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Field induced metamagnetic transition of $ErCo_3$ studied by NMR

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Abstract

Magnetic field dependence of ^{59}Co NMR resonance frequencies in ferrimagnetic $ErCo_3$ was measured in fields parallel and perpendicular to the *c*-axis of the crystal up to 8 T at 4.2 K. The zero field powder spectrum at 4.2 K shows three resolved lines at 23, 65, and 96 MHz, which correspond to 3b, 6c, 18h sites of Co, respectively. When field is applied along the *c*-axis, the resonance frequencies of 96 MHz line increase at about 10.01 MHz/T with increasing field, while those of 23 and 75 MHz lines decrease at the same rate. This means that the hyperfine field H_{hf} is negative only for the Co 18h site, whereas at 3b- and 6c-Co it is positive. The positive H_{hf} is resulted from a large contribution of unquenched 3d orbital moments. When field is applied perpendicular to the *c*-axis, the frequencies of all three resonance lines increase with increasing field, which means that H_{hf} is negative at all the three Co sites. The resonance frequencies abruptly change around the field between 2 and 3 T due to the field induced metamagnetic transitions caused by the rotations of Er and Co magnetic moments towards the direction of the applied field from the *c*-axis.

Keywords: NMR; Ferrimagnet; Rare earth transition-metal compound; Metamagnetism; Itinerant electron metamagnetism

1. Introduction

The RCo_3 compounds (R: rare-earth element) crystallize in the rhombohedral $PuNi_3$-type structure with two and three nonequivalent crystallographic sites for R and Co, respectively [1]. YCo_3 is a very weak itinerant ferromagnet ($T_c = 300$ K). Metamagnetic transition occurs in magnetic field of 82 T. In RCo_3 compounds with magnetic R-elements, the d-sublattice magnetization is modified owing to the strong molecular field of rare-earth sublattice. $ErCo_3$ was found to be a ferrimagnet ($T_c = 401$ K) in which the moments of Er and Co sublattices were oriented in opposite directions along the *c*-axis of the crystal [2].

Recently, a temperature induced phase transition was found at 100 K [3,4]. From the zero field NMR of ^{59}Co in $ErCo_3$ at 4.2 K using powdered sample, three Co resolved lines were obtained at 23, 65, and 96 MHz, which corresponds to 3b, 6c, 18h sites, respectively [5,6]. Temperature induced metamagnetic transition around 100 K was also confirmed from the temperature dependence of the Co sublattice magnetizations obtained by NMR [5,6]. According to the results of neutron diffraction [2], the field induced metamagnetic transition was found around 3 T at 4.2 K when the field was applied perpendicular to the *c*-axis. The moments of one of the two Er sites remains nearly oriented along the *c*-axis while those of the other Er sites rotate through an angle of 55°. In order to investigate the behavior of the magnetic moments in $ErCo_3$, NMR measurements of ^{59}Co in $ErCo_3$ have been carried out focusing on the field dependence of the Co sublattice magnetizations.

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2. Experimental

The polycrystalline $ErCo_3$ sample material was prepared in a high-frequency induction furnace under argon atmosphere in a water-cooled copper boat. The $ErCo_3$ ingot was subsequently annealed at 850 °C for 24 h. The sample used in this investigation was confirmed to be crystallized of the stoichiometric ratio of 1:3. In order to align the magnetic easy axis along the field, powdered sample was oriented in an external field and fixed in paraffin at room temperature. The NMR spectra were measured by frequency and magnetic field sweeps at 4.2 K using a homemade phase-coherent pulsed spectrometer.

3. Results and discussion

The external magnetic field dependence of resonance frequencies of ^{59}Co NMR was carried out in fields parallel and perpendicular to the *c*-axis up to 8 T at 4.2 K (the *c*-axis is the easy axis). Fig. 1 shows the field dependence of the Co NMR frequencies at each Co site when fields are applied along the *c*-axis. The resonance frequencies of 96 MHz line increase at about 10.01 MHz/T with increasing field, while those of 23 and 65 MHz lines decrease at the same rate. All three Co frequencies in external fields change at the rate of 10.01 MHz/T which is in agreement with the gyromagnetic ratio γ of ^{59}Co isotope. This means that all resonance lines are ascribed in Co and all Co-moments are aligned collinear to the applied field. The hyperfine field H_{hf} at Co-nuclei is parallel to the external field for 18h-Co whereas antiparallel at the 3b and 6c sites. The frequency ω changes against the external field as follows,

$$\omega_{\parallel} = \gamma |H_0 - H_{hf}| \quad (1)$$

We find $H_{hf} = +2.3$, +6.5, and −9.6 T for 3b(Co_I), 6c(Co_{II}), and 18h(Co_{III}) sites, respectively, since all Co-moments are antiparallel to the Er-moments. Neglecting transferred and dipolar fields, one has $H_{hf} = A_s\mu_s + A_o\mu_o$ with μ_s for spin and μ_o for orbital moment and the corresponding coupling constants $A_s = -13\,T/\mu_B$ and $A_o = 65\,T/\mu_B$ [7]. The unusual positive sign of H_{hf} is, thereby, due to an unquenched orbital moment. Total Co-moments of $\mu_{Co} = 1.2$, 2.0, and 1.4 μ_B have been determined from neutron diffraction for 3b(Co_I), 6c(Co_{II}), and 18h(Co_{III}) sites, respectively [4]. Therefore, we can estimate the size of μ_s and μ_o from H_{hf} and $\mu_{Co} = \mu_s + \mu_o$. One finds $\mu_s = 0.97$, 1.58, and 1.29 μ_B and $\mu_o = 0.23$, 0.42, and 0.11μ_B for 3b(Co_I), 6c(Co_{II}), and 18h(Co_{III}) sites, respectively.

Fig. 2 shows the field dependence of the Co NMR frequencies at each Co site when field is applied perpendicular to the *c*-axis. The frequencies of all three resonance lines increase with increasing field. They abruptly change around the field between 2 and 3 T due to a field induced metamagnetic transition caused by the rotations of Er and Co magnetic moments towards the direction of the applied field from the *c*-axis. Ninety six and 23 MHz lines are divided into two lines in fields above about 2 T. The upper frequency part corresponds to the resonance line assigned to the majority of Co for both sites with the moments inclining towards the direction of the applied field. The intensities of the resonance lines at the lower frequency part, which is due to the residual magnetic moments keeping in the *c*-axis, decrease gradually with increasing fields. This means that the part of the residual magnetic moments in the *c*-axis are flips towards the direction of the magnetic field. The resonance frequency of 65 MHz line increases almost continuously with increasing field passing through about 2.5 T. Since the shift of frequency versus field for 65 MHz line below 3 T was very small, the measurements of the resonance frequencies could be only carried out by frequency sweep method. Symbols of open circles, squares and lozenges, and solid triangles for each Co site show the resonance frequencies obtained by field-down and field-up process, respectively. The hysteresis in the field dependence of the frequencies is observed in the region below about 1 T and between about 2 and 3 T.

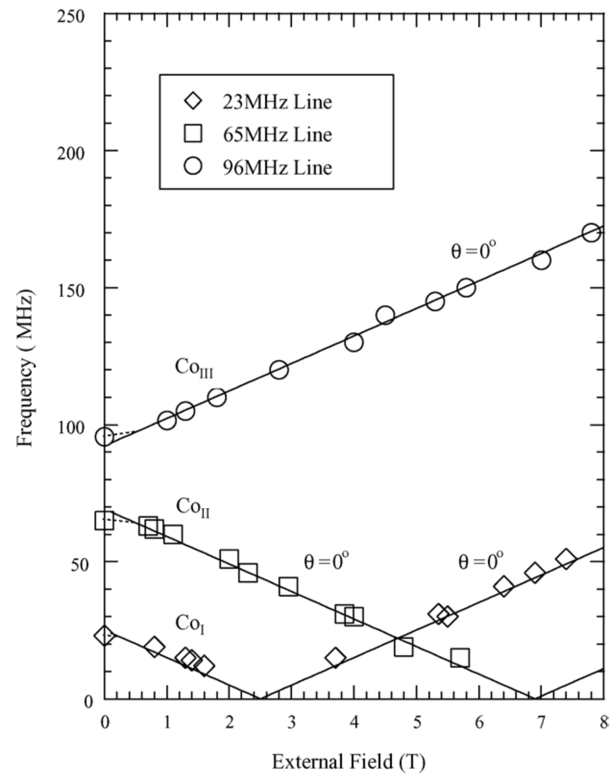

Fig. 1. External field dependence of ^{59}Co NMR frequencies in $ErCo_3$ at 4.2 K in the case of external field parallel to the *c*-axis. Hyperfine field at Co_{III} site is parallel to the external field whereas those at Co_I and Co_{II} are antiparallel to it. Broken lines below 0.5 T show deviations of frequencies from the rigid lines due to the influence of the demagnetization field.

The field induced metamagnetic transitions caused by rotations of Er and Co magnetic moments inclining with an angle θ from the *c*-axis towards the direction of applied field can be estimated by the following equation for the resonance

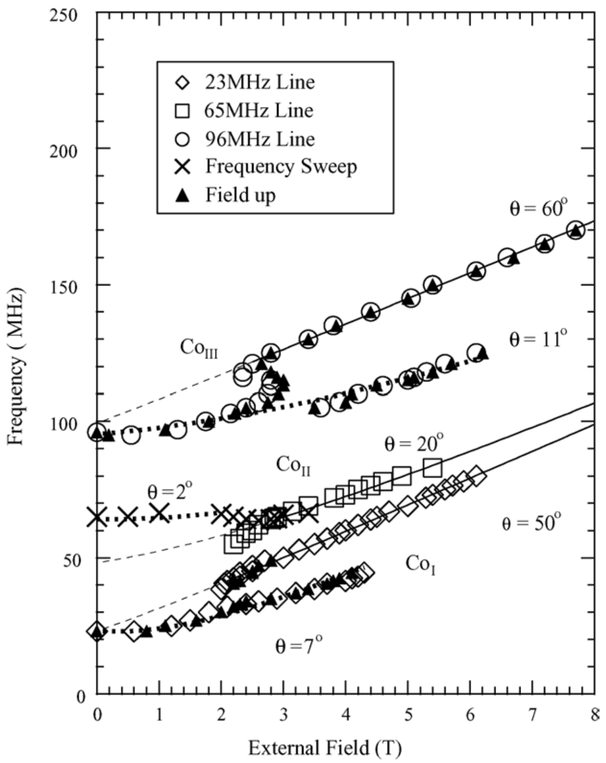

Fig. 2. External field dependence of ^{59}Co NMR frequencies in $ErCo_3$ at 4.2 K in the case of external field perpendicular to the c-axis. The upper branches of 96 and 23 MHz lines above 3 T are due to the moments flipped toward the direction of applied field from the c-axis. The lower branches are due to residual magnetic moments still keeping in the direction of the c-axis. The intensity of those lines decreases with increasing applied field.

frequency,

$$\omega_{\perp} = \gamma \sqrt{H_0^2 - 2H_{\rm hf}H_0 \sin\theta + H_{\rm hf}^2} \tag{2}$$

The moments of the 96 MHz (Co_{III}) and 23 MHz (Co_I) lines are inclined by 60° and 50° from c-axis, respectively, whereas that of 65 MHz(Co_{II}) line is inclined by a small angle of 20°. Also the moments about the lower part lines of 96 and 23 MHz lines above 3 T are only inclined by 11° and 7°, respectively. This means that the moments for the lower part lines remains in the direction of nearly c-axis. With increasing field, the intensity of the lower part decreases and then all of them incline the same angles of 60° for 96 MHz (Co_{III}) and 50° for 23 MHz (Co_I) lines at last. In the case of 65 MHz line, the moments align to nearly c-axis below and above 3 T, and the magnitude of the hyperfine field is changed corresponding to the frequency shift from 65 to 50 MHz.

It was revealed by neutron diffraction [2] that the moments on Er_{II} are flipping by 55° from c direction towards the direction of applied field above 3 T whereas Er_I remains nearly oriented along the c-axis (flipping angle of 15° from the c direction). The moments of Er and Co keep always to align to opposite directions. The average angle of Co-moments is 41°. These results are almost consistent with our Co data obtained by NMR. It is reasonable understood as follows: Co_{II}(6c) sites are surrounding an Er_I site, the moments of both sites remains nearly in the direction of c-axis due to their strong interactions. On the other hand, Co_I(3b) and Co_{III}(18h) sites are in the vicinity of Er_{II} and the moments of Co and Er are tilted by nearly same angle from the c-axis.

From the analysis by Eq. (2), we can obtain $H_{\rm hf} = -2.3$, -4.8, and -9.9 T for 3b(23 MHz)-, 6c(65 MHz)-, and 18h(96 MHz)-Co sites, respectively. The hyperfine fields on ^{59}Co nuclei of all three Co sites have negative values after metamagnetic transitions. The value of hyperfine field for 96 MHz line keeps almost the same one after the metamagnetic transition whereas those for 23 and 65 MHz lines show large variations including their signs. We can try to estimate the magnitude of spin and orbital magnetic moments at each Co site tentatively since we can use the same values obtained from neutron diffraction mentioned above [4], supposing that the total moments do not change by the metamagnetic transition. One finds $\mu_{\rm s} = 1.03$, 1.73, and 1.29 $\mu_{\rm B}$ and $\mu_{\rm o} = 0.17$, 0.27, and 0.11 $\mu_{\rm B}$ for 3b-, 6c-, and 18h-Co sites, respectively. From these results, the contribution of the surviving unquenched orbital angular moments decreases on Co site by the occurrence of the change of magnetic anisotropy at each Co site by the metamagnetic transition when the field is applied perpendicular to the c-axis. Magnitude of spin and orbital moments obtained for 18h(96 MHz) sites is correct because the value of hyperfine field at this site does not change by the transition. However, the values of both moments obtained for other sites would be slightly incorrect because of a fairly large change of the hyperfine fields including their signs. Further investigation will be needed for the correct values of total Co-moment at each site when the magnetic field is perpendicular to the c-axis.

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