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Superexchange interaction behaviors in Cu-doped for chromium based sulphur spinel

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Abstract

The superexchange interaction behaviors in spinel compounds $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ ($0.0 \leq x \leq 0.5$) with magnetic semiconductor are investigated. Rietveld refinement of x-ray diffraction and Mössbauer spectra was concluded that the samples are cubic spinel. The neutron diffractions were measured from 10 K to room temperature. Neutron diffraction on $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ ($0.0 \leq x \leq 0.5$) above 10 K shows that there is no crystallographic distortion and reveal antiferromagnetic ordering. Mössbauer spectra identify that Fe ions occupy tetrahedral sites, the Cr ions occupy octahedral sites with a +3 valence in the $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ ($0.0 \leq x \leq 0.5$). The charge state of Fe ions are ferrous (Fe^{2+}) for the $x=0.1$, while Fe ions are ferric (Fe^{3+}) for the $x=0.5$.

Keywords: Exchange interaction, neutron diffraction, Mössbauer spectroscopy

1. Introduction

Studies of sulphur spinel compounds have suggested that the conduction mechanism in these materials may not be the double exchange of carriers [1]. V. Fritsch *et al.* claimed a triple exchange model in copper doped sulphur spinel [2]. Mössbauer studies on FeCr_2S_4 have been reported already by many workers [3-5]. According to the octahedral (B) site preference of Cr^{3+} , it is believed that the Mössbauer spectra of FeCr_2S_4 arise from the tetrahedral (A) site of

the Fe^{2+} spectra. Samples of $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ ($x \leq 0.5$) have been studied extensively. Lotgering *et al.* developed a monovalence model of Cu^+ ion [6], while Goodenough postulated divalent Cu^{2+} for the concentration range $0.5 < x \leq 1.0$ [7]. Recently, Palmer *et al.* [8] and V. Fritsch *et al.* [2] reported the triple exchange model and suggested the coexistence of the iron ions Fe^{2+} and Fe^{3+} in the tetrahedral sites. Therefore, it is essential to determine the valence state of iron ions in various sulphur spinel compounds to understand the underlying mechanism properly. Therefore, it is necessary to examine the cation

distribution of the various compounds in the sulphur spinel.

2. Experimental

Synthesis of the sample was accomplished by the direct reaction of the high-purity elements Fe, Cr, Cu, and S in an evacuated quartz tube. The crystal structure of the sample was examined by x-ray diffractometer with Cu $K\alpha$ radiation and neutron diffractometer at Korea atomic energy research institute reactor HANARO HRPD. Magnetoresistance (MR) and magnetization were measured with van der Pauw method and vibrating sample magnetometer (VSM), respectively. The Mössbauer spectra were recorded using the conventional spectrometer of the electromechanical type with a ^{57}Co source in a rhodium matrix.

3. Results and Discussion

The x-ray diffraction (XRD) patterns for samples reveal spinel structure. The crystal structure at room temperature is determined by the Rietveld method. It is found that the space group is $Fd3m$ and resulting lattice parameter for $x=0.1$ and 0.5 are $a_0=9.9880 \text{ \AA}$ and $a_0=9.9220 \text{ \AA}$, respectively. Figure 1 shows the results of neutron diffraction patterns for $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ ($0.0 \leq x \leq 0.5$) at 10 K. We cannot find any other different position of magnetic superstructure peaks other than the nuclear peaks at 10 K temperature, in figure 1. Specifically, all magnetic peaks are overlapped on nuclear peaks. Therefore, it is concluded that the intersublattice superexchange interaction of Fe(A)-Cr(B) is antiferromagnetic, while intrasublattice superexchange interaction of Fe(A)-Fe(A) and Cr(B)-Cr(B) is ferromagnetic, respectively. In order to clarify and determine the state of Fe ions in the samples, the Mössbauer spectra were measured. From the Mössbauer results, it is determined that charge state of the iron ions in the samples $x=0.1$ and

0.5 are ferrous and ferric, respectively. The iron and copper ion for the $x=0.5$ show the ferric (Fe^{3+}) and mono valence (Cu^+) characters. Neither the triple exchange model nor the double exchange model can explain these systems.

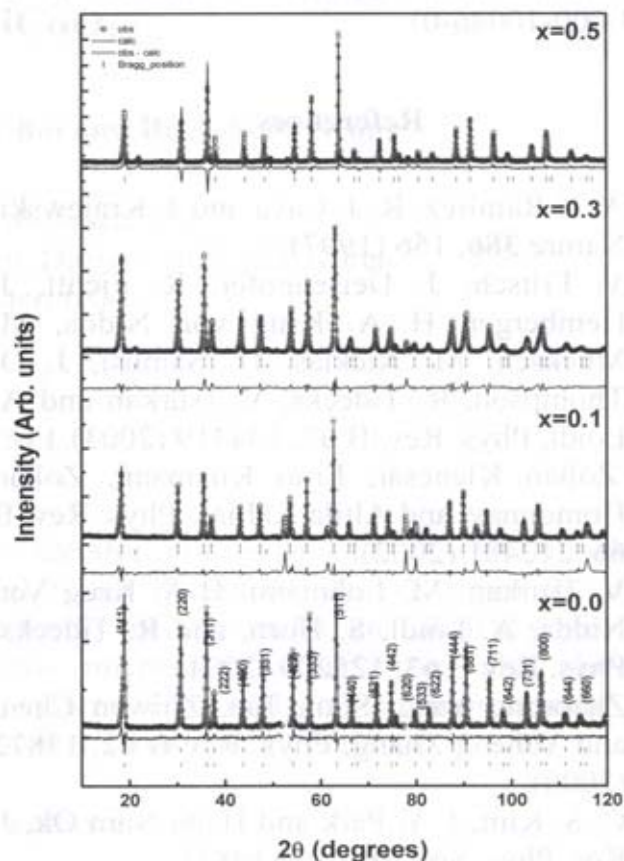


Fig. 1 The neutron diffractions for the $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ ($0.0 \leq x \leq 0.5$) at 10 K

4. Conclusion

In summary the crystal structures of $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ ($x=0.1, 0.5$) are found to be a cubic spinel by Rietveld refinement of XRD and neutron diffraction. The cation distribution is determined by Mössbauer spectra, which reveals that the Fe ions are occupied to the tetrahedral site and Cr ions are occupied to the octahedral site and $\text{Fe}_{1-x}\text{Cu}_x\text{Cr}_2\text{S}_4$ ($x=0.1, 0.5$) belongs to a spinel type. The valence state of the Fe ions for the $x=0.1$ and $x=0.5$ are confirmed to be Fe^{2+}

and Fe^{3+} , respectively, through Mössbauer spectra and neutron diffraction.

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