Journal of Magnetics 12(4), 137-140 (2007)

Magnetic Properties and Crystalline Transition for the $NiCr_{1.7}Fe_{0.3}O_4$

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(Received 30 November 2007)

We have studied the temperature dependent magnetic properties and crystalline phase transitionn in small amount Fe doped nickel chromite. The Crystalline structure of $NiCr_{1.7}Fe_{0.3}O_4$ is spinel cubic (*Fd-3m*) structure with a lattice constant a_0 = 8.317 Å at room temperature. The magnetic Néel temperature (T_N) of the Fe doped nickel chromite sample is determined to be 250 K. The Mössbauer spectra exhibit that there are two magnetic phases with the two different sites for the Cr^{3+} ions. The spectrum at 4.2 K is fitted to two magnetic components of the magnetic hyperfine fields H_{hf} = 496 and 485 kOe. From the spectrum at 295 K, the electric quadrupole splittings are observed with large values of 0.49 and 0.50 mm/s, respectively. The values of the isomer shifts at all temperature ranges show that the Fe ions are ferric states. We are suggested that the dynamic Jahn-Teller distortion and anisotropic magnetic relaxation effects due to the crystalline phase transition.

Keywords : Mössbauer spectroscopy, nickel chromite, crystalline transition

1. Introduction

The chromites materials with spinel structure have been researched because of the multiferroic property. For the spinel chromite materials of ACr_2O_4 (A=Zn, Co etc.) [1, 2], its multiferroic property is due to the geometrical frustration by the B site ions of magnetic coupling. Among these, the $NiCr_2O_4$ exhibits uniqe magnetic properties due to temperature dependent crystalline phase transition. For the small amount Fe doped $NiCr_{2-x}Fe_xO_4$ system, there is a cubic to tetragonal (c/a<1) transition and a tetragonal (c/a<1) to orthorhombic transition for $x \approx 0.3$. [3]

In this paper we have studied the magnetic properties and the crystalline phase transition of the small amount Fe doped Ni chromite with the magnetization and Mössbauer spectroscopy measurements.

2. Experiment

The $NiCr_{1.7}Fe_{0.3}O_4$ was prepared by the sol-gel method. The single phase samples were obtained by annealing 12 hr in atmosphere at 1000°C. The x-ray diffraction pattern of the sample at room temperature was obtained with Cu-$K\alpha$ radiation by an x-ray diffractometer (X'PERT). A scanning speed of 2.4° advance in 2θ/min was used in order to optimize resolution of the closely spaced reflections. The magnetic properties at various temperatures were studied and the temperature dependent moment curve was measured by a vibrating sample magnetometer (VSM). The hyperfine magnetic properties of sample were measured with Mössbauer spectroscopy. A Mössbauer spectrometer of electromechanical type was used in the constant-acceleration mode with a ^{57}Co single-line source in a rhodium (Rh) matrix at room temperature. The liquid helium temperature was obtained with an exchange environment and a closed cycle system for He gas.

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3. Results and Discussion

The crystalline structure of $NiCr_{1.7}Fe_{0.3}O_4$ sample was determined to be a cubic spinel of *Fd-3m* with a lattice constant a_0 = 8.317 Å at 295 K by Rietveld refinement, while the Bragg R_B and R_F factors were 3.25 and 2.79%. It has been reported that with decrease in temperature the crystalline structure is changing from cubic spinel (C) to a tetragonal (T) symmetry and tetragonal to orthorhombic (O) [3].

Fig. 1(a) show the temperature dependence of the zero field cooled (ZFC) and field coold (FC) magnetization curves for the $NiCr_{1.7}Fe_{0.3}O_4$ under external field of 100 Oe. The magnetic Néel temperature (T_N) is determined by comparing the $d\sigma/dT$ curve of the ZFC measurements

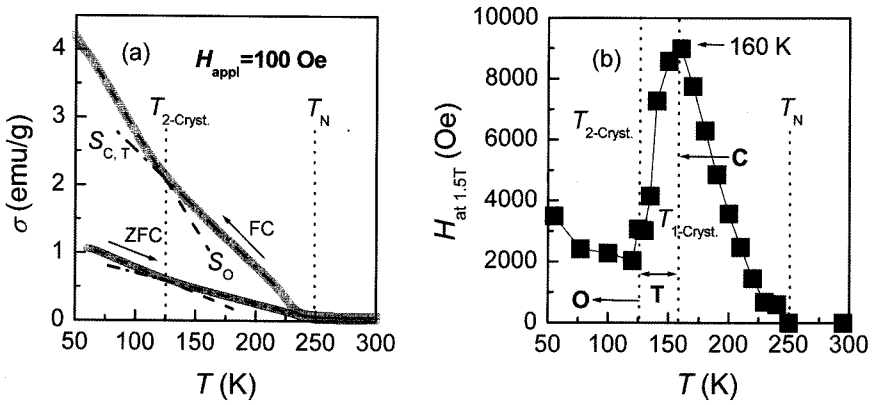

Fig. 1. (a) The temperature dependence of the zero field cooled (ZFC) and field coold (FC) magnetization curves under low external field of 100 Oe and (b) the coercive force at the external field of 1.5 T for the $NiCr_{1.7}Fe_{0.3}O_4$.

with the Mössbauer spectra analysis. The T_N is determined to be 250 K. The ZFC and FC curves are showing abnormal curve phase around 125 K.

Fig. 1(b) shows the temperature dependence of the coercive force under external field of 1.5 T. The value of the coercive force is very large because of the magnetic anisotropy effect below the magnetic Néel temperature. With decreasing temperature, the coercive force reaches the maximum value at 160 K. This temperature corresponds to the crystalline phase transition from cubic to tetragonal symmetry transition ($T_{1\text{-cryst.}}$) [3]. In Fig. 1(b), other abnormal phase are also shown about 125 K, which are present in ZFC and FC curves. This indicates the second crystalline phase transition ($T_{2\text{-cryst.}}$) from tetragonal to orthorhombic. The first crystalline transition is not clearly present in the ZFC and the FC curves in Fig. 1(a).

Mössbauer spectra of the $NiCr_{1.7}Fe_{0.3}O_4$ were measured at various temperatures ranging from 4.2 to 295 K (Fig. 2). The Mössbauer spectra indicate that there are two

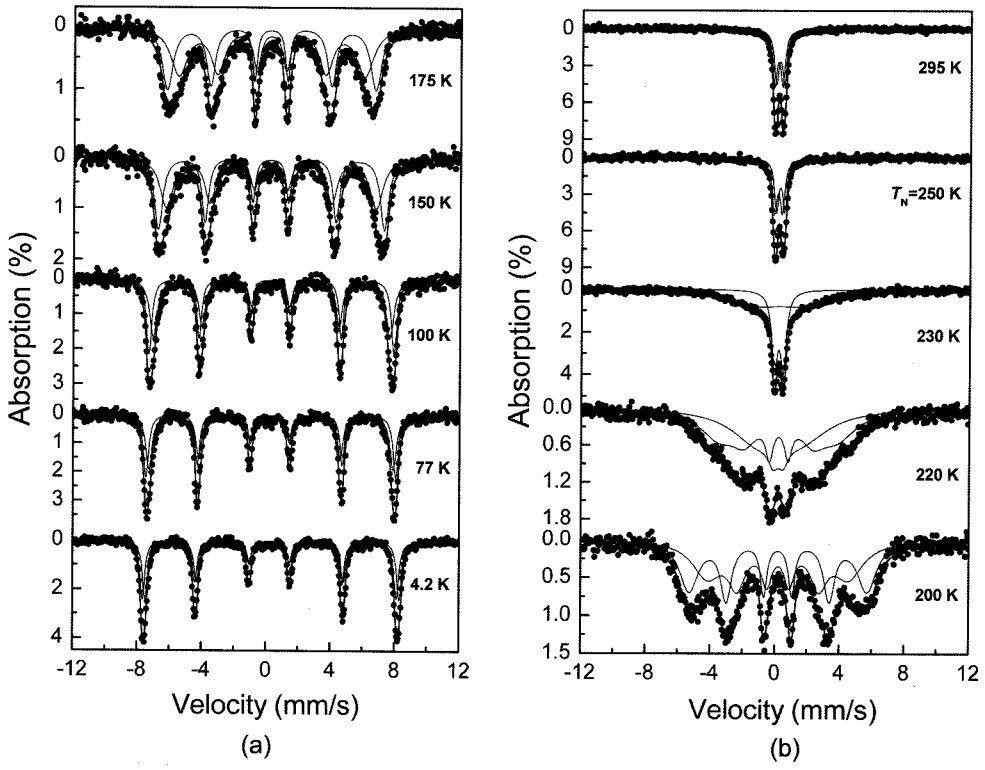

Fig. 2. The Mössbauer spectra for the $NiCr_{1.7}Fe_{0.3}O_4$ at various temperatures ranges.

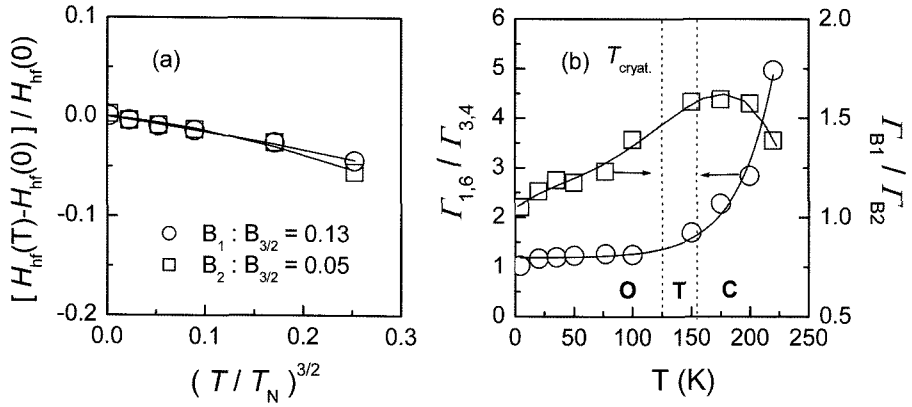

Fig. 3. (a) The Fractional change of the magnetic hyperfine field, H_{hf}, as a function of $(T/T_N)^{3/2}$, and (b) the temperature dependence of the line-widths ratio between 1st-6th and 3th-4th lines and B_1 and B_2 site for Mössbauer spectra of $NiCr_{1.7}Fe_{0.3}O_4$.

magnetic phases, which are due to the two different sites of the Cr^{3+} state [4, 5]. The Mössbauer spectrum of the Fe substituted nickel chromites at 4.2 K was different in its shape and the values of magnetic hyperfine field are different when compared with an inverse spinel Ni ferrite [6]. Namely, the substituted Fe ions make a uniform substitution with two different sites of Cr^{3+}.

The spectrum at 4.2 K was fitted to two magnetic components of the magnetic hyperfine fields $H_{hf} = 496$ and 485 kOe and isomer shifts $\delta = 0.268$ and 0.270 mm/s, respectively. The electric quadrupole splittings (ΔE_Q) have small value about 0.04 mm/s below the $T_{2\text{-cryst.}}$=125 K. In the spectrum between $T_{2\text{-crystl.}}$ (125 K) and T_N (250 K), this values were found to be nearly zero. From the spectrum at 295 K, the ΔE_Q are observed with large values of 0.49 and 0.50 mm/s, respectively. The values of the isomer shifts show that the states are ferric at all temperature ranges. The Mössbauer spectra below T_N show that the large line broadening due to the Jahn-Teller distortion and accompanying relaxation effects as shown in Fig. 2.

Fig. 3(a) shows the fractional change of the magnetic hyperfine field, $[H_{hf}(T)-H_{hf}(0)]/H_{hf}(0)$, as a function of temperature. The average magnetic hyperfine field linearly decrease with increasing temperature for $T/T_N<0.3$, $[H_{hf}(T)-H_{hf}(0)]/H_{hf}(0)=-0.089\ (T/T_N)^{3/2}]$. This value of 0.089 is very small than that of crystalline Fe [7]. This is due to the stabilization of short-wavelength spin waves in crystalline solids. Below the 100 K, the Mössbauer spectra do not show any relaxation effect with anisotropic hyperfine field fluctuations.

As shown in the Fig. 2, the Mössbauer spectra have sharp line shape below 100 K. This result can be explained with very small spin wave values in crystalline solids (Fig. 3(a)). However, above 100 K, we observed the rapid increase in the line broadening with increasing temperature. The asymmetric intensities are different from those of the powder pattern 3:2:1. This may be explained with the anisotropic relaxation effect.

The temperature dependence of the line-widths ratio between 1st-6th and 3th-4th lines and B_1 and B_2 site lines for Mössbauer spectra of $NiCr_{1.7}Fe_{0.3}O_4$ are shown in Fig. 3(b). The line broadening with increasing temperature originates from different temperature dependencies of the magnetic hyperfine fields at various ion sites as determined from the molecular field theory [8]. Also, the line broadening and difference in 1, 6 and 3, 4 line-widths suggest anisotropic hyperfine field fluctuation due to the crystalline phase transition and the dynamic Jahn-Teller distortion effect.

In summary, we have studied the magnetic properties and the crystalline transition for $NiCr_{1.7}Fe_{0.3}O_4$ with the Mössbauer spectroscopy and VSM measurement. The Mössbauer spectra and temperature dependence of magnetization curve measurements show the dynamic Jahn-Teller distortion and anisotropic magnetic relaxation effects due to the crystalline phase transition [3, 9].

Acknowledgements

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (KRF-2005-070-C00050).

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