ISSN (Print) 1226-1750
ISSN (Online) 2233-6656
Journal of Magnetics 19(2), 126-129 (2014) http://dx.doi.org/10.4283/JMAG.2014.19.2.126

Evidence of Spin Reorientation by Mössbauer Analysis

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(Received 21 February 2014, Received in final form 23 April 2014, Accepted 28 April 2014)

We report the crystallographic and magnetic properties of $Ni_{0.3}Fe_{0.7}Ga_2S_4$ by means of X-ray diffractometer (XRD), a superconducting quantum interference device (SQUID) magnetometer, and a Mössbauer spectroscopy. In particular, $Ni_{0.3}Fe_{0.7}Ga_2S_4$ was studied by Mössbauer analysis for evidence of spin reorientation. The chalcogenide material $Ni_{0.3}Fe_{0.7}Ga_2S_4$ was fabricated by a direct reaction method. XRD analysis confirmed that $Ni_{0.3}Fe_{0.7}Ga_2S_4$ has a 2-dimension (2-D) triangular lattice structure, with space group *P-3m1*. The Mössbauer spectra of $Ni_{0.3}Fe_{0.7}Ga_2S_4$ at spectra at various temperatures from 4.2 to 300 K showed that the spectrum at 4.2 K has a severely distorted 8-line shape, as spin liquid. Electric quadrupole splitting, E_Q has anomalous two-points of temperature dependence of E_Q curve as freezing temperature, T_f = 11 K, and Néel temperature, T_N = 26 K. This suggests that there appears to be a slowly-fluctuating "spin gel" state between T_f and T_N, caused by non-paramagnetic spin state below T_N. This comes from charge re-distribution due to spin-orientation above T_f, and T_N, due to the changing E_Q at various temperatures. Isomer shift value (0.7 mm/s ≤ δ ≤ 0.9 mm/s) shows that the charge states are ferrous (Fe^{2+}), for all temperature range. The Debye temperature for the octahedral site was found to be Θ_D = 260 K.

Keywords : mössbauer spectroscopy, spin reorientation, electric quadrupole splitting

1. Introduction

The chalcogenide materials have attracted interest for their various physical properties of colossal magneto-resistance [1], gigantic Kerr effect [2], orbital glass state [3], spin dimerization [4], and spin-frustration [5, 6]. The materials with triangular lattice for AGa_2S_4, (A = Mn, Ni, Fe, Co, Zn), $Gd_3Ga_5O_{12}$, Fe_2OBO_3 and so on, have reported characteristic geometrical frustration phenomena. Their materials have non- conventional magnetic order, arising from the incommensurate spin structure, spin fluctuation, spin-flop, and spin liquid without spin solid below Néel temperature [7-9]. In particular, research interest has focused on triangular lattice antiferromagnet $NiGa_2S_4$, which has a low spin state of S = 1, despite geometrical frustration, spin-fluctuation, and the atomic short-range order in the ground state up to 0.35 K [5]. Meanwhile, it was reported that $FeGa_2S_4$ with geometrical frustration phenomena, like the crystal structure of $NiGa_2S_4$ has a high spin state of spin = 2 at low temperature [10]. Recently, $NiGa_2S_4$ and $FeGa_2S_4$ have magnetic transition with T^* ≅ 9 and 30 K, with presence of spatial inhomogeneity from muon spin rotation and relaxation (μSR) experiments [11]. This coincides almost with Néel temperature T_N of 11, and 33 K of $NiGa_2S_4$ and $FeGa_2S_4$, respectively, by Mössbauer spectroscopy [12-14]. In this paper, we describe crystallographic and magnetic properties of $Ni_{0.3}Fe_{0.7}Ga_2S_4$, when Fe is doped at 70 % in $NiGa_2S_4$ by using an X-ray diffractometer (XRD), a superconducting quantum interference device (SQUID) magnetometer, and a Mössbauer spectroscopy. Especially, we report evidence of spin reorientation of $Ni_{0.3}Fe_{0.7}Ga_2S_4$ by Mössbauer analysis.

2. Experimental Details

The polycrystalline sample of $Ni_{0.3}Fe_{0.7}Ga_2S_4$ was prepared by a standard solid-state reaction method in evacuated 10^{-7} torr quartz ampoules. In order to obtain homogeneous materials, it was necessary to grind the mixed powders of Fe (99.99%), Ni (99.99%), Ga (99.999 %), and S (99.99%), and press the powder into pellet, before the annealing process in evacuated quartz ampoules. A single phase of $Ni_{0.3}Fe_{0.7}Ga_2S_4$ was obtained, by annealing at 1000°C with nitrogen gas in evacuated quartz

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ampoules for ten days. The crystal structure of sample of $Ni_{0.3}Fe_{0.7}Ga_2S_4$ was analyzed, by using Philips X'Pert diffractometer with Cu $K\alpha$ radiation source. The magnetic properties were characterized by superconducting quantum interference device (SQUID) magnetometer. The Mössbauer spectra were recorded by conventional spectrometer of the electromechanical type, with a ^{57}Co source in a rhodium matrix. The obtained Mössbauer spectra were analyzed by a least-squares fitting program.

3. Results and Discussion

The XRD pattern of single-crystal $Ni_{0.3}Fe_{0.7}Ga_2S_4$ at room temperature was analyzed by Rietveld's refinement of the FullProf code, as shown in Fig. 1. The crystalline structure of $Ni_{0.3}Fe_{0.7}Ga_2S_4$ was a 2-dimension triangular lattice of space group *P-3m1*, and the lattice parameters were a_0 = 3.657 Å, and c_0 = 12.058 Å. The Bragg factor R_B and the structure factor R_F were less that 4%. The interlayer path $\theta_{Fe\text{-}S\text{-}Fe}$ (°) for $Ni_{0.3}Fe_{0.7}Ga_2S_4$ is 98.16°, and the lattice parameters of $Ni_{0.3}Fe_{0.7}Ga_2S_4$ are shown in Table 1. Also, we confirmed that the structure of $Ni_{0.3}Fe_{0.7}Ga_2S_4$ consists of a central $Ni_{0.3}Fe_{0.7}S_2$ layer of edge-sharing $Ni_{0.3}Fe_{0.7}S_6$ octahedral site, and top of the bottom sheets of GaS_4 tetrahedral site. The layered structure is formed by four anion sulfur layers, which are stacked in the direction of the c-axis, as in distorted hexagonal structure.

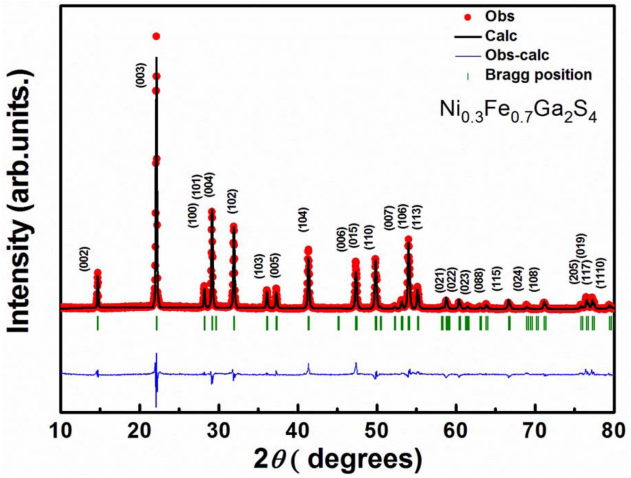

Fig. 1. (Color online) Refined x-ray diffraction pattern of the $Ni_{0.3}Fe_{0.7}Ga_2S_4$ at room temperature. The Bragg factors R_B and the structure factors R_F were under 4%.

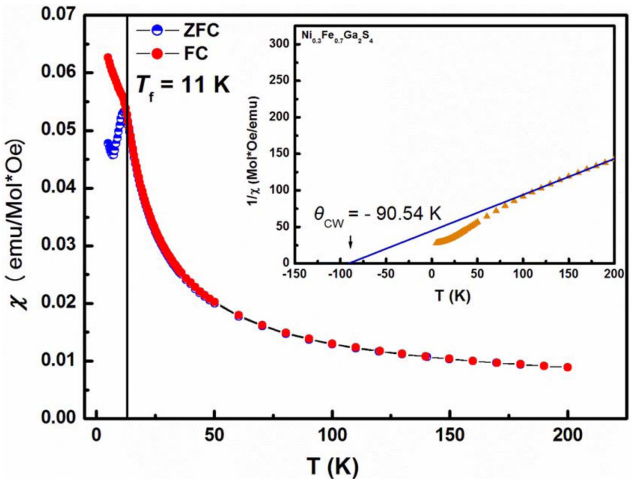

Fig. 2. (Color online) Temperature dependence of molar susceptibility χ of $Ni_{0.3}Fe_{0.7}Ga_2S_4$ in zero-field-cooled (open symbols) and field-cooled (solid symbols) magnetization, at magnetic fields under 100 Oe. Inset shows the inverse molar susceptibility $1/\chi$ in field-cooled (FC) magnetization, at magnetic fields under 5 T.

Fig. 2 presents the temperature dependences of zero-field-cooled (ZFC) and field-cooled (FC) molar susceptibility, in an external magnetic field of H = 100 Oe, measured by SQUID magnetometer. The magnetic irreversibility appears below freezing temperature T_f = 11.0 K, as shown with two different temperature dependencies. This spin-freezing transition temperature, T_f coincides with the temperature of changing from 8-line into 2-line width of Mössbauer spectrum. From the inset of Fig. 2, showing the temperature dependence of inverse susceptibility χ^{-1} in field-cooled (FC) magnetization under 5T, we determined Curie–Weiss temperature for $Ni_{0.3}Fe_{0.7}Ga_2S_4$ to be θ_W = –90.54 K. Also, antiferromagnetic behavior is clearly indicated, and the frustration factor ($|\theta_W|/T_N$) is 8.23.

The Mössbauer spectra for $Ni_{0.3}Fe_{0.7}Ga_2S_4$ were obtained at various temperatures ranging from 4.2 to 300 K as shown in Fig. 3. The Mössbauer spectra show severely distorted 8-line shape from 4.2 K to T_f = 11 K due to the geometrical frustration effect, as spin-fluctuation, incommensurate spin structure, atomic short-range ordering, and liquid spin state. We analyzed the Mössbauer spectra by using the full Hamiltonian for the ^{57}Fe nucleus and considering both the magnetic dipole and the electric

Table 1. XRD refinement parameters of $Ni_{0.3}Fe_{0.7}Ga_2S_4$ at room temperature, for a *P-3m1*, 2-dimensional triangular lattice structure.

sample	a_0 (Å)	c_0 (Å)	V (Å^3)	$d_{Fe\text{-}Fe}$ (Å)	$d_{Fe\text{-}S}$ (Å)	$\theta_{Fe\text{-}S\text{-}Fe}$ (°)
$Ni_{0.3}Fe_{0.7}Ga_2S_4$	3.657	12.058	3.657	3.657	2.420	98.16

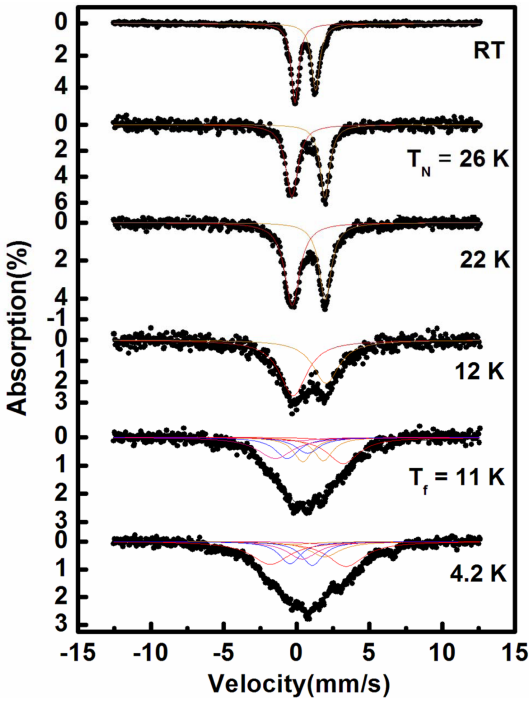

Fig. 3. (Color online) Mössbauer spectra for $Ni_{0.3}Fe_{0.7}Ga_2S_4$ at various temperatures.

quadrupole interactions. From the value of the isomer shift value (0.7 mm/s $\leq \delta \leq$ 0.9 mm/s) at all temperature range, we concluded that the Fe ion is ferrous (Fe^{2+}). We determined that T_f is 11 K, due to the appearance of 2-line from 8-line width of Mössbauer spectrum, in accord with T_f from SQUID magnetometer. We decided on the small gap energy, Δ_1 = 0.208 meV for the doublet levels of $^5T_{2g}$ between $^5T_{2g}$ and ^5E_g states on the ground state of ^5D for Fe^{2+} ion based on crystal field energy theory from electric quadrupole splitting, E_Q = 1.82 mm/s at 4.2 K [15]. Fig. 4 shows the ratio of the intensities, $R_q = A_1/A_2$, between the Mössbauer absorption areas in the two electric quadrupole splitting in the temperature range from 12 to 300 K.

Then, we determined that Néel temperature, T_N is 26 K, since the meeting temperature of the slops is 26 K, when the slopes of R_q at lower and higher temperature are connected. The decreases of R_q from 1.34 to 1.07 with increasing temperature comes from the Goldanskii-Karyagin effect, which is caused by the asymmetric environment, extensive quadrupole splitting and anisotropic thermal vibrations [16].

As shown in Fig. 5, electric quadrupole splitting, E_Q decreases at T_f with frozen disordered-spins around T_f, as in spin-liquid material, and increases of E_Q above T_f shows charge re-distribution due to spin-orientation. However, there is no complete spin-orientation at T_f due to additional increases of E_Q at T_N with evidence of spin-

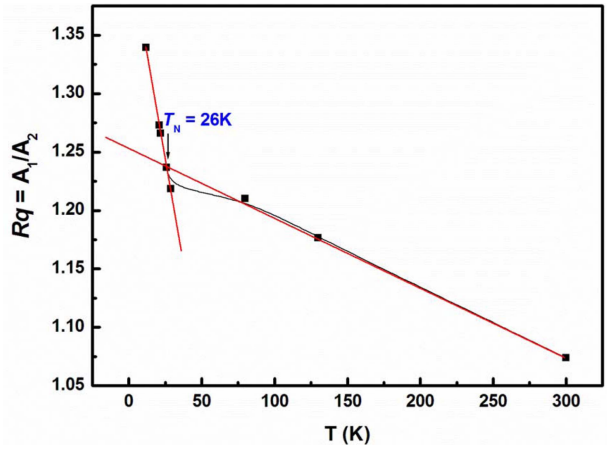

Fig. 4. (Color online) Ratio of the intensities of two lines, $R_q = A_1/A_2$, for $Ni_{0.3}Fe_{0.7}Ga_2S_4$ in the temperature range from 12 to 300 K for the Mössbauer spectra.

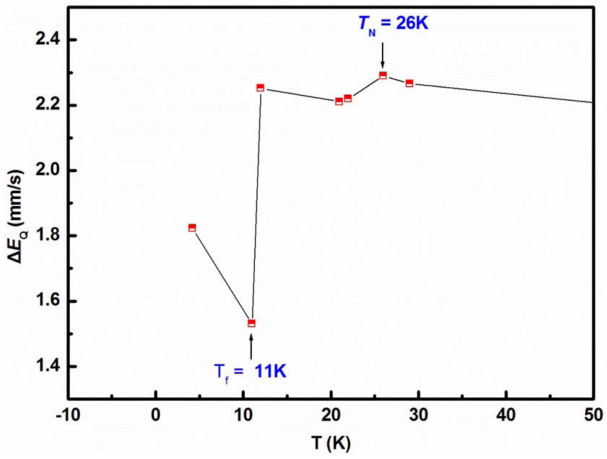

Fig. 5. (Color online) Temperature dependence of the electric quadrupole splitting for $Ni_{0.3}Fe_{0.7}Ga_2S_4$ from 12 to 300 K.

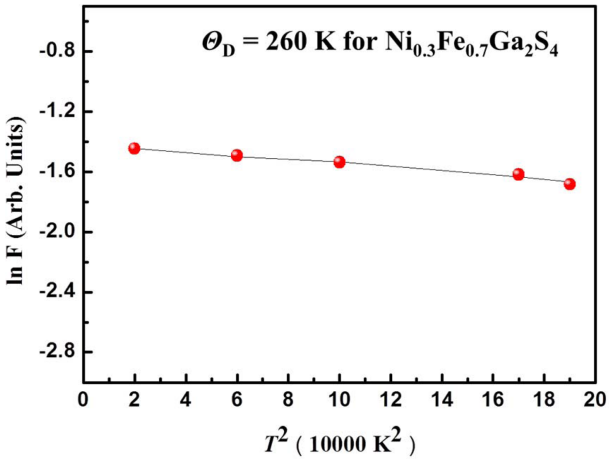

Fig. 6. (Color online) Natural logarithm of the Mössbauer absorption area for $Ni_{0.3}Fe_{0.7}Ga_2S_4$.

reorientation. Finally, this suggests that a viscous "spin gel" regime with nearly-frozen spin state, and slowly fluctuating, exists between T_f and T_N, caused by the absolute paramagnetic disordered-spin at T_N [11]. The Debye temperature for octahedral site can be calculated from the temperature dependence of the resonant absorption area for each sub-spectrum at low temperatures, as shown in Fig. 6. The calculated Debye temperature octahedral site was Θ_D = 260 K.

4. Conclusions

We have investigated the crystallographic and magnetic properties of $Ni_{0.3}Fe_{0.7}Ga_2S_4$. The crystal structure of the sample is found to be 2 D-triangular lattice with space group *P-3m1* from a Rietveld refinement of the XRD data. From SQUID measurements, the sample showed an antiferromangetic behavior with θ_W = –90.54 K, and spin-freezing transition at a freezing temperature is T_f = 11 K. T_N is determined to be 26 K from the ratio of the intensities ($R_q = A_1/A_2$). We found by Mössbauer analysis that spin reorientation appeared at T_f, and T_N due to the changing of E_Q at various temperatures.

Acknowledgment

This work was supported by Mid-career Researcher Program through the National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (MEST) (2013-000671).

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