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Spin ordering transition and distortion of local site in spinel $Fe_{0.9}Cd_{0.1}Cr_2O_4$ by Mössbauer spectroscopy.

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Introduction

When a transition metal oxide has degeneracy, a structural phase transition resulting in crystal symmetry lowering can occur through the coupling between some electronic states and the relevant degrees of freedom to the lattice [1,2]. As has been reported previously spinel $FeCr_2O_4$ exhibits a phase transition from the cubic spinel symmetry to a tetragonal symmetry at around 135 K as a result of the Jahn–Teller effect [3]. The magnetic order of spinel $FeCr_2O_4$ consists of a ferrimagnetic component and a spiral component below T_N = 70 K [4]. It is expected that the substitution of Fe ion by Cd ion with nonmagnetic and relatively large ion radious in $FeCr_2O_4$ will bring about some changes on crystallographic and magnetic properties. In this paper, we report on the crystallographic and magnetic properties of $Fe_{0.9}Cd_{0.1}Cr_2O_4$, especially as studied by Mö ssbauer spectroscopy.

Experiment

A polycrystalline $Fe_{0.9}Cd_{0.1}Cr_2O_4$ sample was prepared with $0.9FeCr_2O_4$-$0.1CdCr_2O_4$ solid-solution. Structural characterization of the $Fe_{0.9}Cd_{0.1}Cr_2O_4$ sample was done with x-ray diffraction (XRD) measurement using Cu $K\alpha$ radiation and analyzed by Rietveld refinement. Magnetization measurement was performed in a vibrating sample magnetometer (VSM). Mö ssbauer spectra were collected to further investigate the magnetic properties of the sample, using a ^{57}Co (Rh) source in a constant acceleration mode.

Results and discussion

The crystal structure of $Fe_{0.9}Cd_{0.1}Cr_2O_4$ is normal cubic spinel with the lattice parameter a_0 = 8.402±0.001Å. Figure 1 shows the Mö ssbauer spectra of $Fe_{0.9}Cd_{0.1}Cr_2O_4$ at various absorber temperatures. Systematic changes in the Mö ssbauer spectrum with decreasing temperature from room temperature were found and attributed to the Jahn-Teller distortion. Below the T_N of 65 K, the spectrum displayed an asymmetric eight-line shape indicating a large electric quadrupole contribution with spin ordering. Magnetic hyperfine and electric quadrupole interactions at 4.2 K have been fitted, yielding the following results: H_{hf} = 186 kOe, ΔE_Q = 3.41 mm/s, $\theta = 75^o$, $\phi = 87^o$, η = 0.02, and R = 2.7, respectively. Each line width of the Mö ssbauer spectra above the T_N increases with increasing temperature and becomes the broadest at the 105 K. This change of line widths in the $Fe_{0.9}Cd_{0.1}Cr_2O_4$ suggest that some structural transition due to Jahn-Teller distortion appear at around 105 K. The appearance of electric quadrupole splitting of spectrum at room temperature can be attributed to the distorted oxygen tetrahedra environment around the Fe ions produced by the substitution of Cd ions. Figure 2 shows the temperature dependence of the magnetic hyperfine field (H_{hf}) for $Fe_{0.9}Cd_{0.1}Cr_2O_4$. As shown in Fig. 2, both the magnitude and slope of the magnetic hyperfine field change below 28 K for $Fe_{0.9}Cd_{0.1}Cr_2O_4$. This result suggests that the change in magnetic structure accompanied by a change in the supertransferred hyperfine field take place abruptly at around 28 K. In the magnetization data as a function of temperature, a weak anomaly is found at around 28 K. It may be attributable to the magnetic phase transition related to the spiral spin structure like that arising from pure $FeCr_2O_4$ [4]. The magnetization curve at 5 K show a ferromagnetic hysteresis loop with a coercivity value (H_c) of 7,950 Oe and a remnant magnetization (M_r) of 5.7 emu/g. The high coercivity and unsaturated magnetization may be a result of the magnetic anisotropy and nonlinear spin structure in sample.

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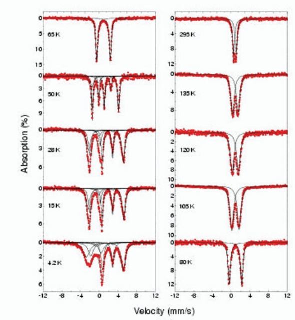

Fig. 1. Mössbauer spectra for $Fe_{0.9}Cd_{0.1}Cr_2O_4$ at various temperatures.

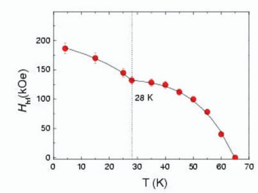

Fig. 2. Temperature dependence of the magnetic hyperfine field (H_{hf}) of $Fe_{0.9}Cd_{0.1}Cr_2O_4$.