text{crit}}$ , the Co moment again increases slightly with increasing  $a$ . The Co spin state changes from a low spin state to a high spin state at the critical lattice volume, indicating the onset of the d itinerant magnetic order. The lattice volume plays a very important role in the formation of the Co moment in RCo<sub>2</sub> compounds. The magnetic moments of Gd and Tb also show a step-wise increase (about  $0.1 \mu_B$ ) as  $a$  approaches  $a_{\text{crit}}$  due to the main contribution of 5d electrons. The magnetic moment per formula unit,  $M_{\text{f.u.}}$ , decreases with increasing  $a$  because of the antiferromagnetic coupling between the moments of the rare earth ion (Gd or Tb) and Co. The Co sublattice is at a stable ferromagnetic state with a moment of about  $1.0 \mu_B/\text{Co}$  at  $a_{\text{calc}}$  or  $a_{\text{exp}}$  for R = Gd and Tb.

In the fixed moment calculations, the total energy,  $E_t(M)$ , is calculated as a function of  $M_{\text{f.u.}}$ , at the calculated stable lattice constant,  $a_{\text{calc}}$ , in RCo<sub>2</sub> with R = Gd and Tb. As shown in figure 4, the total energy,  $E_t(M)$ , show a single minimum corresponding to a Co high spin state ( $1.0 \mu_B$ ). The lattice volume and magnetization dependence of total energies  $E_t(a)$  and  $E_t(M)$  indicate that there is only one stable magnetic state at a high spin state of Co in RCo<sub>2</sub> with R = Gd and Tb.

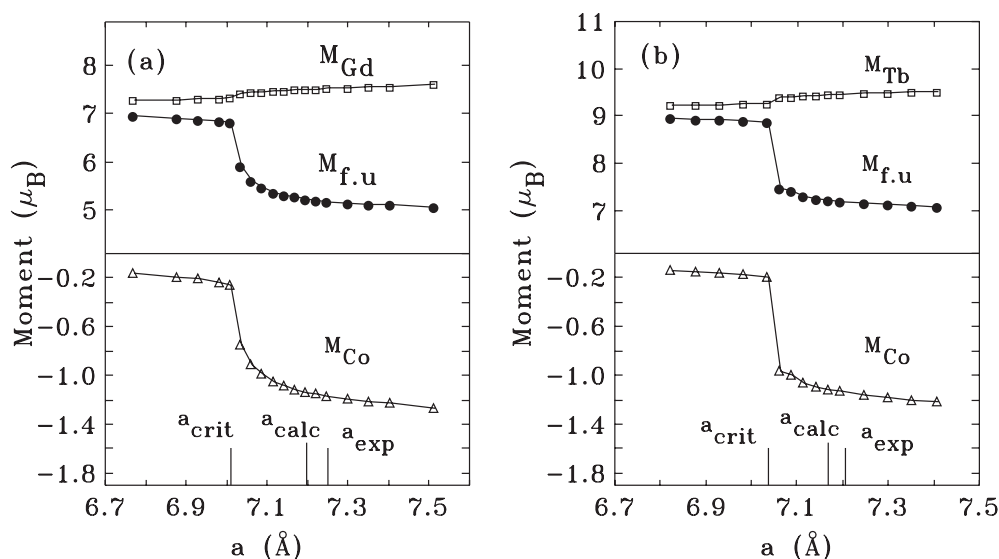


Figure 3. Calculated magnetic moments for GdCo<sub>2</sub> (a) and TbCo<sub>2</sub> (b).

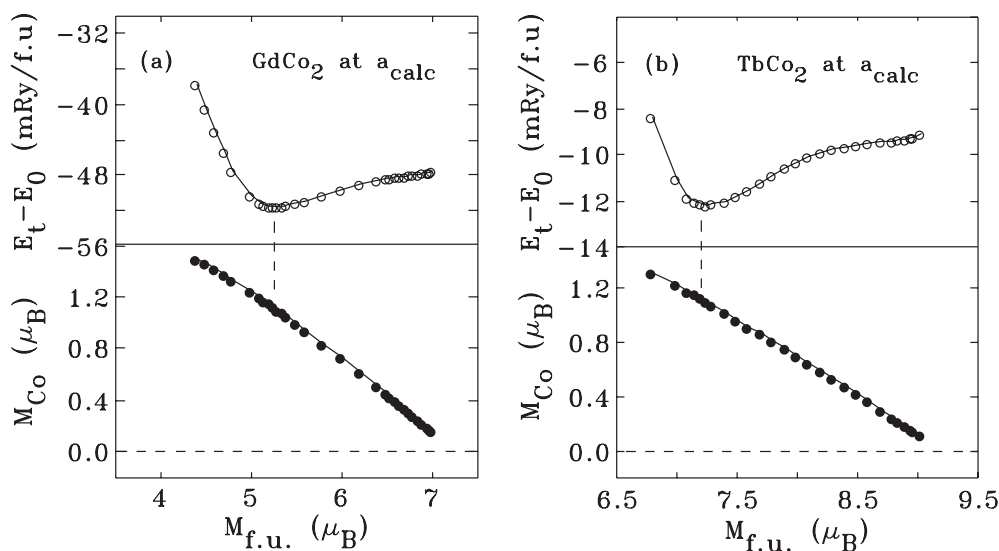
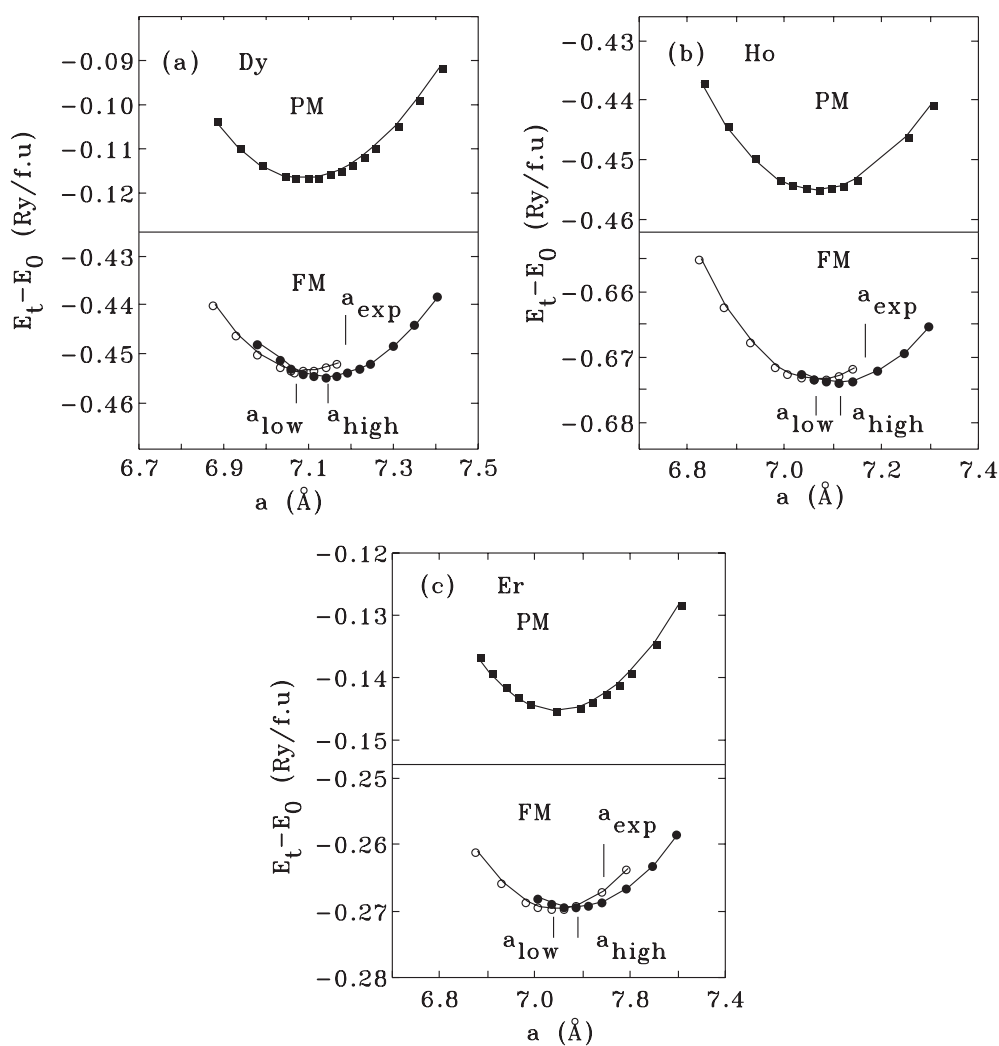


Figure 4. Variation in the total energy and the Co moment as a function of  $M_{\text{f.u.}}$  for RCo<sub>2</sub> at  $a_{\text{calc}}$ : (a) R = Gd,  $E_0 = -28096.4$  Ryd; (b) Tb,  $E_0 = -28971.3$  Ryd.

### 3.2. Magnetic states and magnetic transitions in RCo<sub>2</sub> with R = Dy, Ho, and Er

Figure 5 displays the total energy as a function of lattice constant for RCo<sub>2</sub> with R = Dy, Ho, and Er. The total energy for the PM state is clearly higher than that of the FM state for all the compounds. In contrast to GdCo<sub>2</sub> and TbCo<sub>2</sub> (figure 2),  $E_t(a)$  of the FM state shows a double minimum feature, indicating two stable or metastable magnetic states, depending on the lattice volume.

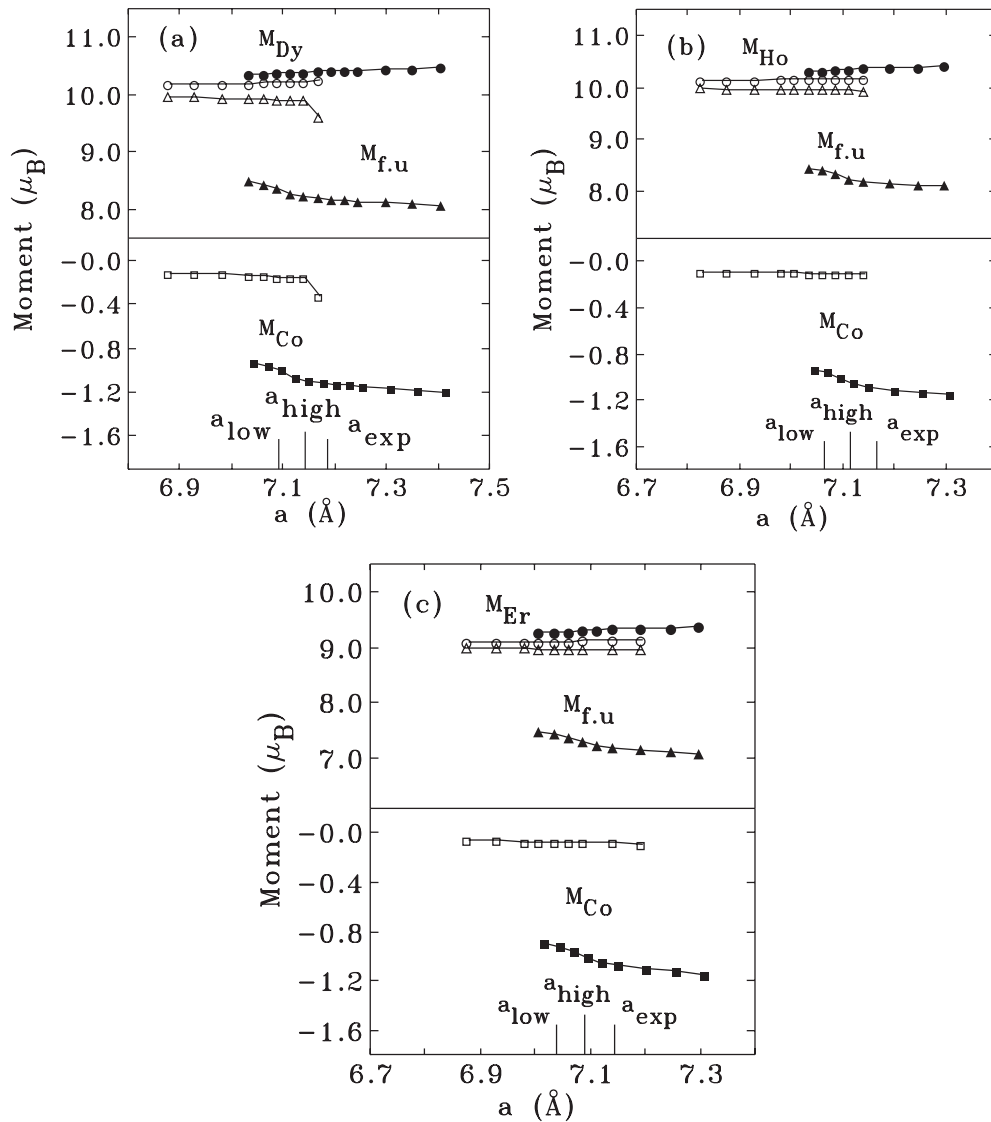


**Figure 5.** Variation in the total energy as a function of lattice constant for RCo<sub>2</sub>: (a) R = Dy,  $E_0 = -29867$  Ryd; (b) Ho,  $E_0 = -30784.5$  Ryd; (c) Er,  $E_0 = -31724.5$  Ryd. PM and FM denote the nonmagnetic and magnetic states, respectively.  $a_{\text{exp}}$  is the experimental lattice constant, while  $a_{\text{low}}$  and  $a_{\text{high}}$  are the calculated values at the low and high Co spin states (LSDA), respectively.

Figure 6 shows the variation in the magnetic moment as a function of lattice constant for these three compounds. Compared with figure 4, there is a high Co moment state ( $M_{\text{Co}} = 1.0 \mu_{\text{B}}$ ) at a lattice constant of  $a_{\text{high}}$  and a low Co moment state ( $M_{\text{Co}} = 0.1 \mu_{\text{B}}$ ) at  $a_{\text{low}}$ , corresponding to the two energy minima, respectively. For R = Dy and Ho, the Co high spin state is a stable state, while the Co low spin state is a metastable state. However, for ErCo<sub>2</sub>, the Co high spin and low spin states are metastable and stable states, respectively. All the calculated lattice constants and Co magnetic moments are also listed in table 1.

In the fixed spin-moment scheme, the total energy,  $E_t(M)$ , is calculated as a function of  $M_{\text{f.u.}}$ , at the calculated lattice constants  $a_{\text{high}}$  and  $a_{\text{low}}$ , respectively. As displayed in figure 7(a),  $E_t(M)$  for DyCo<sub>2</sub> shows two minima, corresponding to a high spin and a low spin state of

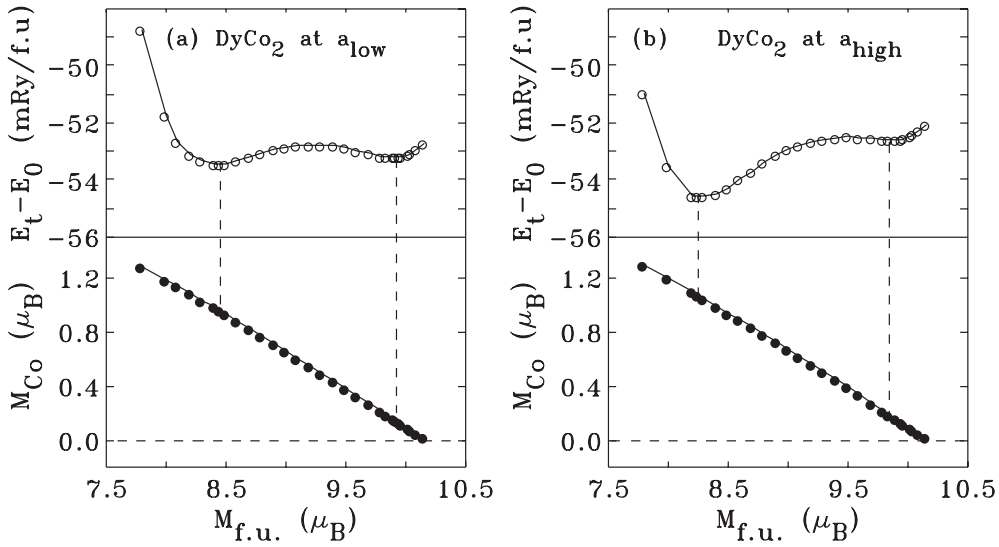




**Figure 6.** Calculated magnetic moments for  $R\text{Co}_2$  with  $R = \text{Dy}$  (a),  $\text{Ho}$  (b) and  $\text{Er}$  (c). The open and solid symbols correspond to the low and high spin Co states, respectively.

Co at the calculated lattice constant  $a_{\text{low}}$ . The minimum of  $E_t(M)$  at the low spin state of Co is slightly lower than that at the high spin state of Co by about 0.2 mRyd for  $\text{DyCo}_2$  at  $a_{\text{low}}$ , which means that the magnetic states are easy to change from one to the other and are not stable.  $E_t(M)$  for  $\text{DyCo}_2$  also shows two minima at  $a_{\text{high}}$  (figure 7(b)). However, the minimum of  $E_t(M)$  at the high spin state is clearly lower than that at the low spin state of Co by about 2 mRyd, indicating that the high spin state is stable. The results are in agreement with the fact that the magnetic state is stable at  $a_{\text{high}}$ , while it is metastable at  $a_{\text{low}}$  in  $\text{DyCo}_2$ . Very similar results are observed in  $\text{HoCo}_2$  (figure 8).

Figure 9 displays the total energies  $E_t(M)$  at the calculated lattice constants  $a_{\text{high}}$  and  $a_{\text{low}}$  in  $\text{ErCo}_2$ . Both  $E_t(M)$  s show a double minimum feature. The two minima of  $E_t(M)$  at  $a_{\text{high}}$



**Figure 7.** Variation in the total energy and the Co moment as a function of  $M_{\text{f.u.}}$  for DyCo<sub>2</sub> at  $a_{\text{low}}$  (a) and  $a_{\text{high}}$  (b);  $E_0 = -29867.4$  Ryd.

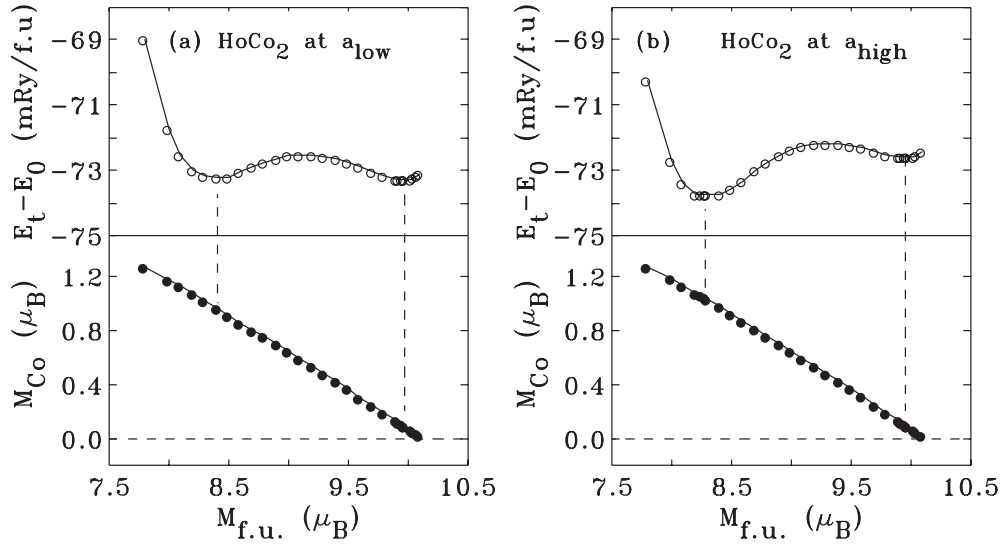
**Table 1.** The calculated and experimental lattice constants and magnetic moments for RCo<sub>2</sub> Laves phases.

R	$a_{\text{calc}}$ (Å)	$a_{\text{exp}}$ (Å)	$M_{\text{exp}}^{\text{Co}}$ ( $\mu_B$ )	$M_{\text{calc}}^{\text{Co}}$ ( $\mu_B$ )	$M_{\text{nom}}^{\text{Co}}$ ( $\mu_B$ )
Gd	7.197	7.258	1.00	1.14	0.90
Tb	7.171	7.206	0.88	1.12	0.89
Dy	7.144	7.188	0.82	1.09	0.89
Dy* <sup>a</sup>	7.070			0.15	0.05
Ho	7.118	7.166	0.78	1.06	0.88
Ho*	7.065			0.10	0.02
Er	7.038	7.154	0.72	0.07	0.02
Er*	7.091			1.00	0.85
Tm	7.017	7.135	0.1	0.05	0.04

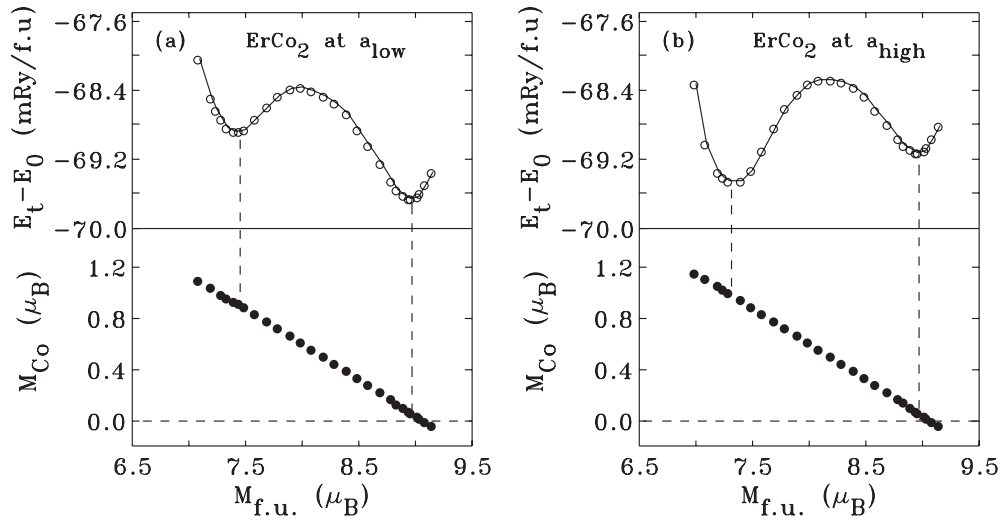
<sup>a</sup> Metastable state.

correspond to a stable high spin state of Co and a metastable low spin state of Co, respectively. On the other hand, the two minima of  $E_t(M)$  at  $a_{\text{low}}$  correspond to a metastable high spin state of Co and a stable low spin state of Co, respectively. In contrast to the situation with R = Dy and Ho, the minimum of  $E_t(M)$  at the high spin state is slightly lower than that at the low spin state by about 0.3 mRyd for ErCo<sub>2</sub> at  $a_{\text{high}}$ , while the minimum of  $E_t(M)$  at the low spin state is lower than that at the high spin state by about 0.8 mRyd for ErCo<sub>2</sub> at  $a_{\text{low}}$ , indicating that the low spin state is stable.

Based on the above calculations, the first-order magnetic transition can be explained as follows: during the cooling process, the magnetic state of the Co sublattice changes from a paramagnetic state to a low spin ferromagnetic state, but immediately the Co moment jumps from the low spin state ( $M_{\text{Co}} = 0.1 \mu_B$ ) to the high spin state ( $M_{\text{Co}} = 1.0 \mu_B$ ) accompanying the unit cell expansion. During the warming process, the magnetic state of Co jumps from the metastable high spin state ( $M_{\text{Co}} = 1.0 \mu_B$ ) to the low spin state ( $M_{\text{Co}} = 0.1 \mu_B$ ) and the



**Figure 8.** Variation in the total energy and the Co moment as a function of  $M_{\text{f.u.}}$  for  $\text{HoCo}_2$  at  $a_{\text{low}}$  (a) and  $a_{\text{high}}$  (b);  $E_0 = -30785.1$  Ryd.

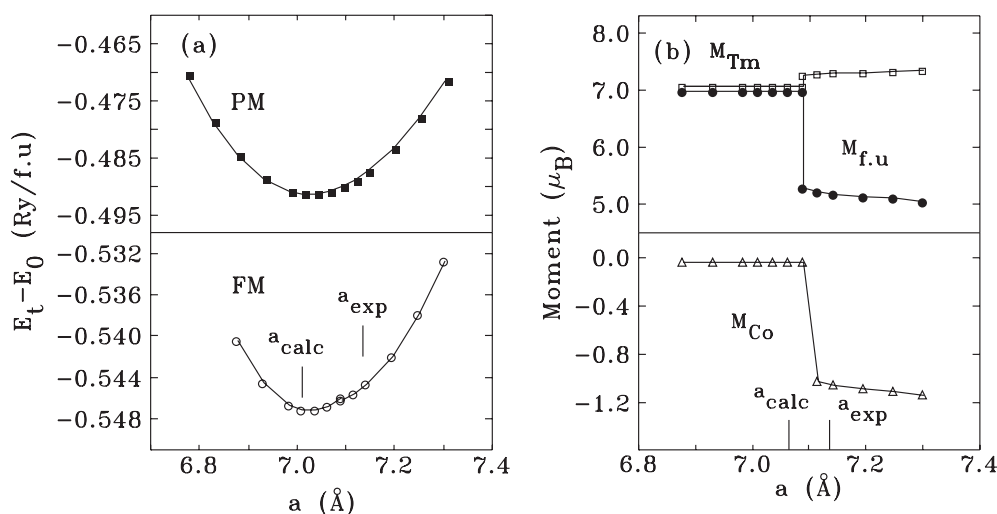


**Figure 9.** Variation in the total energy and the Co moment as a function of  $M_{\text{f.u.}}$  for  $\text{ErCo}_2$  at  $a_{\text{low}}$  (a) and  $a_{\text{high}}$  (b);  $E_0 = -31724.7$  Ryd.

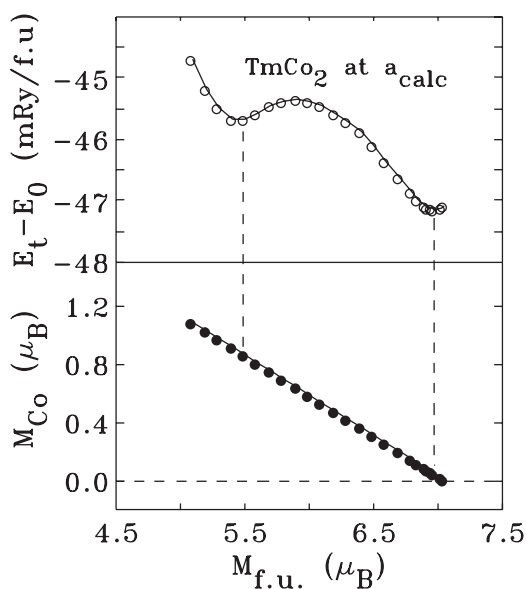
paramagnetic state ( $M_s = 0$ ). This is consistent with the fact that a large negative expansion (0.2%) occurs at  $T_C$  for  $\text{RCO}_2$  with  $R = \text{Dy}, \text{Ho},$  and  $\text{Er}$  [31]. The double minimum feature of  $E_t(a)$ , related to low and high spin states, is also predicted in the Invar alloy,  $\text{Fe}_3\text{Ni}$ , and is responsible for the first-order magnetic transition and the Invar effect [32].

### 3.3. Magnetic states in $\text{TmCo}_2$

Figure 10 describes the calculated total energies and magnetic moments as a function of lattice constant in  $\text{TmCo}_2$ .  $E_t(M)$  shows a single minimum with a Co moment of about  $0.05 \mu_B$ .



**Figure 10.** Calculated total energy,  $E_t$  (a), and magnetic moments (b), as a function of lattice constant,  $a$ , in TmCo<sub>2</sub>;  $E_0 = -32\,686$  Ryd. PM and FM denote the nonmagnetic and magnetic states, respectively.  $a_{\text{calc}}$  and  $a_{\text{exp}}$  are calculated and experimental lattice constant, respectively.



**Figure 11.** Variation in the total energy and the Co moment as a function of  $M_{\text{f.u.}}$  for TmCo<sub>2</sub> at  $a_{\text{calc}}$ ;  $E_0 = -32\,686.5$  Ryd.

As shown in figure 11, the total energy  $E_t(M)$  at  $a_{\text{calc}}$  shows a double minimum feature in TmCo<sub>2</sub>. The low spin state of Co is stable, while the high spin state of Co is metastable. These calculation results explain the experimental fact that the Co sublattice shows no long-range magnetic ordering in TmCo<sub>2</sub> due to a small molecular field of the Tm sublattice, while the partial replacement of Tm by Gd will induce the formation of a Co moment in Tm<sub>1-x</sub>Gd<sub>x</sub>Co<sub>2</sub> [6].

**Table 2.** The calculated Landau expansion coefficients of equation (1) for RCo<sub>2</sub> at  $T = 0$ . The total energy and magnetic moments are given in Ryd/unit cell and  $\mu_B$ /unit cell.

R	$a_1(0)$ Ryd/ $\mu_B^2$	$a_3(0)$ Ryd/ $\mu_B^4$	$a_5(0)$ Ryd/ $\mu_B^6$	$a_1(0)a_5(0)/a_3(0)^2$
Gd	$-2.5607 \times 10^{-3}$	$1.6272 \times 10^{-4}$	$7.9538 \times 10^{-6}$	
Tb	$-7.9333 \times 10^{-4}$	$-2.5044 \times 10^{-4}$	$2.7093 \times 10^{-5}$	
Dy	$1.1689 \times 10^{-4}$	$3.9441 \times 10^{-4}$	$3.2224 \times 10^{-5}$	0.024
Dy*	$9.4968 \times 10^{-4}$	$4.1184 \times 10^{-4}$	$3.3782 \times 10^{-5}$	0.189
Ho	$5.4216 \times 10^{-4}$	$3.7075 \times 10^{-4}$	$2.7086 \times 10^{-5}$	0.107
Ho*	$1.0892 \times 10^{-3}$	$3.9009 \times 10^{-4}$	$2.7501 \times 10^{-5}$	0.197
Er	$2.4734 \times 10^{-3}$	$7.8432 \times 10^{-4}$	$5.1708 \times 10^{-5}$	0.208
Er*	$1.9196 \times 10^{-3}$	$0.7489 \times 10^{-4}$	$5.0021 \times 10^{-5}$	0.171
Tm	$3.4414 \times 10^{-3}$	$1.0361 \times 10^{-5}$	$6.8074 \times 10^{-5}$	0.218

\* Metastable state.

### 3.4. Discussion

Table 1 displays the calculated and experimental lattice constants and magnetic moments in RCo<sub>2</sub> compounds. The experimental data are taken from the literature [19]. The calculated lattice constant and magnetic moments correspond to the minimum of the total energy. Table 1 also shows the calculated lattice constant and magnetic moment for the metastable state of RCo<sub>2</sub> with R = Dy, Ho, and Er.

As expected, the calculated lattice constant,  $a_{\text{calc}}$ , decreases with increasing atomic number of the 4f elements because of the lanthanide contraction. The experimental lattice constant,  $a_{\text{exp}}$ , shows the same exact variation. However, the calculated lattice constants,  $a_{\text{calc}}$ , are underestimated by about 0.7% in comparison with the corresponding experimental lattice constants, which is ascribed to the LSDA treatment for the exchange–correlation effect in the calculation.

Both the calculated and experimental Co magnetic moments,  $M_{\text{Co}}$ , show the same variation tendency with different R. The Co magnetic moment decreases with decreasing R spin. The calculated Co moment seems to be overestimated by about 0.2–0.33  $\mu_B$ . However, the experimental Co moments,  $M_{\text{exp}}^{\text{Co}}$ , are generally derived from the magnetic measurement by  $M_{\text{exp}}^{\text{Co}} = 1/2(M_{\text{exp}}^{\text{f.u.}} - M_{\text{R}^{3+}})$ , where it is assumed that R possesses the moment of the isolated ion of R<sup>3+</sup>. Similarly, the nominal Co moments  $M_{\text{nom}}^{\text{Co}}$  are also derived from  $M_{\text{calc}}^{\text{f.u.}}$ , by  $M_{\text{nom}}^{\text{Co}} = 1/2(M_{\text{calc}}^{\text{f.u.}} - M_{\text{R}^{3+}})$ . As shown in table 1, the calculated nominal Co moments,  $M_{\text{nom}}^{\text{Co}}$ , are in very good agreement with those of the experimentally obtained ones,  $M_{\text{exp}}^{\text{Co}}$ , except for R = Er. The experimental  $M_{\text{exp}}^{\text{Co}}$  equals the calculated  $M_{\text{nom}}^{\text{Co}}$  at the metastable state for R = Er.

In order to gain more insight into the magnetic transitions in RCo<sub>2</sub> Laves phases, the Landau coefficients,  $a_i(T)$ , at  $T = 0$  K are derived by fitting the calculated fixed-spin-moment total energy as a function of the band magnetic moment using equation (1). As shown in table 2,  $a_1(0)$  is negative for R = Gd and Tb, indicating that the famous Stoner criterion for the appearance of ferromagnetism is met in these compounds. These results explain the second-order magnetic transition in the compounds. However, the calculation results are different from those given by Khmelevskiy *et al* [17], where the value of  $a_1(0)$  is positive for R = Gd and Tb. The most likely explanation is that the authors have replaced the 4f elements R with the nonmagnetic element Y in the calculations. In fact, Diviš *et al* [18] studied the influence of the local R 4f moments on the stability of the magnetic states for RCo<sub>2</sub> with R = Y, Nd, Ho, and Er using a self-interaction corrected LSDA method. They found that the induced spin splitting

of the rare earth 5d states by the R 4f states couple antiferromagnetically with the Co 3d states, playing a crucial role in driving the stability of the magnetism in RCo<sub>2</sub>.

On the other hand, the Landau coefficients show  $a_1(0) > 0$ ,  $a_3(0) < 0$ , and  $a_5(0) > 0$  for R = Dy–Tm (table 2). As stated above, the total energy  $E_t(a)$  shows two minima at a smaller and a larger lattice volume, corresponding to a low and a high spin state of Co, respectively. As shown in table 2, for R = Dy, Ho, and Er at high spin Co states (larger lattice volume),  $a_1(0)a_5(0)/a_3(0)^2$  is less than 5/28 and it seems that a second-order magnetic transition is to be expected at  $T_C$ . However, the value of  $a_1(0)a_5(0)/a_3(0)^2$  is only slightly larger than 3/16 and near the boundary between the first-order transition and the metamagnetic transition for R = Dy, Ho, and Er at low spin Co states (smaller lattice volume). This means that the difference in total energy for FM and PM states is very small in this case, although the PM state is stable while the FM state is metastable. It is expected that a strong metamagnetic transition from paramagnetic to ferromagnetic states will be induced by a small lattice expansion or in an external field. Again, it indicates that the large negative lattice expansion near  $T_C$  plays an important role in understanding the first-order magnetic transitions for R = Dy, Ho, and Er. In addition, the value of  $a_1(0)a_5(0)/a_3(0)^2$  for TmCo<sub>2</sub> (0.218) is clearly larger than 3/16 but less than 9/20. A field-induced itinerant electronic metamagnetic transition is possible in this compound. Due to the small molecular field of Tm (about 50 T [1]), no long-range magnetic ordering of the Co sublattice is formed.

#### 4. Conclusion

The first-principle density functional theory calculations indicate that the order of the magnetic transition in the Laves phase RCo<sub>2</sub> depends on the type of rare earth. For R = Dy, Ho, and Er, the total energy  $E_t(a)$  shows two minima at a smaller and a larger lattice volume, corresponding to a low and a high spin state of Co, respectively. Further, the total energy  $E_t(M)$  at the calculated equilibrium lattice constant also shows two minima, corresponding to a low and a high spin state of Co, respectively, for R = Dy, Ho, and Er. The double minimum feature of  $E_t(a)$  and  $E_t(M)$  is responsible for the first-order magnetic transition at  $T_C$  in RCo<sub>2</sub> with R = Dy, Ho, and Er. On the other hand, for R = Gd and Tb,  $E_t(a)$  and  $E_t(M)$  show a single minimum feature, which displays a second-order magnetic transition at  $T_C$ . The above results are also confirmed by the analysis of the Landau expansion coefficient derived from the fixed spin-moment band structure calculations using Landau–Ginzburg theory including the spin fluctuation effect.

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