

STUDY OF THE CONDUCTION PHENOMENON IN THE SYSTEM $Zn_{(1-x)}FeCrO_4Ni_x$

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ABSTRACT

In order to explore an "anomalous" conduction phenomenon in the system $Zn_{(1-x)}FeCrO_4Ni_x$ which was investigated with Mossbauer spectra, X-rays diffraction, Infrared spectra and other methods. The results show that the conductivity anomaly is not an intrinsic behavior but arises from the moisture-adsorption. Their native conduction is similar to that of semiconductors, obeying the relationship $\sigma = \sigma_{\infty} \exp(-E_a/KT)$. All samples crystallize in cubic symmetry and their lattice parameters increase with x . The cation distribution is $(Zn_{(1-x)}Fe_x)[Fe_{(1-x)}Ni_xCr]O_4$. No phase change occurs in the temperature range from 283 to 423 K.

Keywords: Resistivity anomaly $Zn_{(1-x)}FeCrO_4Ni_x$ Mossbauer effect

1 INTRODUCTION

The variable magnetic, electrical and crystallographic properties of spinels have attracted some interest because of both the theoretical meaning and practical use. Some experiments have been done on the electrical properties of $ZnFeCrO_4$ ^[1,2], but Al-Saie^[3] reported an "anomalous" conduction behavior, which is different from those discovered either in the metals or in the semiconductors. We present here our results of the conduction phenomenon in this system and explain the apparent anomalous behavior based on the detailed structural investigation.

2 EXPERIMENTAL

$Zn_{(1-x)}FeCrO_4Ni_x$ were prepared from the mixtures of Analar grade ZnO , Fe_2O_3 , NiO and Cr_2O_3 with acetone. The molar proportions of the components in solid solution were varied with x from 0 to 1. The mixtures were ground in an agate mortar and the dried mass was compressed into pellets under the pressure of 9.8×10^7 Pa using polyvinyl alcohol as a binder. The samples were put into the programmable electric furnace and heated at 723 K for 24 h, then 1193 K for 72 h in air, at last quenched to

room temperature at rate of 0.6 K/min. The powdered samples were analyzed by X-ray diffraction, Mossbauer spectra and IR spectra.

Mossbauer measurements were performed with a 555 MBq ^{57}Co in a Rh matrix in the temperature range of 283 K up to 473 K. The isomer shift is relative to natural iron at room temperature. The IR spectra were recorded in KBr on a Beckman double beam spectrophotometer from 2000 cm^{-1} to 400 cm^{-1} .

DC resistivities were measured by using four probe technique in the temperature range of 283—423 K on a Model ZC-43 resistancemeter. The measurements were carried out in vacuum, in inert atmosphere, or in moisture of N_2 and air, respectively.

3 RESULT AND DISCUSSION

The X-ray diffraction (XRD) patterns reveal that the samples crystallized in single phase belonging to spinel structure and the lattice parameter a decreases with x (see Table 1). The result shows $a = 0.838\text{ nm}$ for ZnFeCrO_4 , which is in good agreement with the data taken from Ole's^[1] and Jain^[2]. The XRD patterns prove that the no phase change occurs in the range of 283—423 K.

The Mossbauer spectra obtained at room temperature are showed in Fig.1. The spectra are constituted of two doublets for $x > 0$, one corresponding to the Fe^{3+} cations at the octahedral(B) sites and the other to the Fe^{3+} cations at the tetrahedral(A) sites. The parameters derived from the fitting are given in Table 1. The larger quadrupole splitting at A sites might be associated with the variety of ions in the B sublattice inducing deformations of oxygen tetrahedral. For $\text{ZnFeCrO}_4(x=0)$ all Fe^{3+} cations occupy B sites. As $x > 0$, Ni^{2+} cations preferentially enter octahedral positions while the Fe^{3+} cations displaced from these octahedral sites enter the tetrahedral sublattice. The intensity ratios of the A sites to B sites are in agreement with the cation distribution $(\text{Zn}_{(1-x)}\text{Fe}_x)^{\text{A}} [\text{Fe}_{(1-x)}\text{Ni}_x\text{Cr}]^{\text{B}}\text{O}_4$ given in Table 2. No abrupt changes of Mossbauer parameters (showed in Fig.2 and 3) were observed in this temperature range.

The infrared spectra (see Fig.4) gives another evidence for above distribution. There are two absorption bands in 612 cm^{-1} and 500 cm^{-1} representing the overlap of frequencies for different cations with oxygen band at A-sites and B-sites. According to Tarte's report^[4], the vibration frequency of Cr^{3+} , Fe^{3+} and Ni^{2+} on B-sites is 650—550, 550—400 and 400 cm^{-1} respectively, that of Zn^{2+} and Fe^{3+} on A-sites is 500 and 570 cm^{-1} . The intensity of high-frequency band near 620 cm^{-1} keeps constant with x , corresponding to the constant contents of Cr^{3+} cations on B sites. However, the intensity of low frequency band near 500 cm^{-1} decreases with x and the absorption peak near 450 cm^{-1} appears for low x . They come from following results: the Fe^{3+} cations replaced by Ni^{2+} on B-sites enter into A-sites, leading to the variation of the

intensity for corresponding components. At same time, the reduction of Zn^{2+} contents lowers the intensity of the band near 500 cm^{-1} and thus results in the broaden of band near 600 cm^{-1} . In conclusion, the IR spectra supports the cation distribution $(Zn_{(1-x)}Fe_x)^A [Fe_{(1-x)}Ni_xCr]^B O_4$. The cation distribution above is also further supported by the preference energy values of the cation site: Zn^{2+} , -132.1 ; Fe^{3+} , -55.6 ; Ni^{2+} , $+37.6$ and Cr^{3+} , $+69.4\text{ kJ/g at.wt.}^{[6]}$

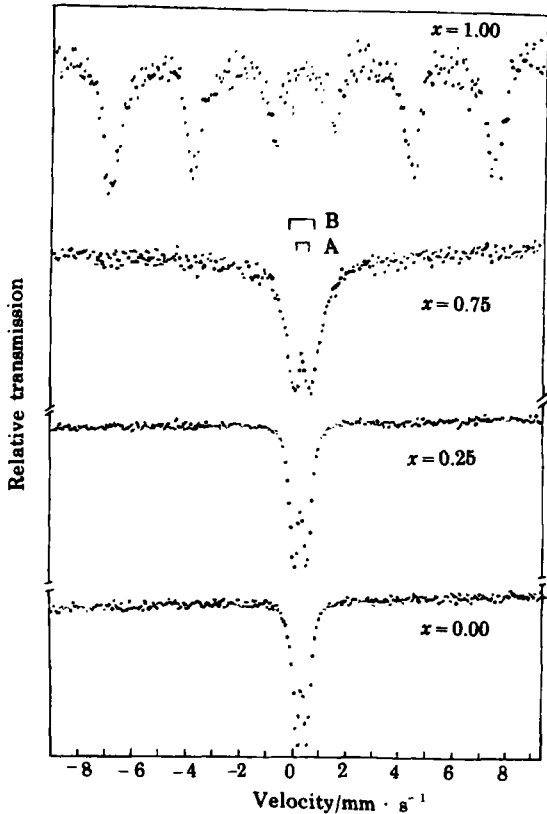


Fig.1 Mossbauer spectra for the system $Zn_{(1-x)}FeCrO_4Ni_x$ at room temperature

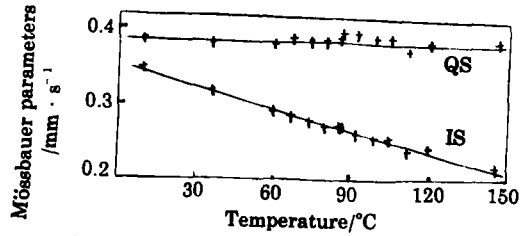


Fig.2 Temperature dependence of Mossbauer parameters for $ZnFeCrO_4$

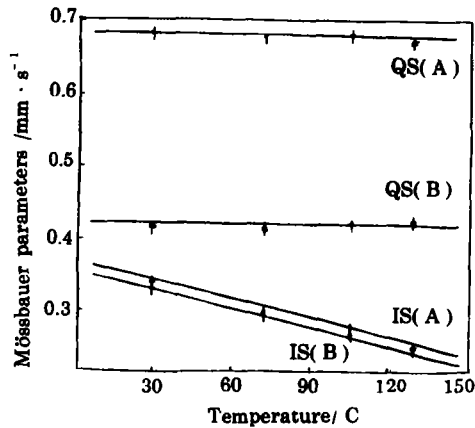


Fig.3 Temperature dependence of Mossbauer parameters for $Zn_{0.75}Fe_{0.25}CrO_4$

Table 1

Lattice constant a , activity energy E_a , transition temperature T_c and room temperature resistivity ρ_0 for the system $Zn_{(1-x)}FeCrO_4Ni_x$

x	a/nm	E_a/eV	T_c/K	$\rho_0/\Omega \cdot cm$
0.00	0.838 ± 0.001	0.85	328	2.9×10^{10}
0.25	0.837 ± 0.001	0.61	318	2.6×10^9
0.75	0.835 ± 0.001	0.46	308	1.1×10^8

The DC resistivities for different temperatures are showed in Fig.5. In the air, the resistivity of $ZnFeCrO_4$ vs the reciprocal of temperature shows clearly an "anomaly" (Fig.5b) around the transition temperature T_c ($T_c \approx 328\text{ K}$ for $x=0$) as Al-Saie's report^[9].

The transition temperature T_c moves to lower and the maximum resistivity decreases with x for $Zn_{(1-x)}FeCrO_4Ni_x$. But in vacuum environment, their intrinsic resistivities with temperature obeyed the relationship $\rho = \rho_x \exp(-E_a/KT)$, where E_a refers to the activity energy showed in Table 1. The Fig.6 shows that the experimental results in the condition of dry nitrogen and of dry oxygen quite agree with that in vacuum. On the other hand, the conduction behavior in the moisture nitrogen and in air are different from above mentioned. The fact suggests that "the resistivity anomaly" is not intrinsic and it arises from moisture-adsorption on the surface of samples.

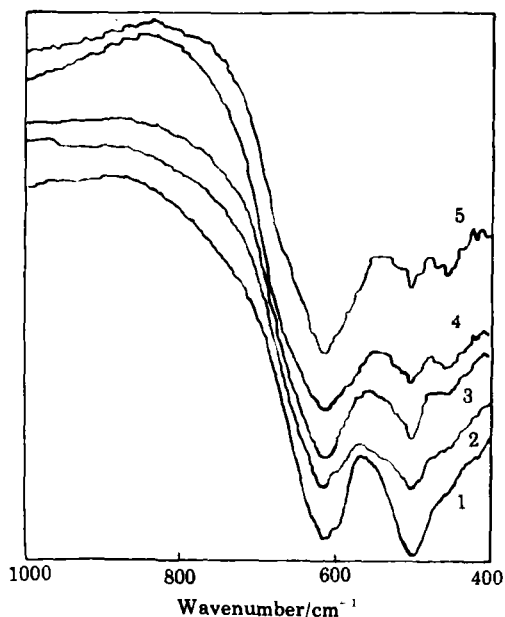


Fig.4 IR spectra for the system $Zn_{(1-x)}FeCrO_4Ni_x$ at room temperature
1) $x=0.0$ 2) $x=0.25$ 3) $x=0.75$
4) $x=0.80$ and 5) $x=0.90$

Table 2
Quadrupole splitting (QS), isomer shift (IS), relative absorption area (S) for A and B sites of the system $Zn_{(1-x)}FeCrO_4Ni_x$ mm/s

x	QS _A	QS _B	IS _A	IS _B	S _A	S _B
0.00	—	0.39	—	0.39	—	1.00
0.25	0.68	0.40	0.31	0.32	0.39	0.61
0.75	0.88	0.48	0.28	0.28	0.69	0.31

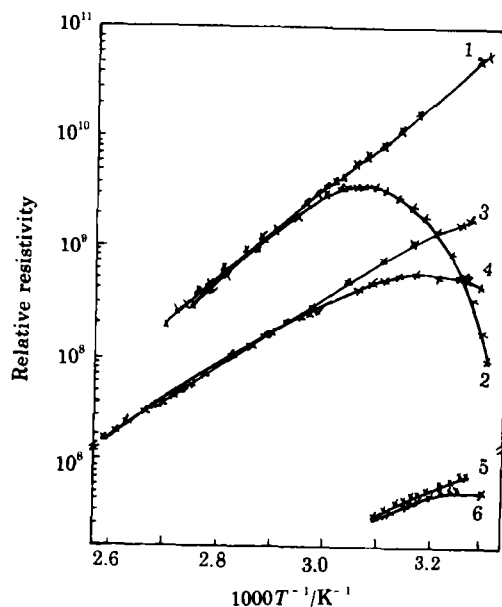


Fig.5 Temperature dependence of resistivity for the system $Zn_{(1-x)}FeCrO_4Ni_x$ under different conditions

1) $x=0.0$ in vacuum 2) $x=0.0$ in air 3) $x=0.25$ in vacuum 4) $x=0.25$ in air 5) $x=0.75$ in vacuum and 6) $x=0.75$ in air

The resistivity of the samples at room temperature and the activation energy decrease with x (see Table 1) could be ascribed to the fact that completely filled Zn^{2+} d-orbitals have much lower energy and are more contracted than the Ni^{2+} orbits. The

system $Zn_{(1-x)}FeCrO_4Ni_x$ is transition-metal-oxides with the spinel structure, which is known to be low-mobility materials^[3,6-9]. Their transport properties are often considered occurring from charge transfer between octahedral cations through the hopping of localized d electrons. This hopping mechanism is confined to the valence distribution of the cations that occupy the oxygen octahedral sites.^[9] The activation energy is often associated with the mobility of charge carriers rather than their concentration. The charge carriers are considered as localized on cations or vacant sites. Due to lattice vibration cations occasionally come close enough for the transfer of charge carriers. The conduction is induced by lattice vibration and as a result the carrier mobility μ shows an exponential temperature dependence with activation energy, i.e. $\mu = \mu_0 \exp(-E_a/KT)$.

This type of behavior arises from the presence of significant energy separations between 3d, 4s and oxygen 2p band in transition-metal oxides. Owing to this large separation, unlike that occurring in metals, there is less hybridization of 3d, 4s and oxygen 2p orbital in the system $Zn_{(1-x)}FeCrO_4Ni_x$. Therefore it exhibits itinerant conduction behavior.^[10] It is concluded that dependence of resistivity on the temperature obeys

$$\rho = 1/ne\mu = \rho_x \exp(E_a/KT)$$

According to our experiments, the resistivity behavior (see Fig.5) follows the above formula, indicating semiconductor nature.

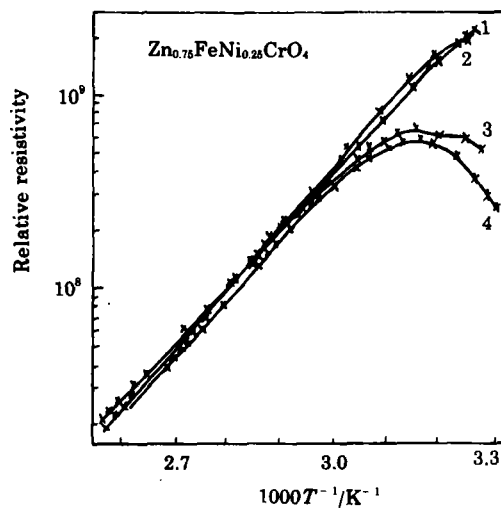


Fig.6 Temperature dependence of resistivity for $Zn_{0.75}Fe_{0.25}CrO_4$ under different conditions

a) in dry N_2 b) in dry O_2
c) in air d) in the moisture N_2

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