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A neutron diffraction study of the hexagonal Laves phases, $Ho(Co_{0.667}Ga_{0.333})_2$ and $Er(Co_{0.667}Ga_{0.333})_2$: Co/Ga site preferences and magnetic structure

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ABSTRACT

$RE(Co_{0.667}Ga_{0.333})_2$ (*RE* = Ho, Er) were characterized by neutron powder diffraction (NPD). Rietveld refinement of the NPD data at 280 K confirms the hexagonal $MgZn_2$-type structure ($P6_3/mmc$), in accordance with the previous XRD results. Co/Ga occupancies on the 2*a* and 6*h* sites were refined to be 0.46/0.54(2) and 0.74/0.26(2), respectively, indicating a preference of Ga for the 2*a* site and of Co for the 6*h* site. Both materials are ferromagnetic, $\boldsymbol{k}$ = (000), with measureable moments only on the *RE* sites. The magnetic (Shubnikov) space group is $P6_3/mm'c'$ for the Er phase. Co moments refined to values of 0.1–0.3 μ_B and are effectively zero within 3σ. The Er moment, 6.07(8) μ_B at 3.5 K is parallel to the *c* axis and this orientation persists up to T_C = 18.5 K, while the Ho moment has components along both the *a* and *c* axes with a total moment of 6.3(1) μ_B at 3.5 K. Both moments are much reduced from the free ion values, 9 μ_B (Er) and 10 μ_B (Ho), which is attributed to crystal field effects. In addition, the Ho moment angle with the *c* axis is strongly temperature dependent, being roughly constant, ~ 24(6)° from *T* = 29 K to ~25 K, then increasing with decreasing temperature to 44(1)° at 3.5 K. Magnetic small angle neutron scattering (MSANS) was observed over a *Q*-range from 0.14 $Å^{-1}$ to 0.50 $Å^{-1}$ in both samples. The integrated MSANS of the Er phase peaks near T_C, then decreases monotonically with decreasing temperature, behavior typical for a simple ferromagnet. On the other hand, the integrated MSANS for the Ho phase exhibits a weak peak around T_C = 31 K, followed by a plateau to 25 K and a strong increase with decreasing temperatures, which tracks the evolution of the Ho moment angle with the *c* axis.

1. Introduction

The $RECo_2$ (*RE* = rare earth) compounds have been well studied [1–5]. While all $RECo_2$ adopt the same cubic $MgCu_2$-type structure, their magnetic properties are quite different with regard to the rare-earth element. A novel type of short-range order, an exchange enhanced paramagnetism, has been identified in nonmagnetic $ScCo_2$, YCo_2, and $LuCo_2$, while a long-range magnetic order is found in $RECo_2$ with magnetic rare-earth elements [6]. In the latter case, the Co sublattice is driven into a ferromagnetic state by an *f-d* exchange field and the moment in the ordered state is between 0.8 and 1 μ_B. The light $RECo_2$ phases are ferromagnetic with the Co and *RE* sublattice coupling parallel. On the other hand, the heavy $RECo_2$ phases are best characterized as ferrimagnetic wherein the *RE* moments couple anti-parallel to the Co moments [7]. The magnetic phase transition for at least some members of the series, *RE* = Dy, Ho and Er, is apparently first order and thus, these have been evaluated recently as potential magnetocaloric materials [3,8]. Therefore, the studies on the heavy $RECo_2$-based phases have been attracting increasing attention.

While the $RECo_2$ materials adopt the cubic ($Fd\bar{3}\ m$) Laves phase structure, substitution of Ga for Co induces the formation of the hexagonal ($P6_3/mmc$) $MgZn_2$-type structure in the $RE(Co_{0.667}Ga_{0.333})_2$ series [9]. All studied $RE(Co_{0.667}Ga_{0.333})_2$ (*RE* = Gd, Tb, Dy, Ho and Er) phases show a long-range order but the Curie temperatures are reduced by a factor of ~ 2.5 from the parent $RECo_2$ phases [3,9] (Fig. 1). Apparent ferromagnetic behavior is observed for *RE* = Gd, Tb and Dy, whose Weiss temperature/Curie temperature ratios are near unity, which is typical for ferromagnets. Also, the effective magnetic moments, μ_{eff} were equal to the *RE* only values, suggesting zero contribution from the Co/Ga sublattice in the paramagnetic region. Exceptions to this trend occur for *RE* = Ho and Er, whose Weiss temperature/Curie temperature ratios are 0.66 and −0.65, respectively

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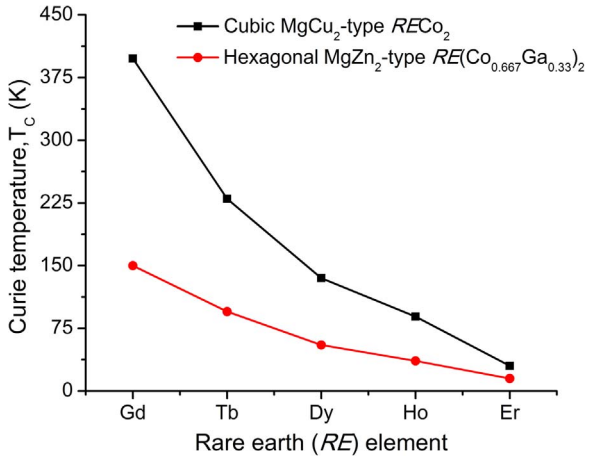

Fig. 1. The Curie temperature of cubic $RECo_2$ and hexagonal $RE(Co_{0.667}Ga_{0.333})_2$ (RE = Gd, Tb, Dy, Ho, and Er).

(the Weiss temperature is negative for Er). As well, μ_{eff} values exceeded those for the RE ions only, suggesting a non-zero Co/Ga contribution and the possibility of a moment on that sublattice.

Finally, there are two Co/Ga sites in the $MgZn_2$-type structure, and the Co/Ga occupancies could not be refined due to their similar X-ray atomic scattering factors. On the other hand, the neutron scattering lengths, b, are significantly different for Co (b = 2.49 fm) and Ga (b = 7.29 fm), and thus they are readily distinguished by neutron diffraction [10]. In this work, neutron powder diffraction (NPD) was used to determine the magnetic structures and the magnetic moments at each site of the hexagonal $MgZn_2$-type $RE(Co_{0.667}Ga_{0.333})_2$ (RE = Ho, Er) phases and the Co/Ga occupancies.

2. Experimental section

2.1. Synthesis

The starting materials of $RE(Co_{0.667}Ga_{0.333})_2$ (RE = Ho, and Er) phases are RE (99.9 wt%, distilled grade, Metal Rare Earth Limited, China), Co (99.98 wt%, Alfa Aesar), and Ga (99.999 wt%, Alfa Aesar) pieces. The $RE(Co_{0.667}Ga_{0.333})_2$ alloys with a total mass of ~3 g were arc-melted 3 times to ensure homogeneity. During re-melting process, the samples were turned over as fast as possible to prevent sample cracking during cooling. The cast $RE(Co_{0.667}Ga_{0.333})_2$ (RE = Ho, and Er) alloys were wrapped in Ta foil, sealed in evacuated silica tubes, heated to 1000 °C at 100 °C/hour in the box furnaces and annealed for 72 h before being quenched in cold water.

2.2. Neutron powder diffraction

Neutron powder diffraction was performed on the C2 diffractometer at the Canadian Neutron Beam Centre at Chalk River, Ontario. The samples of ~ 2 g were mounted on a cylindrical vanadium container with a top-loading closed-cycle refrigerator. The data were collected using the neutron beams with a wavelength of 2.369(1) Å at 3.5 K, 280 K, and other temperatures between 3.5 K and Curie temperature (T_C) for 2θ = 3.0–83.1°, and with a wavelength of 1.327(1) Å at 3.5 K and 280 K for 2θ = 36.9–117.0°. The 2θ step size was 0.1° for all the data collection. The FullProf program [11] was used to refine the crystal and magnetic structures.

2.3. Electronic band structure calculations

To study the band structure of hexagonal $MgZn_2$-type $Er(Co_{0.667}Ga_{0.333})_2$ phase and understand the absence of Co moments, tight-binding, linear-muffin tin orbital calculations with the atomic sphere approximation [12] (TB-LMTO-ASA) as implemented in the Stuttgart program [13] were performed. The lattice parameters and atomic coordinates were taken from the previous single crystal X-ray refinements [9]. All 4f electrons were treated as core electrons. Exchange and correlation were treated by the local density approximation (LDA) [14]. A scalar relativistic approximation [15] was used to account for all relativistic effects except spin-orbit coupling. According to the atomic sphere approximation (ASA), overlapping Wigner-Seitz (WS) cells were constructed with radii making the overlapping potential to be the best approximation to the full potential. To satisfy the overlap criteria of the TB-LMTO-ASA model, space-filling empty spheres were included in the unit cell by the automatic sphere generation [16]. The basis set included 6s, 6p and 5d orbitals for Er, 4s, 4p, 3d, orbitals for Co, 4s, 4p, and 4d orbitals for Ga.

3. Results and discussion

3.1. Crystal structure

Rietveld refinement of the neutron powder diffraction data of $RE(Co_{0.667}Ga_{0.333})_2$ (RE = Ho, and Er) are consistent with the $MgZn_2$-type structure, conforming the previous X-ray diffraction results [9] (Table 1). There are three crystallographic sites in the hexagonal $MgZn_2$-type structure: 2a, 4f and 6h. The RE atoms occupy the 4f site, while Co/Ga are distributed over the 2a and 6h sites but their occupancies could not be previously refined due to their similar X-ray atomic scattering factors (Z_{Co} = 27 and Z_{Ga} = 31). However, as already noted, there is significant neutron scattering length contrast [10]. Herein, the Co/Ga occupancies were refined employing the neutron powder diffraction with a wavelength of 1.327(1) Å at 280 K.

Due to strong correlations, the site occupancy and displacement parameter were not refined simultaneously. The occupancies of RE atom sites were fixed at 100%, which was confirmed by the single crystal X-ray diffraction in our previous work [9]. Displacement parameters for the three sites were varied for a set of fixed occupancies for the 2a site, which spanned the full range of possibilities. The results for both materials in terms of the Ga fraction, x, of the 2a site are shown in Fig. 2. The χ^2 value is minimized when the isotropic displacement parameters on the 2a and 6h sites are roughly equal. At the point of intersection, x is about 13/24, i.e. Ga occupies 13/24 (0.54) of the 2a sites, while the remaining 11/24 (0.46) fraction is taken by Co. Because the total Co/Ga ratio is 2, the Co and Ga occupancies on 6h sites are 53/72 (0.74) and 19/72 (0.26), respectively (Table 2). Note that the results are essentially the same for Ho and Er

Table 1
Unit cell parameters of the $MgZn_2$-type $RE(Co_{0.667}Ga_{0.333})_2$ phases (RE = Ho and Er, XRD and NPD were collected at room temperature and 280 K, respectively).

Sample	Method	λ/Å	Structure type	a/Å	c/Å	R_P
$Ho(Co_{0.667}Ga_{0.333})_2$	XRD	1.5406	$MgZn_2$-type	5.2064(1)	8.4228(1)	6.22
$Ho(Co_{0.667}Ga_{0.333})_2$	NPD	1.327 (1)	$MgZn_2$-type	5.2027(3)	8.4248(7)	3.89
$Ho(Co_{0.667}Ga_{0.333})_2$	NPD	2.369 (1)	$MgZn_2$-type	5.2048(6)	8.429(1)	3.52
$Er(Co_{0.667}Ga_{0.333})_2$	XRD	1.5406	$MgZn_2$-type	5.1851(1)	8.4115(1)	5.53
$Er(Co_{0.667}Ga_{0.333})_2$	NPD	1.327 (1)	$MgZn_2$-type	5.1853(4)	8.4159(9)	3.76
$Er(Co_{0.667}Ga_{0.333})_2$	NPD	2.369 (1)	$MgZn_2$-type	5.1871(6)	8.418(1)	4.46