Deviation from the stoichiometric composition of single-crystal 'Er$_2$Co$_{17}$'

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Abstract. The deviation from the stoichiometric composition of single-crystal 'Er$_2$Co$_{17}$' has been determined by theoretical analysis. It is found that the composition of this single-crystal 'Er$_2$Co$_{17}$' is rich in cobalt, and its real composition is suggested to be Er$_{2-\delta}$Co$_{17+2\delta}$ ($\delta = 0.14$) on the basis of a comparison of calculations based on the single-ion model with a series of experiments. The values of the Er–Co exchange field H_{ex} and the crystalline-electric-field (CEF) parameters A_n^m at the rare-earth (R) site in the 'Er$_2$Co$_{17}$' compound are also evaluated at the same time. The experiments provide the following data: the temperature dependence of the spontaneous magnetization of the compounds and the normalized magnetic moment of the Er ion, the magnetization curves along the crystallographic axes at 4.2 K and 200 K, and the temperature dependence of the magnetization along the crystallographic axes in a field of 4 T.

1. Introduction

It is known that an excess amount of rare earth relative to the stoichiometric composition has to be added to compensate the preferential evaporation losses of the rare-earth material during the growth process for single-crystal rare-earth–transition metal (R–T) intermetallic compounds [1]. If the starting constituents are melted together in an ideal ratio or the excess amount of rare earth added is not sufficient, the actual composition of the single-crystal compound being grown will be rich in the transition metal. If the excess amount of rare earth added is too high, the single-crystal compound will be rich in the rare earth. Only when the excess amount of rare earth added is in a suitable range is the composition of the single-crystal compound grown quite near to the stoichiometric composition.

On one hand, chemical analysis methods sometimes cannot be used to determine the actual composition of a single-crystal compound, because large-size single crystals are not easy to obtain for some R–T intermetallic compounds; in some special conditions a single crystal a few millimetres long can be obtained, but such a small sample is only sufficient for measuring crystallographic and magnetic properties when the single crystal is undamaged. On the other hand, the usual physical measurement methods, such as the x-ray diffraction technique, and energy spectrum analysis with a scanning electron microscope (SEM) or a transmission electron microscope (TEM), cannot be used to determine the deviation from the stoichiometric composition in a single-crystal compound accurately when this deviation is very small.

It is also known that the lattice parameters and intrinsic magnetic properties of a single-crystal compound will show fluctuations relative to those of an ideal single-crystal compound

if deviation from the stoichiometric composition occurs in the sample. It is believed that the deviation from the stoichiometric composition of a single-crystal compound can be determined by theoretical analysis of the fluctuation in the intrinsic magnetic properties. In this work, it is found that the composition of single-crystal 'Er$_2$Co$_{17}$' [1] is rich in cobalt, and its real composition is suggested to be Er$_{2-\delta}$Co$_{17+2\delta}$ ($\delta = 0.14$) as obtained from a comparison of calculations based on the single-ion model with a series of experiments.

2. Method of calculation

The Er$_2$Co$_{17}$ compound has a Th$_2$Ni$_{17}$-type hexagonal structure with space group $P6_3/mmc$. There are two rare-earth crystallographic sites, b and d, in this hexagonal structure. Each site splits into two magnetically inequivalent sites A and B. In the coordinate system with the z- and x-axes along the c- and a-axes, the Hamiltonians of the CEF interaction for the Er ions at the A and B sites are closely related; they are expressed as

$$H_{CEF}(A) = \sum_{n=2,4,6} A_n^0 C_n^0 + \sum_{n=4,6} A_n^3(C_n^3 + C_n^{-3}) + A_6^6(C_6^6 + C_6^{-6}) \tag{1}$$

$$H_{CEF}(B) = \sum_{n=2,4,6} A_n^0 C_n^0 - \sum_{n=4,6} A_n^3(C_n^3 + C_n^{-3}) + A_6^6(C_6^6 + C_6^{-6}) \tag{2}$$

where

$$C_n^m = \sum_j \left[\frac{4\pi}{2n+1}\right]^{1/2} Y_n^m(\vartheta_j, \varphi_j). \tag{3}$$

$Y_n^m(\vartheta_j, \varphi_j)$ are the spherical harmonics, and ϑ_j and φ_j are the polar and azimuthal angles of the position vector of the jth 4f electron. The sign of the second term in the right-hand side of equation (1) is opposite to that of equation (2), and the contributions of each of them to the total free energy of the compound largely cancel each other. Neglecting the second terms, the Hamiltonian of the CEF interaction, averaged over the crystallographic and magnetic inequivalent sites, is therefore represented simply as

$$H_{CEF} = \sum_{n=2,4,6} A_n^0 C_n^0 + A_6^6(C_6^6 + C_6^{-6}). \tag{4}$$

The total Hamiltonian of the Er ion in the compound consists of the Er–Co exchange interaction, the CEF interaction, and the Zeeman energy; that is,

$$H_{\text{Er}} = 2\mu_B \mathbf{S} \cdot \mathbf{H}_{ex} + H_{CEF} + \mu_B[\mathbf{L} + 2\mathbf{S}] \cdot \mathbf{H}. \tag{5}$$

The Er–Er exchange interaction, which is much weaker than the Er–Co exchange interaction, is neglected.

$\mathbf{H}_{ex}(T)$ is assumed to be proportional and antiparallel to the magnetic moment of the Co sublattice $\mathbf{M}_{\text{Co}}(T)$. The matrix elements of equation (5) are calculated by using the irreducible-tensor-operator technique [2]. For a given applied magnetic field $\mathbf{H}$ and direction of $\mathbf{H}_{ex}(T)$, the eigenvalues E_n and eigenfunctions $|n_i\rangle$ ($i = 1, 2, \ldots, \sum_J(2J+1)$) are obtained by diagonalizing the $\sum_J(2J+1) \times \sum'_J(2J+1)$ matrix of equation (5). The diagonalization was carried out within the subspace consisting of the ground J-multiplet, $J = 15/2$, for the Er ion.

The free energy for Er$_2$Co$_{17}$ is given by

$$F(\mathbf{H}, \mathbf{H}_{ex}, T) = -2k_B T \ln Z + K_{1\text{Co}} \sin^2 \theta_{\text{Co}} - \mathbf{M}_{\text{Co}}(T) \cdot \mathbf{H} \tag{6}$$

where

$$Z = \sum_i \exp\left(\frac{-E_i}{k_B T}\right) \tag{7}$$

and K_{1Co} is the magnetocrystalline anisotropy constant of the Co sublattice. The values of $M_{Co}(T/T_C)/M_{Co}(0)$ and $K_{1Co}(T/T_C)/K_{Co}(0)$ are taken as those of Y$_2$Co$_{17}$ [1]. T_C is the Curie temperature. The equilibrium direction of H_{ex} is determined from minimization of the free energy. The magnetic moments of the Er ion, Er$_2$Co$_{17}$, and Er$_{2-\delta}$Co$_{17+2\delta}$ are respectively given by

$$M_{Er}(T) = -\frac{1}{Z} \sum_i \mu_B \langle n_i | L + 2S | n_i \rangle \exp\left(\frac{-E_i}{k_B T}\right) \tag{8}$$

$$M(T) = 2M_{Er}(T) + M_{Co}(T) \tag{9}$$

$$M(T) = (2 - \delta)M_{Er}(T) + (17 + 2\delta)m_{Co}(T) \tag{10}$$

where $m_{Co}(T)$ is the average atomic magnetic moment per cobalt atom.

The values of the parameters H_{ex} and A_n^m are obtained from the best fit of the calculations to the experimental data. The values of $M_{Co}(0)$ and $K_{1Co}(0)$ are also adjusted around the values for Y$_2$Co$_{17}$ to obtain a better fit to the experimental values of $M_{Co}(0)$: 28.05 [1], 27.3 [3], and 28.00 μ_B FU^{-1} [4], and $K_{1Co}(0)$: -8.66 [1], -9.94 [3], and -6.77 K FU^{-1} [4]. The experimental studies provide the following data: the temperature dependence of the spontaneous magnetization of Er$_2$Co$_{17}$ and the normalized magnetic moment of the Er ion, the magnetization curves along the crystallographic axes at 4.2 K and 200 K, and the temperature dependence of the magnetization along the crystallographic axes in a given field of 4 T applied along the crystallographic axes.

3. Results and discussion

The fitted values of $2\mu_B H_{ex}$ and A_n^m, together with $M_{Er}(0)$, $M_{Co}(0)$, and $K_{1Co}(0)$ for the compound Er$_2$Co$_{17}$, at $T = 0$ K, are listed in table 1. The corresponding fitted values for the compounds R$_2$Co$_{17}$ (R = Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm) at $T = 0$ K reported by Han *et al* [5] are also included in table 1 for reference.

Table 1. The fitted values of $2\mu_B H_{ex}$, A_n^m, $K_{1Co}(0)$, $M_{Co}(0)$, and the values of $M_{Er}(0)$ calculated by using the parameters for Er$_2$Co$_{17}$. The corresponding fitted values of the parameters and the values of $M_R(0)$ for R$_2$Co$_{17}$ are also listed for reference.

R	$2\mu_B H_{ex}$ (K)	A_2^0 (K)	A_4^0 (K)	A_6^0 (K)	A_6^6 (K)	$K_{1Co}(0)$ (K FU^{-1})	$M_{Co}(0)$ (μ_B FU^{-1})	$M_R(0)$ (μ_B/R atom)	From:
Er	210	-260	-130	50	-100	-9.0	27.9	9.00	This work
Pr	600	-80	-260	10	-300	-8.0	27.7	3.10	[5]
Nd	500	-250	-270	30	-350	-8.0	27.6	3.13	[5]
Sm	350	-220	0	0	-300	-8.0	26.9	0.40	[5]
Gd	260					-8.0	27.7	7.00	[5]
Tb	250	-200	-100	50	-130	-9.0	27.9	8.99	[5]
Dy	230	-220	-230	50	-120	-9.0	27.4	10.00	[5]
Ho	210	-200	-150	50	-110	-9.0	27.7	9.93	[5]
Er	210	-260	-130	50	-100	-9.0	29.6	9.00	[5]
Tm	200	-200	-120	50	-100	-9.0	27.6	7.00	[5]

It was found that the Co atomic magnetic moment, $M_{Co}(T = 0 \text{ K}) = 29.6 \ \mu_B \ \text{FU}^{-1}$ (i.e. the average cobalt magnetic moment $m_{Co}(T = 0 \text{ K}) = 1.74 \ \mu_B/\text{Co}$), calculated by fitting the experimental results for $M(H, T)$ according to the stoichiometric composition for single-crystal Er_2Co_{17} [1], was larger than those for other R_2Co_{17} compounds (R = Pr, Nd, Sm, Gd, Tb, Dy, Ho, and Tm). It is not credible that the quantitative difference between M_{Co} for Er_2Co_{17} and the values for other R_2Co_{17} compounds is about 2 $\mu_B \ \text{FU}^{-1}$. The calculated values of the spontaneous magnetization $M_S^{cal}(T)$ evaluated with $M_{Co}(T = 0 \text{ K}) = 29.6 \ \mu_B \ \text{FU}^{-1}$ were also greater than the experimental values of $M_S^{exp}(T)$ [6, 7] over the temperature range from 0 to 600 K. The quantitative difference between $M_S^{cal}(T)$ and $M_S^{exp}(T)$ for Er_2Co_{17} is also about 2 $\mu_B \ \text{FU}^{-1}$ over this temperature range. This shows that the composition in the single-crystal 'Er_2Co_{17}' compound [1] is rich in cobalt. The high content of cobalt leads to the unusual value of the magnetic moment of the Co sublattice, $M_{Co}(T)$. The real composition of this single-crystal sample is suggested to be $Er_{2-\delta}Co_{17+2\delta}$ ($\delta = 0.14$), on the basis of the random replacement of a fraction of the rare-earth sites in the Er_2Co_{17} by a pair of transition metal atoms (a Co dumb-bell). This stochastic replacement process can be illustrated by the formula $Er_{2-\delta}(2Co)_\delta Co_{17} \rightarrow Er_{2-\delta}Co_{17+2\delta}$.

The experimental $M_S^{exp}(T)$ and $M_R(T)/M_R(0)$ curves for Er_2Co_{17} [6–8], and the $M(H, 4.2 \text{ K})$, $M(H, 200 \text{ K})$, and $M(T, 1 \text{ T})$ magnetization curves for $Er_{2-\delta}Co_{17+2\delta}$ ($\delta = 0.14$) [1] can be calculated at the same time as the Er–Co exchange field H_{ex} and the CEF parameters A_n^m, which are given in table 1, and it is found that $M_{Co}(T = 0 \text{ K}) = 27.9 \ \mu_B \ \text{FU}^{-1}$ (i.e. the average Co magnetic moment $m_{Co}(T = 0 \text{ K}) = 1.64 \ \mu_B/\text{Co}$) in the compound Er_2Co_{17}. This fitted value of the Co atomic magnetic moment, $M_{Co}(T = 0 \text{ K}) = 27.9 \ \mu_B \ \text{FU}^{-1}$, for Er_2Co_{17}, is in quite good agreement with the experimental values of $M_{Co}(0)$: 28.05 [1], 27.3 [3], and 28.00 $\mu_B \ \text{FU}^{-1}$ [4] for Y_2Co_{17}.
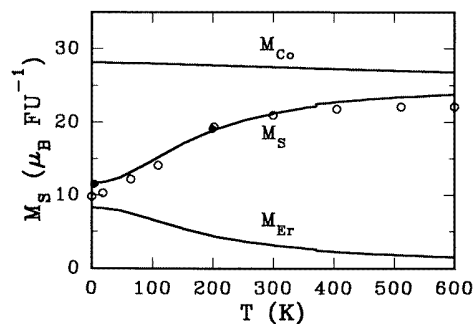

Figure 1. The temperature dependence of the spontaneous magnetization for the compound Er_2Co_{17}. The solid lines represent the calculations. The experimental data are taken from references [7] (open circles) and [1] (closed circles), respectively.
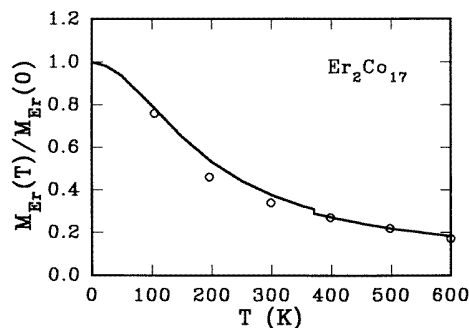
Figure 2. The temperature dependence of the normalized magnetic moment for the Er ion in the compound Er_2Co_{17}. The solid lines represent the calculations. The experimental data (open circles) are taken from references [7] and [8].

It is noticeable that the single-crystal studies of the Th_2Zn_{17}-type rhombohedral structure in the early work on R_2T_{17} (T = transition metal) compounds confirm an $RT_{8.5}$ stoichiometry [9, 10], but, in contrast, certain studies made of the Th_2Ni_{17}-type hexagonal structure can lead to different compositions, e.g. $ErCo_{9.0}$, $YNi_{9.4}$, $ThNi_{9.5}$, and $LuFe_{9.5}$ [11, 12]. These studies showed that enrichment with the transition metal in the growth process of a single-crystal compound with the Th_2Ni_{17}-type hexagonal structure in the range from Er_2Co_{17} to Er_2Co_{18} is allowable for Er–Co compounds and in the range from Lu_2Fe_{17} to Lu_2Fe_{19} is allowable for Lu–Fe compounds, owing to the random replacement of a fraction of the

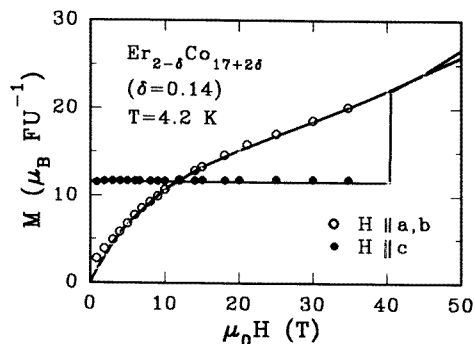**Figure 3.** Magnetization curves along the crystallographic axes at 4.2 K for Er$_{2-\delta}$Co$_{17+2\delta}$ (δ = 0.14). The solid lines represent the calculations. The experimental data (open and closed circles) are taken from reference [1].

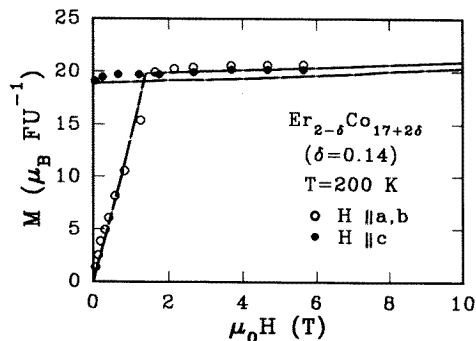**Figure 4.** Magnetization curves along the crystallographic axes at 200 K for Er$_{2-\delta}$Co$_{17+2\delta}$ (δ = 0.14). The solid lines represent the calculations. The experimental data (open and closed circles) are taken from reference [1].

rare-earth sites in the R$_2$T$_{17}$ compounds by pairs of transition metal atoms.

Figure 1 shows the temperature dependence of the spontaneous magnetization, $M_S(T)$, of Er$_2$Co$_{17}$. For the antiferromagnetically coupled Er$_2$Co$_{17}$ compound, $M_S(T)$ increases with increase of the temperature, since $M_{Er}(T)$ decreases more quickly than $M_{Co}(T)$. Figure 2 shows the temperature dependence of the normalized magnetic moment, $M_{Er}(T)/M_{Er}(0)$, for Er$_2$Co$_{17}$. The experimental $M_{Er}(T)$ curve has been obtained as the difference between $M_S(T)$ for Er$_2$Co$_{17}$ and $M_S(T)$ for Y$_2$Co$_{17}$ [7, 8]. The small discontinuities near 370 K in figures 1 and 2 are caused by the spin reorientation from the c-axis to the c-plane.

Figures 3 and 4 show the magnetization curves along the crystallographic axes at 4.2 K and 200 K, respectively. The results of the calculation show that the first-order magnetic process (FOMP) manifested by the magnetization curves along the c-axes at 4.2 K is in existence at 40.5 T as shown in figure 3. Figure 5 shows the temperature dependence of the magnetization along the crystallographic axes in a given field of 4 T applied along the crystallographic axes. The calculations reproduce the experimental data fairly well.

4. Conclusions

The deviation from the stoichiometric composition for single-crystal Er$_2$Co$_{17}$ [1] has been determined by theoretical analysis. The composition of this single-crystal 'Er$_2$Co$_{17}$' is rich in cobalt, and its real composition is suggested to be Er$_{2-\delta}$Co$_{17+2\delta}$ (δ = 0.14) on the basis of a comparison of calculations based on the single-ion model with a series of experiments. The experimental $M_S^{exp}(T)$ and $M_R(T)/M_R(0)$ curves for Er$_2$Co$_{17}$ [6–8], and the $M(\mathbf{H}, 4.2$ K), $M(\mathbf{H}, 200$ K), and $M(T, 1$ T) magnetization curves for Er$_{2-\delta}$Co$_{17+2\delta}$ (δ = 0.14) [1] can be calculated at the same time as the Er–Co exchange field H_{ex} and the CEF parameters A_n^m,
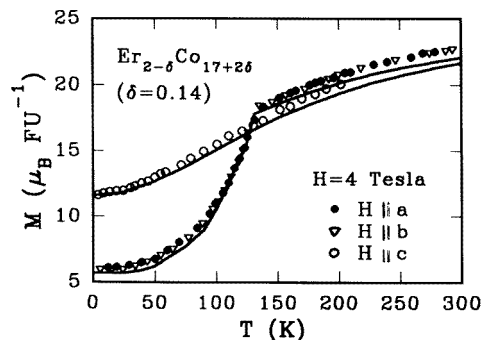
Figure 5. The temperature dependence of the magnetization along the crystallographic axes in a given field of 4 T applied along the crystallographic axes for $Er_{2-\delta}Co_{17+2\delta}$ ($\delta = 0.14$). The solid lines represent the calculations. The experimental data (open and closed circles, open triangles) are taken from reference [1].

which are given in table 1, and it is found that $M_{Co}(T = 0 \text{ K}) = 27.9 \ \mu_B \text{ FU}^{-1}$ (i.e. the average Co magnetic moment $m_{Co}(T = 0 \text{ K}) = 1.64 \ \mu_B/\text{Co}$) in the compound Er_2Co_{17}.

Acknowledgments

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