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Charge structure and cation distribution on Fe-Ga chalcogenide spinel by neutron diffraction and Mössbauer spectroscopy

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Abstract

$FeGa_xCr_{2-x}S_4$ (x=0.1 and 0.3) have been studied with x-ray, neutron difraction, and Mössbauer spectroscopy. Rietveld refinement of x-ray, neutron diffraction, and Mössbauer spectroscopy lead to the conclusion that the samples are in inverse spinel type, where the majority of Ga ions are present at tetrahedral site (A). The neutron diffractions on $FeGa_xCr_{2-x}S_4$ (x=0.1) above 10 K show long range interaction behaviors and reveal an antiferromagnetic ordering, with the magnetic moment of Fe^{2+}(-3.45 μ_B) aligned antiparallel to Cr^{3+} (+2.89 μ_B) at 10 K. Fe ions migrate from the tetrahedral (A) site to the octahedral (B) site with increase of Ga substitutions. The electric quadrupole splittings of the A and B sites in Mössbauer spectra give a direct evidence that Ga ion stimulate asymmetric charge distribution of Fe ions in the A site.

Keywords: Mössbauer spectroscopy, Cation distribution, Neutron diffraction, Magnetic structure, Charge structure

1. Introduction

Since the discovery of the colossal magnetoresistance (CMR) effect perovskite manganite, a great interest has been attracted to investigate these ferromagnetic compounds. Ramirez *et. al.* reported the existence of CMR effect in Cr-based chalcogenide spinel such as $FeCr_2S_4$[1]. V. Tsurkan *et. al.*[2] reported a spin-glass-like anomalies from a structural lattice transformation. Authors published on anomalous magnetic behaviors of ferrimagnetic properties on Ga-doped sulphur spinel by magnetoresistance and Mössbauer studies.[3] Very recently, ultrafast photoemission spin dynamics has been reported by time resolved magneto optical Kerr spectroscopy for Cr based chalcogen spinel compunds.[4] Here, we present the results of X-ray, neutron diffraction Mössbauer experiments on Ga doped sulphur spinel compounds.

2. Experimental

$Fe_1Cr_{2-x}Ga_xS_4$ (x=0.1, 0.3) were prepared by the direct reaction of the high-purity elements Fe, Cr, Cu, and S in an evacuated quartz tube. The crystal structures of the samples were

examined by x-ray diffractometer with Cu Kα radiation. The magnetic structures of the samples were examined neutron diffractometer at Korea Atomic Energy Research Institute HANARO HRPD (high resolution powder diffractometer, λ=1.8348 Å) reactor. The Mössbauer spectra were recorded using a conventional spectrometer of the electromechanical type with a ^{57}Co source in a rhodium matrix.

3. Results and Discussion

Fig. 1 (a) and (b) show the results of Rietveld refinement of the x-ray diffraction for the $FeCr_{1.9}Ga_{0.1}S_4$ (x=0.1) and $FeCr_{1.7}Ga_{0.3}S_4$ (x=0.3), at 295 K, respectively. We could not find any different positions of peaks other than cubic spinel in Fig. 1 (a) and (b).

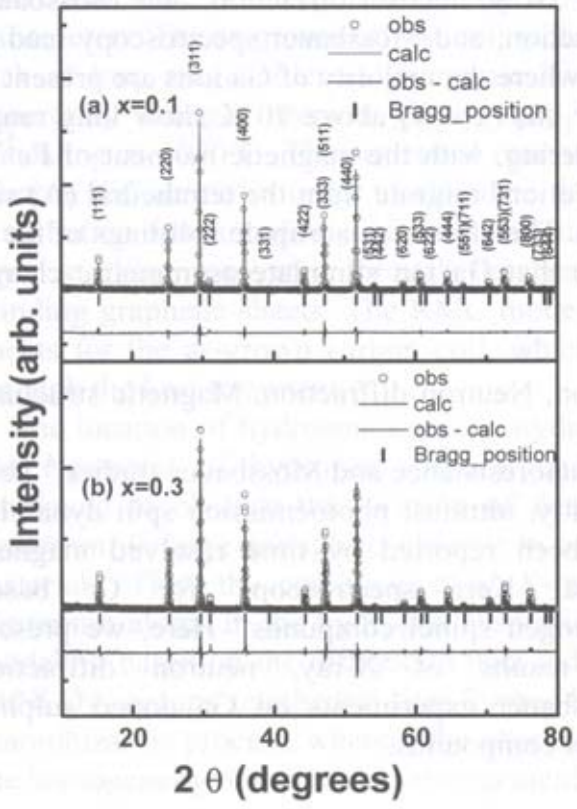

Fig. 1. Refined x-ray diffraction pattern of the $FeGa_xCr_{2-x}S_4$ (a) x=0.1, (b) x=0.3 at 295 K. Tick marks show the Bragg positions.

Table 1. Results of refinement parameters of x-ray diffraction on $FeGa_xCr_{2-x}S_4$ (x=0.1 and 0.3) [*Fd3m*: Fe, Ga (8a); Fe, Ga, Cr (16d); S(32e (*u*, *u*, *u*))]

	x=0.1	x=0.3
a/Å	10.0067(3)	9.9962(3)
u (S)	0.7401(3)	0.7409(3)
Fe (A)-occ	0.98	0.90
Ga (A)-occ	0.02	0.10
Fe (B)-occ	0.02	0.10
Ga (B)-occ	0.08	0.20
R_B	2.66 %	7.39 %

Crystal structure is determined to be *Fd3m*. The determined lattice constants, oxygen parameter *u*, cation occupancy, and Bragg factor R_B, are listed in Table 1. The Cr ions enter into the B site for strong preference of the octahedral symmetry. It is noticeable that Ga ions enter into the both B and A sites, simultaneously the same amounts of Fe ions migrate from the A to the B site.

In order to examine crystallographic and magnetic structure in $FeCr_{1.9}Ga_{0.1}S_4$ (x=0.1), we obtained neutron diffraction patterns from 10 to 300 K. Magnetic structure is determined by Rietveld refinement of the Fullprof program. Fig. 2 shows the results of refined neutron diffraction patterns for $FeCr_{1.9}Ga_{0.1}S_4$, at verious temperatures. For all the temperature range below 300 K, it was observed, as one lowered the temperature, the intensity of the inner Bragg reflections, namely, (111), (220), (222), and (331), increased significantly, denoting important magnetic contribution to these reflections. As can be seen in Fig. 2, the diffraction peaks were found to be remain very sharp and indicating the presence of magnetic long-range order (LRO) in this sample. The observed magnetic moments of Fe^{2+}(A) and

Cr^{3+}(B) as well as net magnetic moments of $FeCr_{1.9}Ga_{0.1}S_4$ are listed in Table 2. Neutron diffraction at 10 K revealed a cubic spinel structure of ferrimagnetic ordering, with magnetic moments of Fe^{2+}(A)(-3.45 μ_B), Cr^{3+}(B)(2.89 μ_B), and net moment (2.04 μ_B), respectively.

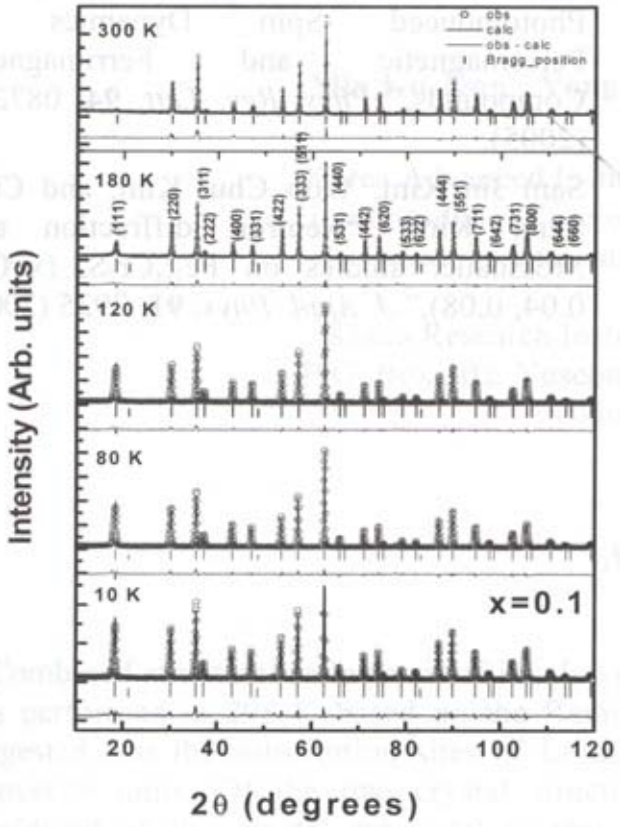

Fig. 2 Neutron diffraction patterns of $FeCr_{1.9}Ga_{0.1}S_4$ at various temperatures. Upper and lower tick marks show the Bragg and magnetic reflection positions.

Table 2. Results of refinement parameters of neutron diffraction on $FeCr_{1.9}Ga_{0.1}S_4$.

T (K)	Fe (μ_B)	Cr (μ_B)	Net (μ_B)
10	-3.45	2.87	2.04
80	-3.86	3.12	2.07
120	-3.58	2.86	1.86
180	-2.28	1.62	0.79
300	0	0	0

The Mössbauer spectra were collected from 12 to 295 K. Fig. 3 (a), (b), and (c) show the Mössbauer spectra for the sample x=0.0, 0.1, and 0.3, respectively, at room temperature.

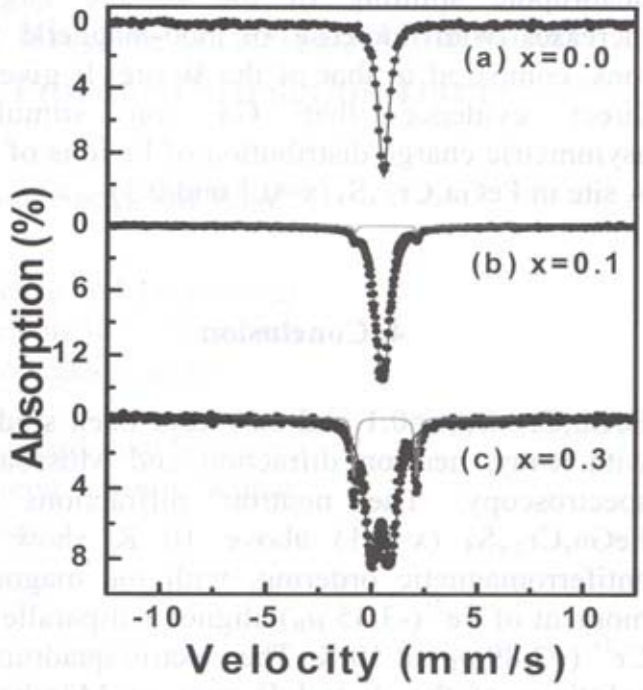

Fig. 3 Mössbauer spectra of $FeGa_xCr_{2-x}S_4$ (a) x=0.0, (b) x=0.1 and (c)x= 0.3 at 295 K.

$FeCr_2S_4$(x=0.0) has a single line at room temperature, while the both spectra Fig. 3 (b) and (c) consist of two doublets at room temperature. The one corresponds to the iron ions at the A sites (inner doublet), the other corresponds to the iron ions at the B sites (outer doublet). The electric quadrupole splitting of the outer and inner sets are 0.30 and 2.93 mm/s, for the sample x=0.1, respectively. While, they are 0.83 and 2.94 mm/s, for the sample x=0.3, respectively. The isomer shifts and area ratio of the A and B sites, for the x=0.1, are 0.66 and 0.53 mm/s, 2.0 and 98.0 %, respectively. While, those of the sample x=0.3 are 0.65 and 0.50 mm/s, 10.3 and 89.7 %, respectively. The Mössbauer absorption area ratio accords with the results of the x-ray diffraction refinement, too. The covalence of the A-site is lager than that of B site in spinel structure. Therefore the isomer shift of the A site is smaller than that of the B site. In addition, the crystal symmetry of

the octahedral site is slightly tilted. Hence, one can guess a large quadrupole splitting in B sites. Reminding that $FeCr_2S_4$ has a single line at room temperature, it is abnormal that it has large quadrupole splitting[5]. We notice that the quadrupole splitting of the A site largely increases with increase of non-magnetic Ga ions, compared to that of the B site. It gives a direct evidence that Ga ion stimulate asymmetric charge distribution of Fe ions of the A site in $FeGa_xCr_{2-x}S_4$ (x=0.1 and 0.3).

4. Conclusion

$FeGa_xCr_{2-x}S_4$ (x=0.1 and 0.3) have been studied with x-ray, neutron difraction and Mössbauer spectroscopy. The neutron diffractions on $FeGa_xCr_{2-x}S_4$ (x=0.1) above 10 K show an antiferromagnetic ordering, with the magnetic moment of Fe^{2+}(-3.45 μ_B) aligned antiparallel to Cr^{3+} (+2.89 μ_B) at 10 K. The electric quadrupole splittings of the A and B sites in Mössbauer spectra give a direct evidence that Ga ion stimulate asymmetric charge distribution of Fe ions in the A site.

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