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Magnetism in $HoCo_2$ and $ErCo_2$ under high pressure

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Abstract

Temperature dependencies of the electrical resistivity $\rho(T)$ was studied on $HoCo_2$ and $ErCo_2$ under the hydrostatic pressure up to 8 GPa. At ambient pressure the resistivity drops dramatically at the Curie temperature T_C (=78 and 33 K, respectively) as a result of the Co 3d-band moment formation in these two $RECo_2$ compounds (RE=rare earth). The applied pressure P affects considerably both, T_C and the $\rho(T)$ anomaly in the vicinity of T_C. Initially, the value of T_C becomes reduced linearly with increasing P up to approximately 1.5 GPa. The measurements in pressure beyond 1.5 GPa, however, reveal that the real T_C vs. P dependence gradually deviates from the initial linear trend. Simultaneously, the $\rho(T)$ drop at T_C becomes gradually reduced and vanishes for higher pressures ($P>4$ GPa) where T_C becomes nearly pressure independent. We conclude that these phenomena reflect the pressure induced suppression of Co metamagnetism. This behavior will be discussed within a model assuming that for $P>P_c$ the projected Co-3d density of states in the vicinity of E_F decreases critically and the RE–Co–RE exchange channel becomes ineffective to induce the metamagnetic splitting of the Co 3d majority and minority subbands. This scenario is corroborated by results of ab initio electronic structure calculations.

Keywords: RE–T compounds; Curie temperature; Electrical resistivity; Pressure effects

1. Introduction

$HoCo_2$ and $ErCo_2$ belong to the family of $RECo_2$ (RE=3D rare earth) compounds crystallizing in the cubic Laves phase structure. Since the Co 3d-band states in these materials appear on the verge of magnetism, materials of this type are frequently subjected to intensive experimental and theoretical studies of various aspects of the itinerant electron metamagnetism. The compounds with nonmagnetic rare-earth elements (Y, Lu or Sc) are exchange-enhanced paramagnets and exhibit metamagnetic behavior in high external magnetic fields larger than 70 T (at least for YCo_2 and $LuCo_2$) [1]. This behavior can be explained in terms of Landau theory, which allows to define the necessary conditions for the appearance of itinerant electron metamagnetism (IEM) as proposed by Wohlfarht and Rhodes [2]. YCo_2 and $LuCo_2$ are also frequently quoted as archetype spin–fluctuation systems with a high characteristic temperature T_{sf}. In $HoCo_2$ and $ErCo_2$, the Co metamagnetic state can be induced in zero external field by employing a large effective exchange field mediated by the 5d (RE)–3d (Co) hybridization from the ferromagnetically ordered RE4f magnetic moments at T_C (=78 and 33 K, respectively) [3]. The related first-order magnetic phase transition at T_C is accompanied by a dramatic drop of the electrical resistivity, and a sudden volume expansion due to the abrupt change of the density of Co-3d states at E_F, partial localization of the 3d states and the Co moment formation. Magnetic ordering in both, the RE (=Ho or Er) and Co sub-lattice is collinear ferromagnetic with an antiparallel inter-sublattice coupling.

Based on the s–d model [4], in which the coexistence of the localized moment of the RE atoms and the itinerant d electrons of Co atoms is assumed, Bloch et al. [5] explained the first-order transition in $HoCo_2$ and $ErCo_2$ and pointed out that it is closely related to the metamagnetic behavior of the d-electrons and the temperature variation of the spin susceptibility of the d-electrons $\chi_d(T)$. The metamagnetism of d electrons has been confirmed by many experiments [6–10]. It has been shown that the value of M_{Co} is about 1 μ_B/atom when the effective field H_{eff} acting on d electrons is higher than a critical value H_c (~100 T), but it is dramatically reduced when $H_{eff}<H_c$. The first-order transition of $HoCo_2$ and $ErCo_2$ at T_C is

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changed to the second-order one by diluting the magnetic RE atoms by nonmagnetic Y atoms because of the reduction of the H_{eff} value. It has been suggested by Bloch et al. [4,5] that the first-order magnetic phase transition in $HoCo_2$ and $ErCo_2$ could be changed to the second-order one by applying high pressure. Later, Inoue and Shimizu [11] extended the s–d model and provided conditions under which the first-order phase transition would change to the second-order one on substitution or with pressure.

In his theoretical work, Yamada [12] has considered the effect of pressure on the itinerant d-electron subsystem at finite temperatures. The effect of spin fluctuations has been taken into account in the phenomenological Landau–Ginzburg theory. He has found that the critical field H_c of the metamagnetic transition (MT) increases with increasing pressure and the MT vanishes at a critical pressure P_0. The critical-pressure value P_0 decreases with increasing temperature and becomes zero at a critical temperature T_0. A value of P_0 of 1–5 GPa for YCo_2 at 0 K has been estimated.

In order to reveal effects of variation of interatomic distances on magnetism in $HoCo_2$ and $ErCo_2$ we have studied in this work pressure effects on the electrical resistivity anomaly associated with the magnetic phase transition at T_C. Moreover, we have performed ab initio electronic structure calculations in order to investigate Co magnetism in these two materials theoretically.

2. Experimental details

The polycrystalline $HoCo_2$ and $ErCo_2$ samples were synthesized by melting stoichiometric mixtures of components (minimum purity of 3N5) under argon atmosphere. A ratio of 1:1.95 has been chosen to avoid formation of $RECo_3$, which is ferromagnetic already at room temperature. The melted buttons were wrapped in Ta foil, sealed under vacuum in silica tubes and annealed at 600–850°C for 14 days. The X-ray diffraction analysis revealed only the expected cubic C15 phase. The lattice constants obtained are found to be in a good agreement with data reported in literature. Additionally, the samples have been checked by DC-susceptibility measurements. The resistivity has been measured as a function of temperature ($4.5 < T < 300$ K) on bar-shaped samples (size: $\sim 0.2 \times 0.2 \times 0.8$ mm^3) using the DC four-terminal measuring technique. The hydrostatic pressure up to 8 GPa has been applied using a tungsten–carbide pressure cell with mixture of mineral oils as a pressure-transmitting medium.

3. Results and discussion

The $\rho(T)$ curves for $HoCo_2$ and $ErCo_2$ at ambient pressure are shown on Fig. 1. The data are in good agreement with those reported earlier (see, for example, Refs. [3,13,14]). The first-order magnetic phase transitions to magnetic ordering at T_C (=78 and 33 K, respectively) is reflected by the step-like resistivity drop in the $\rho(T)$ dependence. The magnetic-ordering temperatures deduced from resistivity data are in a good agreement with those obtained from DC-susceptibility measurements. The additional resistivity anomaly at $T_R \ll T_C$ in $HoCo_2$ case is the effect attributed to the reorientation of the easy-magnetization axis in this material [15].

Figs. 2 and 3 shows the resistivity data measured on $HoCo_2$ and $ErCo_2$, respectively, exerted to various pressures up to 8 GPa. From the evolution of resistivity

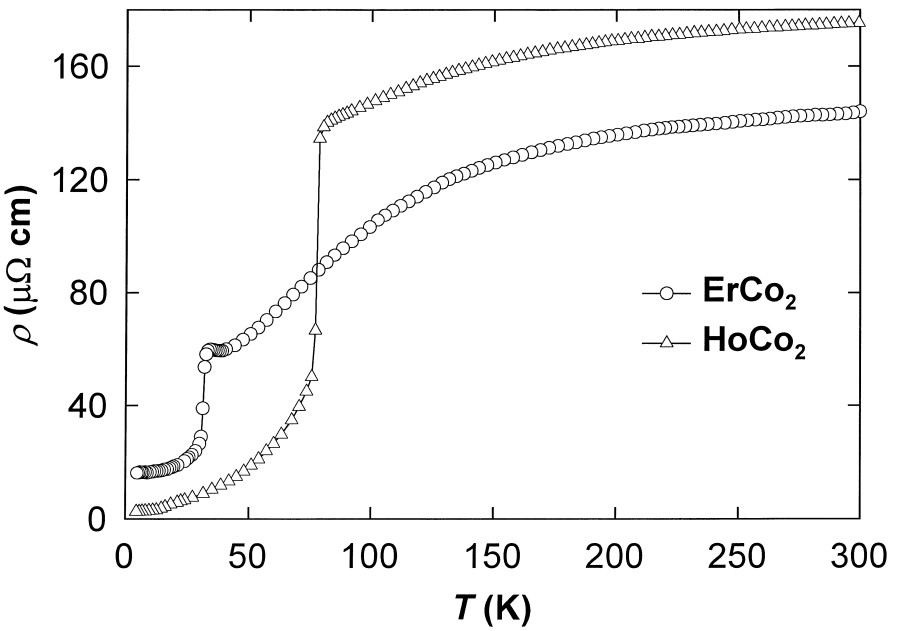

Fig. 1. Temperature dependence of electrical resistivity $\rho(T)$ of $RECo_2$ compounds for RE = Er, Ho at ambient pressure.

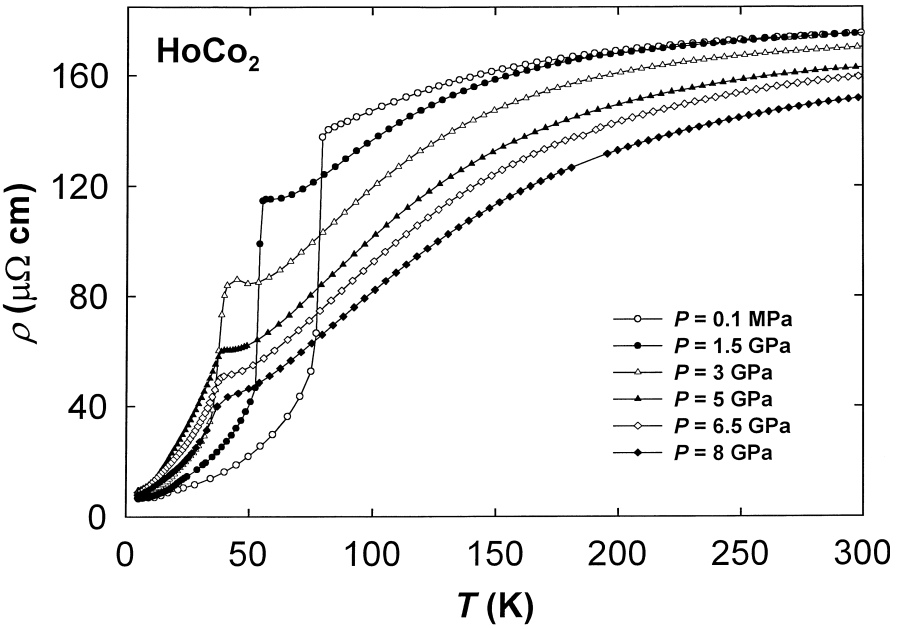

Fig. 2. Temperature dependence of electrical resistivity $\rho(T)$ of $HoCo_2$ compound at different pressures.

behavior with increasing pressure one may deduce that the value of T_C becomes initially reduced linearly with increasing pressure up to approximately 1.5 GPa. When a linear extrapolation of the lower pressure data of T_C (varying with $\partial T_C/\partial P = -16.6$ and -7.9 K GPa^{-1}, respectively) to higher pressures is made, a value of the critical pressure $P_c \approx 4.7$ and 4.2 GPa for disappearance of magnetic ordering is estimated for $HoCo_2$ and $ErCo_2$, respectively. Our data are in good agreement with those from literature [14]. The measurements in pressures beyond 1.5 GPa, however, reveals that the real T_C vs. P data gradually deviate from the linear dependence and T_C becomes almost nearly pressure independent for $P > 4$ GPa ($T_C \approx 35$ and 13 K, respectively). The latter value is significantly lower than 22 K derived in the recent paper of Hauser et al. [16]. Simultaneously with the pressure induced evolution of the Curie temperature, the shape of the $\rho(T)$ anomaly in the vicinity of T_C becomes dramatically modified although the shape of high-temperature ($T \ll T_C$) $\rho(T)$ curve is little affected.

Note that the resistivity anomaly for $HoCo_2$ at T_R, which is connected with the reorientation of the easy-

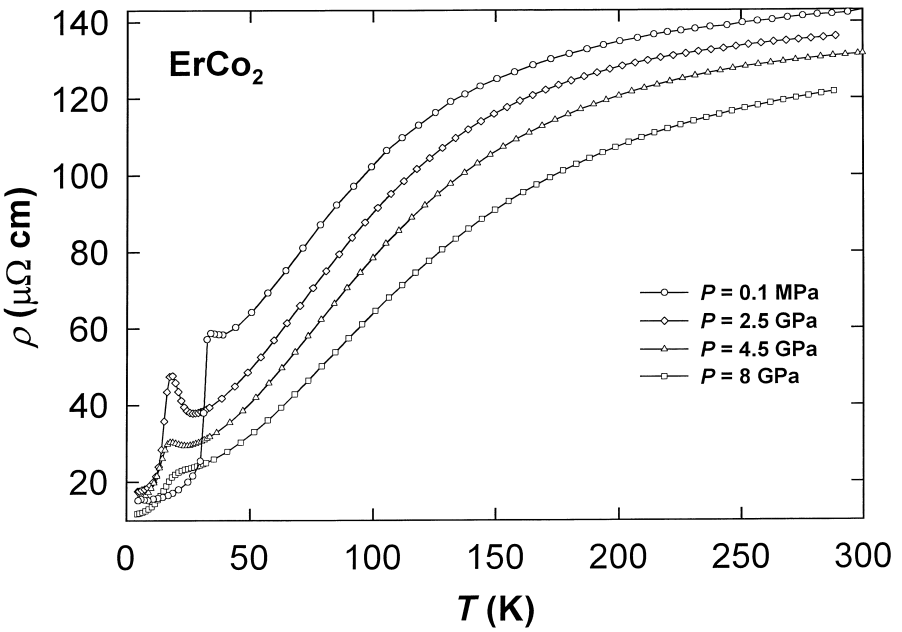

Fig. 3. Temperature dependence of electrical resistivity $\rho(T)$ of $ErCo_2$ compound at different pressures.

magnetization axis, is shifted with the pressure to the higher temperatures with the approximate rate $+3.2$ K GPa^{-1} but it cannot be recognized already at 3 GPa.

According to Bloch et al. [4,5] and Yamada [12] the first-order magnetic phase transition in $HoCo_2$ and $ErCo_2$ could be changed to the second-order one by applying high pressure. The $\rho(T, P)$ curves for $HoCo_2$ and $ErCo_2$ clearly show the change in the type of magnetic phase transition (Fig. 4). The pressure necessary to change the type of transition is about 3 GPa for $HoCo_2$ and about 2.5 GPa for $ErCo_2$ the values roughly comparable to those proposed in Ref. [12].

In the case of $ErCo_2$ the enhancement of resistivity at temperatures approaching T_C, which is ascribed to a critical conduction-electron scattering on spin-fluctuations in the itinerant d band, becomes more pronounced with increasing the pressure approximately up to $P=2.5$ GPa and then starts to decrease as the pressure is further increased. Analogous evolution of the resistivity behavior for temperatures just above T_C is observable also for $HoCo_2$ but in this case the enhancement is much smaller. Note that a formally similar development of the T_C related anomaly is observed in Y diluted $Er_{1-x}Y_xCo_2$ [14,16] and $Er_{1-x}Y_xCo_2$ [8] systems around the critical concentration x_c. This similarity is probably due to the fact that in both cases, in the vicinity of P_c and x_c, the value of effective exchange field due to ferromagnetically ordered RE moments becomes comparable to the critical field for the metamagnetic transition, $H_{eff} \approx H_c$. Also the residual resistivity for both of the compounds is changed with the pressure, namely it is increased with the increasing of the pressure up to approximately 5 GPa in the case of $HoCo_2$ and 2.5 GPa in the case of $ErCo_2$ and then starts to decrease.

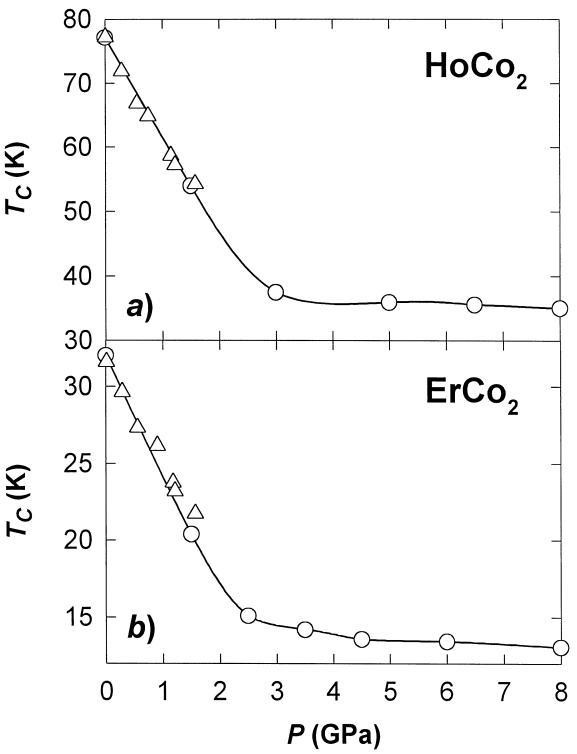

Fig. 4. T_C–P phase diagrams of $HoCo_2$ and $ErCo_2$. The triangles are the data taken from Ref. [14].

The resistivity behavior of $HoCo_2$ and $ErCo_2$ in the critical region around T_C is usually explained within the following scenario in which the stability of Co magnetism is principally involved. The resistivity above T_C is mainly affected by a spin-disorder scattering on paramagnetic rare-earth moments influenced by the crystal field interaction and by an spin-fluctuation scattering depending on the dynamics of spin fluctuations in the Co 3d-band [17]. When lowering the temperature, the 4f-moments, which order ferromagnetically at T_C, produce via the 5d (RE)–3d (Co) a strong uniform exchange interaction acting on the Co 3d states. When this action is sufficient to split the 3d majority and minority sub-bands, the spin fluctuation at the Co-sites are quenched and the 3d-band metamagnetic state is induced by a first order magnetic phase transition. Consequently, the scattering is drastically suppressed, which yields the resistivity drop. The obvious effect of a dramatic reconstruction of the Fermi surface on transport properties at the magnetic transition should be considered as well.

The loss of Co magnetism is indicated by vanishing resistivity drop at T_C for pressures where $T_C = \text{const}$. This behavior could be explained by a model assuming that for $P > P_c$ the projected Co-3d density of states in the vicinity of E_F decreases, the itinerant Co moment vanishes because the RE–Co–RE exchange channel becomes ineffective to induce splitting of the Co 3d majority and minority subbands, a.e. the conditions of the first order magnetic phase transition is not fulfilled and transition becomes a second order. The RE moments order at the 'residual' T_C (value roughly comparable to T_C of $RENi_2$) due to the persisting RKKY-type exchange interaction between localized RE moments with a low value of $\partial T_C / \partial P$.

To check this scenario we performed first principles electronic structure calculations in the framework of density functional theory (DFT). In our case we employed the full potential linearized augmented plane wave method (LAPW) [18]. Exchange and correlation effects are treated within local spin density approximation and scalar relativistic Kohn–Sham equations are used to obtain self-consistent solution of the DFT functional. To simulate localized 4f states we switched off the hybridization of the 4f states with all other valence states and treat the holmium (erbium) 4f-states in the spherical part of the crystal potential as atomic-like core states. The integer number 10 (11) was fixed for the occupation of erbium 4f-states at Er site. The non-spin-polarized DFT calculations (see Fig. 5) leads the Co-atom projected density of states (DOS) $N_{Co}(E_F) = 1.22$ states eV^{-1} atom ($N_{Co}(E_F) = 1.2$ states eV^{-1} atom) at the Fermi level (E_F), which manly originates from Co 3d-states ($N_{Co\text{-}3d}(E_F) = 1.1$ states eV^{-1} atom). From our

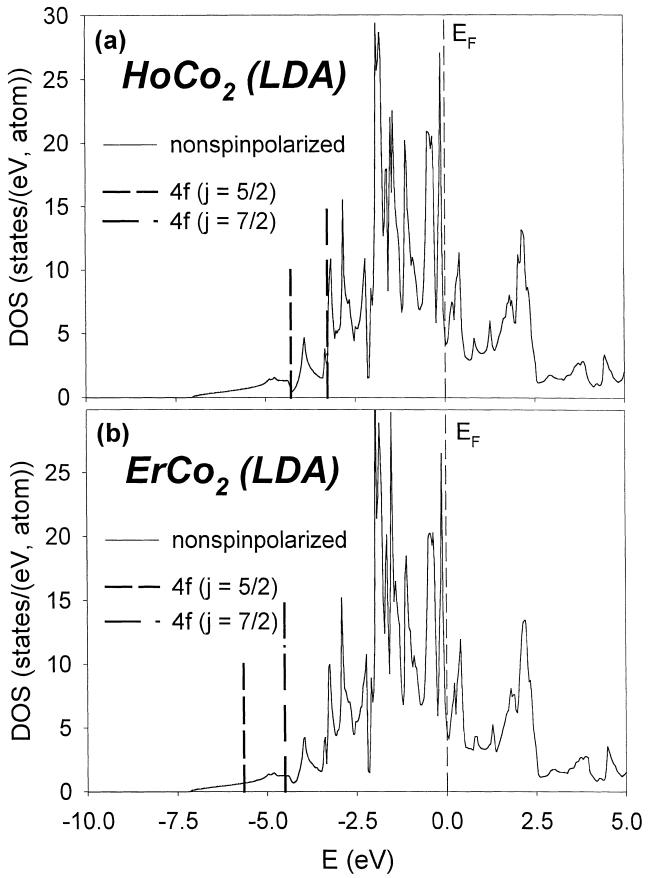

Fig. 5. Total non spin-polarized DOS of $HoCo_2$ (a) and $ErCo_2$ (b). The Fermi energy is set to zero for both compounds. The energy levels of the fully occupied localized $4f_{5/2}$ and $4f_{7/2}$ states are indicated by full vertical lines. The empty localized $4f_{5/2}$ and $4f_{7/2}$ states are not shown.

selfconsistent calculations we also deduced Stoner exchange parameter $I_{Co}=0.41$ eV for both compounds studied. Therefore the calculated Stoner product $I_{Co}\cdot N_{Co}(E_F)$ equals to 0.49 and does not favor the spontaneous ferromagnetic instability of itinerant Co states. In contrast the spin-polarized calculations with antiparallel alignment of holmium (erbium) 4f spin moments and cobalt 3d spin moments converged to stable magnetic state, which has lower total energy than the non spin-polarized state. In addition we performed a large number of numerical experiments with different values of initial exchange splitting originating from Ho (Er) 4f-states and Co 3d-states and found that the crucial factor driving the stability of the magnetism in $HoCo_2$ and $ErCo_2$ is the induced spin splitting of rare-earth 5d states which couples antiferromagnetically with the Co 3d-states. The selfconsistent calculations provide the spin magnetic moments of $M_S^{Co}=1.15\ \mu_B$, ($M_S^{Co}=1.13\ \mu_B$), $M_S^{Ho}=-4.26\ \mu_B$ ($M_S^{Er}=-3.25\ \mu_B$) and $M_S^{I}=-0.21\ \mu_B$ ($M_S^{I}=-0.19\ \mu_B$) in the interstitial region of the $HoCo_2$ ($ErCo_2$) crystal.

In the case of $ErCo_2$ we have also calculated the spin-polarized electronic structure for the set of ten lattice parameters smaller than the ambient-pressure value $a_{exp}=714.4$ pm. We have found that the M_S^{Co} is smoothly decreasing to the value of 0.78 μ_B for the $a\geq 692$ pm but for values $a\leq 688$ pm it suddenly drops to the small value of $M_S^{Co}<0.1\ \mu_B$. In the critical region $692>a>688$ pm we were not able to obtain stable selfconsistent solution of our DFT calculations. Considering the compressibility value for $ErCo_2$ (8.9×10^{-3} GPa^{-1}) the calculations point to the critical pressure for loss of Co metamagnetism of approximately 11 GPa. This value is more than two times larger than the experimentally observed P_c. We are aware of the fact that our calculations cannot involve spin fluctuations, which should play an important role in the physics of $ErCo_2$ and therefore consider the agreement between the calculated and experimentally determined critical pressure satisfactory at the present stage.

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