JOURNAL OF APPLIED PHYSICS **105**, 07E119 (2009)

Moment variation in Er$(Co_{1-x}Fe_x)_2$ Laves phase: Magnetic measurements and Mössbauer spectroscopy study

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(Presented 14 November 2008; received 14 September 2008; accepted 3 December 2008; published online 5 March 2009)

Er$(Co_{1-x}Fe_x)_2$ cubic Laves phases have been studied by magnetic measurements and ^{57}Fe Mössbauer spectroscopy. With increasing x from 0 to 0.8, the magnetization decreases from 6.8 to $4.8\mu_B$/f.u. (5 K), then it slightly increases to $5.2\mu_B$/f.u. as x increases from 0.8 to 1.0. Assuming a fixed Er moment of $9\mu_B$ (Er metal value), the corresponding moment of Co(Fe) shows a maximum at $x=0.8$ due to the antiparallel coupling between the Er and Co(Fe) sublattices in the compounds. The ^{57}Fe spectra can be analyzed in terms of two distinct six-line ^{57}Fe patterns with intensities in the ratio of 1:3, indicating that the easy magnetization direction is along [111] in these compounds. The Fe content dependence of the hyperfine fields at the ^{57}Fe nuclei in Er$(Co_{1-x}Fe_x)_2$ shows the same tendency as that of the moment variation of Co(Fe), following a 3*d*-type Slater–Pauling dependence. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3073936]

I. INTRODUCTION

The cubic Laves phases RM_2 (R=rare earth elements and M=Co, Fe, and Ni) have long been studied for their interesting magnetic properties, which arise from the coexistence and interaction of the magnetic moments of the highly localized 4*f* electrons of the rare earth elements and of the itinerant 3*d* electrons of the transition elements.[1–3] In RFe$_2$ Laves phase, Fe possesses an intrinsic magnetic moment and the Fe sublattice is ferromagnetically ordered. In RCo$_2$ compounds, the Co 3*d* band states are "nearly magnetic" and at the borderline of the onset of 3*d* magnetism. For R=Dy, Ho, and Er, the Co moment is induced by the exchange field, H_{fd}^{Co}, due to the ferromagnetically ordered 4*f* magnetic moments and the magnetic phase transition is first order. The structure and magnetic properties of RCo$_2$ are sensitive to the substitution of Co by other elements such as Fe, Ni, Al, Si, etc.[2] For the system with Fe and Ni, a solid solubility exists. The Curie temperature T_C and the average magnetic moment of 3*d* elements increases rapidly with the replacement of Co by Fe.[4] Mössbauer measurements show that both the ^{57}Fe and ^{161}Dy magnetic fields strongly depend on the number of 3*d* electrons in the band in Dy(Fe,Co)$_3$. Moreover, these fields form two different Slater–Pauling curves.[5]

Recently, much more attention has been paid to RCo$_2$ based alloys with R=Dy, Ho, and Er, which show a large magnetocaloric effect (MCE) due to a first order magnetic transition at T_C.[6–12] In our previous work, we investigated the MCE in Er$(Co_{1-x}Fe_x)_2$ compounds and found that the MCE and the order of magnetic transition at T_C were very sensitive to the Fe content.[13] In order to gain more insights on the magnetic state of 3*d*(Co,Fe) sublattice, we study the effect of Fe content on the magnetic properties in Er$(Co_{1-x}Fe_x)_2$ by magnetic measurements and Mössbauer spectroscopy.

II. EXPERIMENTAL METHODS

Alloys with nominal composition Er$(Co_{1-x}Fe_x)_2$ (x=0–1) were prepared in purified Ar atmosphere by a triarc melting method. The ingots were annealed at a temperature of 1073 K for a week in evacuated quartz tubes. The results of x-ray diffraction analysis indicate a single phase with the MgCu$_2$ cubic structure for all compounds. The lattice constants were determined by Rietveld method using GSAS code.[14] Samples with Curie temperatures higher than 300 K were measured by thermomagnetometry to determine T_C using a Perkin–Elmer thermogravimetric analyzer (TGA-7) in a small magnetic field gradient. For samples with Curie temperatures less than 300 K, T_C was determined from the temperature dependence of the ac-susceptibility (χ_{ac}), using a Quantum Design physical property measurement system magnetometer. The magnetometer was also used for dc-magnetization measurements in fields of up to 9 T.

The Mössbauer spectra for Er$(Co_{1-x}Fe_x)_2$ samples were obtained in a standard transmission geometry with a 1 GBq ^{57}CoRh source on a constant acceleration spectrometer, which was calibrated against an α-iron foil at room temperature. The ^{57}Fe spectra are measured at room temperature for the samples of Er$(Co_{1-x}Fe_x)_2$ with x=0.25–1.0. Spectra were fitted using a standard nonlinear least-squares minimization method.

III. RESULTS AND DISCUSSION

A. Structure and magnetic moments of Er$(Co_{1-x}Fe_x)_2$ compounds

As expected, x-ray diffraction analyses confirmed that all the annealed compounds Er$(Co_{1-x}Fe_x)_2$ were of single

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0021-8979/2009/105(7)/07E119/3/$25.00

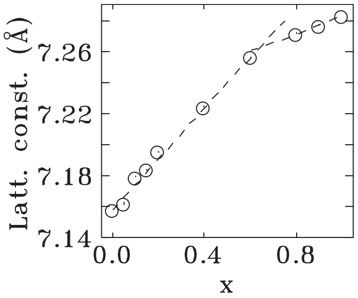

FIG. 1. Lattice constants for $Er(Co_{1-x}Fe_x)_2$ compounds. The line is drawn as a guide to the eye.

phase with the cubic $MgCu_2$ structure. As shown in Fig. 1, the lattice constant a, increases almost linearly from 7.1578(4) to 7.2560(6) Å for $0 \leq x \leq 0.6$, then increases slowly and reaches 7.2827(3) Å at $x=1.0$.

All the samples with $x \geq 0.25$ have a Curie temperature higher than 435 K, as indicated by magnetic measurements. Magnetization at 5 K was measured under a maximum magnetic field of 6 T for $Er(Co_{1-x}Fe_x)_2$ compounds. The alloys display a typical soft ferromagnetic behavior. The magnetization approaches its saturation value M_s at low magnetic fields. M_s, derived from $M-1/H$ plots, are shown in Fig. 2. In $Er(Co_{1-x}Fe_x)_2$ Laves phase, the $3d$(Co,Fe) magnetic moments are oriented antiparallel to the Er moments. Assuming that the magnetic moment of Er remains unchanged ($9.0\mu_B$/Er, the theoretical value in the ferromagnetic Er metal), the Co(Fe) magnetic moments, derived from $M_{\text{Co,Fe}} = (M_R - M_s)/2$, are also displayed in Fig. 2.

As shown in Fig. 2, with increasing x from 0 to 0.8, the magnetization decreases from 6.8 to $4.8\mu_B$/f.u. (5 K), then it slightly increases to $5.2\mu_B$/f.u. unit as x increases from 0.8 to 1.0. The corresponding moment of Co(Fe) shows a maximum at $x=0.8$ due to the antiparallel coupling between the Er and Co(Fe) sublattices in the compounds.

B. Mössbauer spectra for $Er(Co_{1-x}Fe_x)_2$ Laves phases

All $Er(Co_{1-x}Fe_x)_2$ alloys have cubic $MgCu_2$-type structure. The substitution of Co by Fe is randomly distributed at the $16d$ sites. In the absence of a magnetic field, all the iron sites are equivalent, and the nuclear quadrapole interaction is axially symmetric. However, the iron atoms may no longer be equivalent in the magnetic ordering state due to the magnetic crystalline anisotropy. The ^{57}Fe spectra split into two six-line patterns with intensities in the ratio 1:3 for all these samples. This results from the presence of a nonzero quadrapole interaction due to the magnetic crystalline anisotropy axis along the [111] direction in the compounds. As an example, Fig. 3 shows the Mössbauer spectra for $Er(Co_{1-x}Fe_x)_2$ with $x=0.25$, 0.4, 0.6, and 1.0.

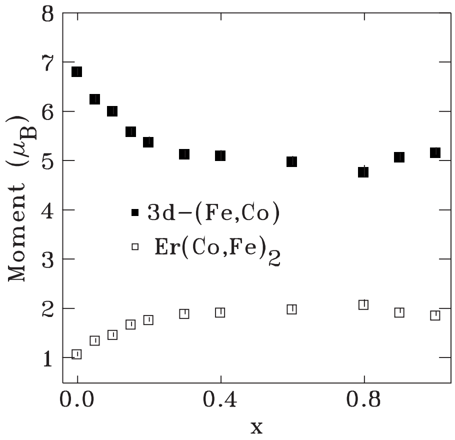

FIG. 2. Magnetic moments for $Er(Co_{1-x}Fe_x)_2$ as a function of Fe content. The open and close square symbols stand for the moment for $Er(Co_{1-x}Fe_x)_2$ per formula unit and for $3d$ atom (Fe,Co), respectively.

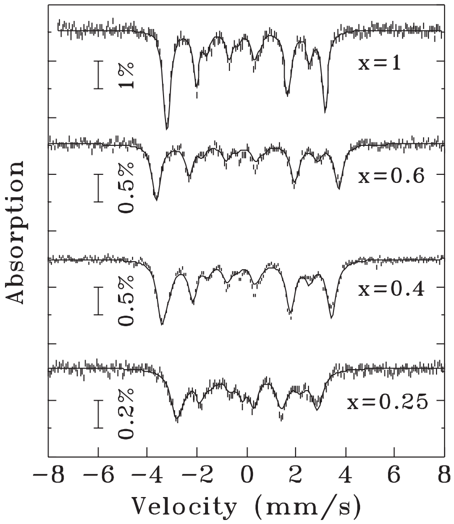

FIG. 3. Mössbauer spectra for $Er(Co_{1-x}Fe_x)_2$ with $x=0.1$, 0.4, 0.6, and 1.0, recorded at room temperature.

There is an approximately linear correlation between the mean hyperfine field B_{hf} and the mean magnetic moment. The $3d$ atomic moments could be estimated from the measured hyperfine field B_{hf}. A conversion constant of 12.5 T/μ_B was reported for cubic Laves phase of AFe_2 ($A=4f$ elements, Y, Zr, etc.) by Wallace.[15] Here, a slightly lower conversion constant of $C=10.8$ T/μ_B is adopted due to the fact that the Mössbauer and magnetic measurements are done at room temperature and 5 K, respectively. Figure 4 displays the $3d$ atomic magnetic moments derived from the measured hyperfine field B_{hf} with a conversion constant of

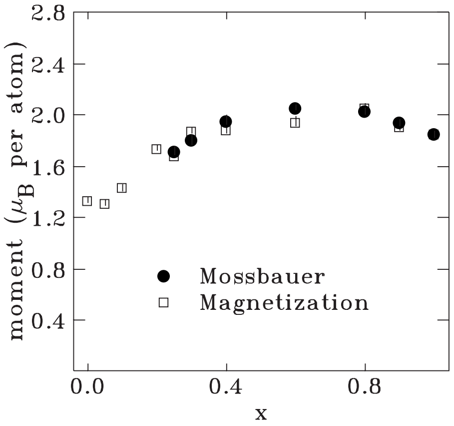

FIG. 4. Magnetic moments of $3d$ atoms (Fe,Co) as a function of Fe content. The square and circle symbols stand for the moment values derived from magnetic measurement and Mössbauer measurements, respectively.

$C=10.8\ \mathrm{T}/\mu_B$. For comparison, the $3d$ moments derived from magnetic measurements (Fig. 2) are also shown in Fig. 4. The $3d$ moments derived from the two methods are, within error, in good agreement. The $3d$ moments of $\mathrm{Er(Co_{1-x}Fe_x)_2}$ show a maximum near $x=0.7$ (or as x is between 0.6 and 0.8). In fact, the magnetic moments for $\mathrm{Co_{1-x}Fe_x}$ alloys show a maximum at $x=0.7$, which could be explained based on Slater–Pauling curves. It could be concluded that the moment variation of Co(Fe), following a $3d$-type Slater–Pauling dependence in $\mathrm{Er(Co_{1-x}Fe_x)_2}$ Laves phases. Similar situations are also observed in $\mathrm{Dy_x(Fe,Co)_y}$ alloys with the ratio of $x/y=1:2$, 1:3, and 2:17.[5]

The results mean that the Fe and Co seem having the same value of magnetic moments in $\mathrm{Er(Co_{1-x}Fe_x)_2}$ Laves phases. The theoretical calculation of $3d$-moments in pseudobinary $\mathrm{Y(Fe_xCo_{1-x})_2}$ are performed by Eriksson *et al.*[16] The authors have shown that the Slater–Pauling curve of the $3d$-moments with a maximum can be explained in a rigid-band model by the increase of the number of $3d$-electrons and the simultaneous decrease of the width of the exchange splitted $3d$-bands with increasing Co concentration. The calculation results are in good agreement with the experiment results.[17,18] It is therefore conceivable that the same mechanism as in $\mathrm{Y(Fe_xCo_{1-x})_2}$ Laves phase is also responsible for the concentration dependence of the $3d$-moment in $\mathrm{Er(Co_{1-x}Fe_x)_2}$ system. A quantitative explanation of the observed Slater–Pauling behavior will have to await detailed calculations for the $\mathrm{Er(Co_{1-x}Fe_x)_2}$ Laves phases.

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