

Study of slow cooled and quenched samples of $Zn_xCu_{1-x}FeCrO_4$ spinel ferrite system

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Received 12 June 1995, accepted 17 January 1996

Abstract : The structural and magnetic properties of the Zn substituted slow cooled and quenched samples of $Zn_xCu_{1-x}FeCrO_4$ ferrite system with chosen values of concentration (x) have been investigated by means of X-ray diffraction, a.c. susceptibility, magnetization and Mossbauer spectroscopic measurements. The X-ray results confirm the single phase spinel structure for all the concentrations. The electrical measurements confirmed non-existence of mixed valence in the samples. The results of slow cooled samples suggest that the system under investigation exhibits ferrimagnetic spin glass type of magnetic ordering for $x \leq 0.4$ while for $x > 0.4$ it shows only a cluster spin glass type of magnetic ordering. The results of quenched samples suggest that the present system approaches the cluster spin glass type of magnetic ordering for $x > 0.1$.

Keywords : Ferrites, cluster spin glass, structural and magnetic properties.

PACS Nos. : 75.50.Lk, 75.25.+z, 75.30.Cr

1. Introduction

The possibility of continuously changing the concentration of nonmagnetic ions in different sublattices makes ferrite a very interesting material to study the appearance of various magnetic structures [1–8]. This is due to fact that, in the spinel intra-sublattice (J_{BB}, J_{AA}) interactions are weaker than the inter-sublattice (J_{AB}) interaction; as a result there are unsatisfied bonds in the ferrimagnetic phase. Because of the these unsatisfied bonds, increasing the magnetic dilution accentuates the competitions between the various exchange interactions resulting in a variety of magnetic structure. The structural and magnetic properties of ferrites depend upon the cooling rate employed during the synthesis of samples. It is particularly interesting to study the change in the properties of spinel systems containing Cu^{2+} ions.

The present communication aims to study the effect of cooling rate on structural and magnetic properties of $Zn_xCu_{1-x}FeCrO_4$ spinel system by means of X-ray diffraction, a.c. susceptibility, magnetization and Mössbauer spectroscopic techniques.

2. Experimental

The seven slow cooled samples ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 0.6) and four quenched samples ($x = 0.0, 0.1, 0.2$ and 0.3) of the spinel series $Zn_xCu_{1-x}FeCrO_4$ were prepared by the usual double sintering ceramic method. The starting materials were AR grade (99.3%) oxides, ZnO, CuO, Fe_2O_3 and Cr_2O_3 . These oxides were mixed in proper proportion and pre-sintered at $950^\circ C$ for 12 h. In final sintering process, for slow cooled samples, the materials were held at $1100^\circ C$ for 12 h and slowly cooled to room temperature. For the quenched samples, materials were held at $1100^\circ C$ for 12 h and then quenched in liquid nitrogen (80 K). The X-ray diffractograms were recorded using CuK_α radiation on a Phillips X-ray diffractometer, model PM 9220. The diffraction pattern showed sharp lines corresponding to a single phase spinel structure for all the concentrations. The low field a.c. susceptibility measurements for powdered samples were made in the temperature range 80 K to 600 K using the double coil set-up [9]. The applied field was 40 A/m. Room temperature magnetization measurements were performed using the high field hysteresis loop technique [10]. The Mössbauer spectra were obtained at 298 K in transmission geometry with a constant acceleration transducer and a 256 multichannel analyser operating in time mode. A gamma source of ^{57}Co (Rh) of 10 mCi was used.

3. Results and discussion

The lattice parameter a (Å) of the slow cooled samples and quenched samples of the $Zn_xCu_{1-x}FeCrO_4$ system plotted as a function of Zn content (x) is shown in Figure 1. The

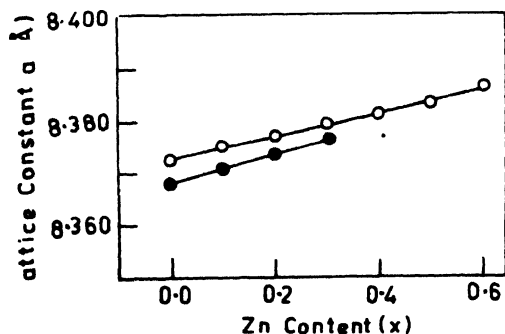
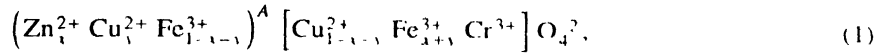


Figure 1. Variation of the lattice constant a (Å) with Zn content (x), slow cooled samples (○), quenched samples (●) of $ZnCuFeCrO$ system.

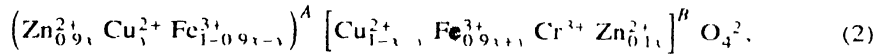
lattice constant increases linearly with zinc content (x) for both the set of slow cooled and quenched samples thus obeying the Vegard's law [11]. It is seen from Figure 1 that the values of lattice constant of quenched samples are lower than those of the slow cooled samples. This happens because in quenched samples, the fraction of bigger Zn^{2+} (0.74 \AA) ions replaces the smaller Fe^{3+} (0.63 \AA) ions on larger octahedral sites [12]. Thus, the replacement of bigger ion (Zn^{2+}) from A-site to B-site results in a decrease of the lattice constant.

Comparing site preference energies of the constituent ions and from our earlier results [13], the cation distribution for slow cooled system can be written as :



where $y = 15\%$ of Cu ions on A-site [14].

The X-ray intensity analysis on quenched system shows that for $x \geq 0.1$, Zn replaces Fe ions from the B-site to A-site. Therefore, the cation distribution for quenched system can be as :



where $y = 15\%$ of Cu ions on A-site [14].

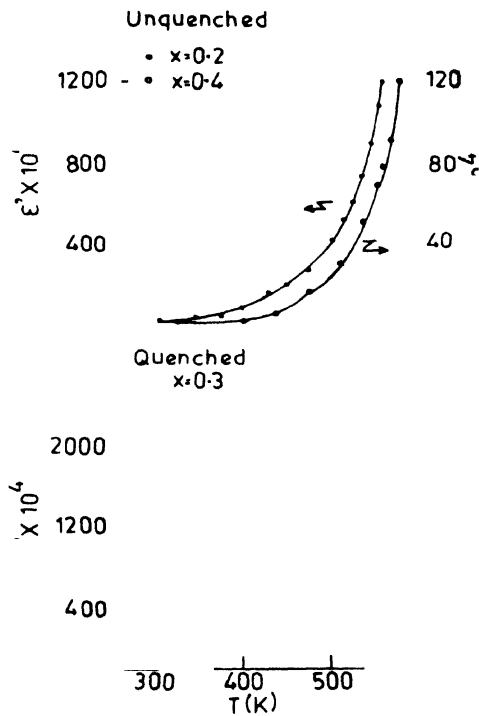


Figure 2. Dielectric constant (ϵ') as a function of temperature for ZnCuFeCrO system

In order to check the possibility of Cu^{1+} ions in the systems, d.c. resistivity and dielectric constant measurements were performed. Typical curves of dielectric constant versus temperature are depicted in Figure 2 for slow cooled and quenched samples. The room temperature resistivity (ρ) for all the samples was found to be of the order of 10^6 ohm-cm indicating absence of mixed valency in samples. The temperature dependence of dielectric constant [$\epsilon'(T)$] exhibits no relaxation peak even at higher temperatures, unlike

the ferrite systems containing Cu^{1+} ions [15]. In light of above results it can be inferred that the present systems does not show mixed valence behavior.

The saturation magnetization per formula unit $n_B(\mu_B)$ obtained from magnetization data for slow cooled and quenched samples are summarized in Table 1. The $n_B(\mu_B)$ decreases with increasing Zn-content (x) ($x > 0.1$) indicating ferrimagnetic behaviour decreases with increasing x . The lower values of saturation magnetization per formula unit for all quenched samples are due to the presence of Zn^{2+} ions on octahedral sites.

Table 1. Magneton number $n_B(\mu_B)$, Canting angle (θ), Freezing temperature (T_f), Neel temperature (T_N), Mössbauer parameters (298K) for $\text{Zn}_x\text{Cu}_{1-x}\text{FeCrO}_4$ system

x	Magnetization		a.c. susceptibility		Mössbauer parameters	
	$n_B(\mu_B)$	Canting angle (θ) in degree	$T_f(K)$	$T_N(K)$	I.S. (mm/sec)	Q.S. (mm/sec)
Slow cooled samples						
0.0	0.33	0.00	—	575	—	—
0.1	0.43	27.29	—	545	0.27	0.36
0.2	0.28	43.97	—	510	0.18	0.27
0.3	0.23	53.92	—	460	0.18	0.27
0.4	0.17	61.81	—	420	0.18	0.27
0.5	0.04	69.17	—	375	0.27	0.18
0.6	0.02	74.45	—	350	0.36	0.09
Quenched samples						
0.0	0.25	0.00	395	520	—	—
0.1	0.32	27.69	330	475	0.27	0.36
0.2	0.21	40.48	198	455	0.18	0.27
0.3	0.17	51.57	150	420	0.18	0.27

Isomer shift (I.S.) with respect to Fe metal, error ± 0.02 . Quadrupole splitting (Q.S.), error ± 0.06 $T_N(K)$ and $T_f(K)$, error ± 5 K

The observed low values of $n_B \approx 0.5$ to $0.04 \mu_B$ for slow cooled samples and $n_B \approx 0.4$ to $0.2 \mu_B$ for quenched samples (compared with the spin only moments $5 \mu_B$, $3 \mu_B$, $1 \mu_B$, for Fe^{3+} , Cr^{3+} and Cu^{2+} respectively in the Neel configuration) (Table 1) suggests that no long range ordering contributes by transverse component but it exists only for the longitudinal component with completely disordered transverse component. This supports the random freezing of 'spin cluster' in the systems rather than freezing of individual spin as in the case of conventional spin glasses.

According to Neel's two sub-lattice model of ferrimagnetism (16), the Neel's magnetic moment per formula unit in μ_B , n_B^N is expressed as,

$$n_B^N(x) = M_B(x) - M_A(x), \quad (3)$$

where M_B and M_A are B- and A-site magnetic moments, respectively in μ_B .

The experimental values of saturation magnetization per formula unit $n_B(\mu_B)$ are found to be lower as compared to calculated values obtained by using eq. (3) for both slow cooled and quenched systems indicating that significant canting exists on B -sites suggesting magnetic structure to be non-collinear (canted) which leads to canted spin type of magnetic ordering in both the systems. Therefore, the canting angle (θ) can be calculated by using the relation

$$n_B^C = M_B \cos \theta - M_A.$$

The experimental values of canting angle (θ) can be obtained using observed n_B values for slow cooled samples with the help of relation :

$$n_B = 4(x + 1 + y) \cos \theta - [5(1 - x) - 4(y)],$$

while for quenched it can be obtained using relation :

$$n_B = (4 + 3.5x + 4y) \cos \theta - [5 - 4.5x - 4y].$$

The thermal variation of a.c. susceptibility [$\chi_{ac}(T)$] for slow cooled samples with $x = 0.1, 0.2, 0.3, 0.4, 0.5$ and 0.6 is shown in Figure 3. It can be seen from Figure 3

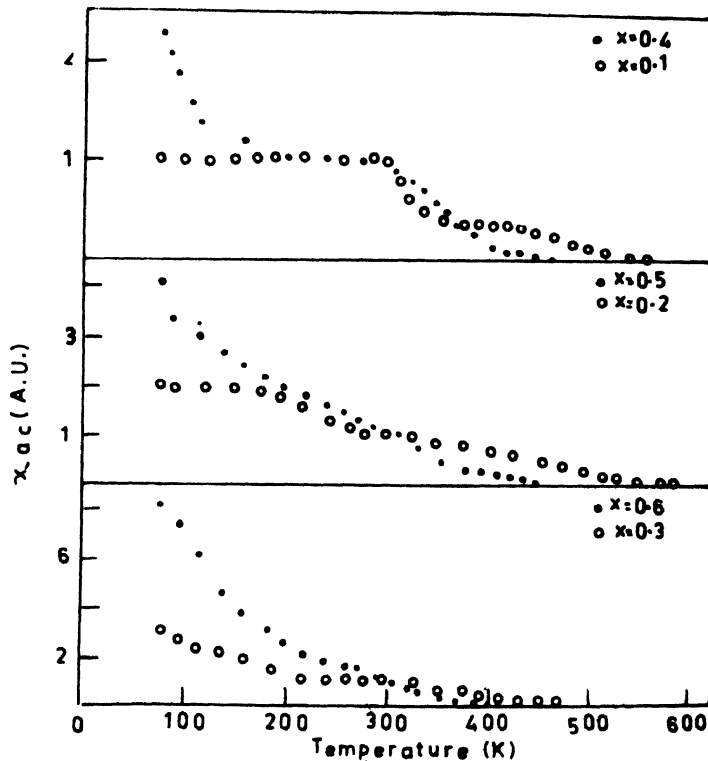


Figure 3. Thermal variation of a.c. susceptibility for slow cooled samples of ZnCuFeCrO system.

that upto $x \leq 0.4$ the behaviour is similar to that of ferrimagnetic samples but for $x > 0.4$ there is sudden change in nature as well as rise in the value of susceptibility at 77 K as

compared to its value at 298 K (Figure 4). These observed features can be explained as follows.

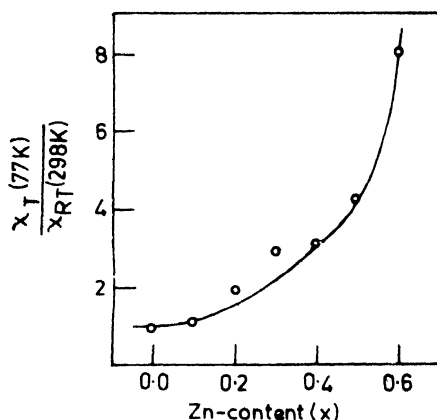


Figure 4. Relative susceptibility with Zn-concentration (x)

From eq. (1) it can be seen that for $x = 0.5$ and 0.6 , the magnetic ion concentration on the A-site $[M(A)]$ is near to the A-sublattice percolation threshold (0.429) [17]. Therefore, no long range ordering is possible in the system. However, if we assume the short range interactions are present and these are limited to first neighbour then according to mean field theory the interacting spins form clusters which behave as single entities below a certain temperature. These clusters may not have the collinear spin configuration within, as the nearest neighbours are at random.

It is found that for $x \geq 0.4$ the canting angle is greater than 60° (Table 1) so it is expected that a transverse component is much larger than longitudinal component. As a result now observed nature of $[\chi_{ac}(T)]$ (Figure 3) can be explained on the basis of gradual increase of spin-spin correlation as the temperature is lowered. From Figure 3 it can be seen that no peak is observed up to 80 K, which suggests that inter-cluster interaction is not comparable to the thermal energy, otherwise there should be a rapid increase in the magnetic viscosity resulting in the freezing of clusters. Therefore, sudden increase in susceptibility for $x > 0.4$ (Figure 4) indicates that the system is approaching the cluster spin glass type magnetic ordering.

Figure 5 shows the thermal variation of a.c. susceptibility $[\chi_{ac}(T)]$ for quenched samples with $x = 0.0, 0.1, 0.2$ and 0.3 . The results of $[\chi_{ac}(T)]$ (Figure 5) show an asymmetrical peak centered around its respective freezing temperature (T_f), which is an indication of some degree of magnetic ordering or net result of competing anisotropies in these chosen samples. Similar asymmetrical peak have previously reported for other diluted systems [18–20]. The observed sharp maxima at $T_f \approx 395$ K and 330 K for $x = 0.0, 0.1$ respectively and broad maxima at $T_f \approx 198$ K and 150 K for $x = 0.2, 0.3$ respectively, have been found to shift to lower temperature upon application of an external magnetic field of the order of 4 K Am^{-1} . The maximum observed in $[\chi_{ac}(T)]$ curves can be explained as arising from the strength of the local anisotropy field becoming larger than applied external field at T_f . In $\text{Zn}_x\text{Cu}_{1-x}\text{FeGrO}_4$ system as Zn concentration

increases from $x = 0.1$ to 0.3 the interaction energy ($ZJ_{AB} S_A S_B$) which gives rise to ferrimagnetic ordering at Neel temperature (T_N), decreases, as a result, the frustration and disorder also increases. These two parameters lead to the random freezing of cluster moments. This can be clearly seen from the decrease in the Neel temperature (T_N) and freezing temperature (T_f) deduced from thermal variation of a. c. susceptibility measurements (Table 1).

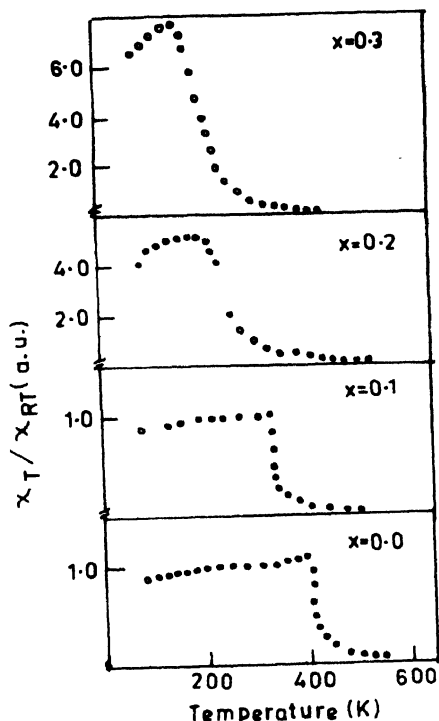


Figure 5. Thermal variation of a. c. susceptibility for quenched samples of ZnCuFeCrO system

The magnetic behaviour of the $x = 0.1$ to 0.3 samples is particularly interesting. These samples show nearly only one ordering in $[\chi_{ac}(T)]$ curves at T_f (Figure 5) corresponding to a maximum and the shifting of T_f to lower temperature upon application of external field are general features of cluster spin glass type of ordering. The sudden rise in value of χ_{ac} for $x > 0.1$ can be explained on the similar basis as in the slow cooled samples.

The Neel temperatures for quenched samples are found to be lower as compared to the slow cooled samples attributed to the replacement of Zn^{2+} ion on B -site which dilutes the magnetic linkages and results in lower values of Neel temperature.

In order to confirm the concept of cluster spin glass, further the Mössbauer spectra of the slow cooled and quenched samples were taken at room temperature (298 K). Typical

Mössbauer spectra for slow cooled sample with $x = 0.2, 0.5$ and 0.6 are displayed in Figure 6. Mössbauer spectra for quenched sample with $x = 0.1$ and 0.3 are displayed in Figure 7. In both the cases, spectra exhibits the presence of an intense central quadrupole

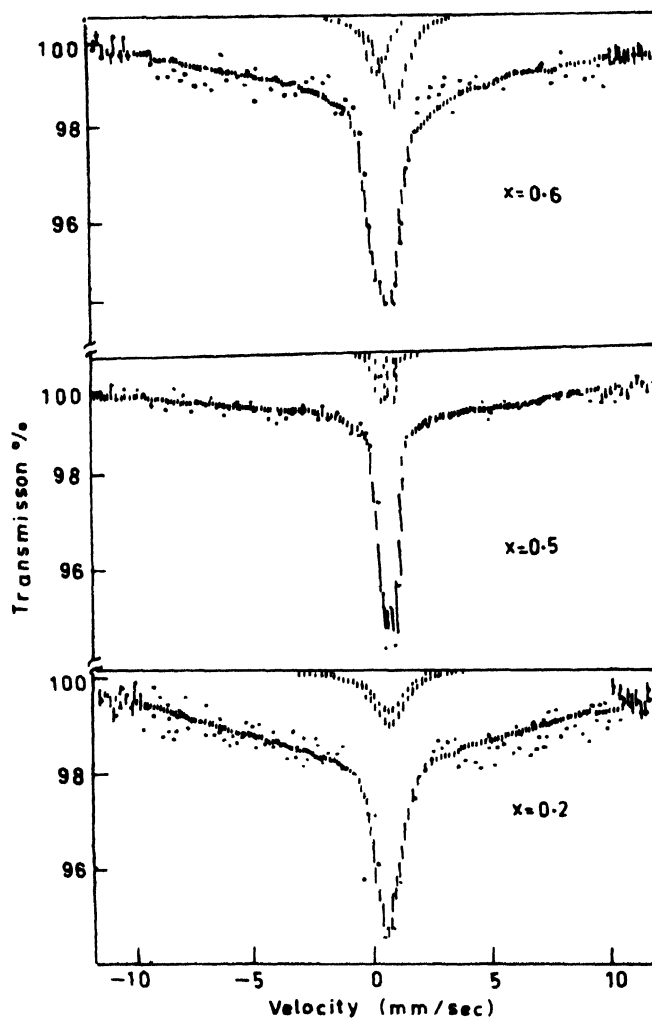


Figure 6. Typical Mössbauer spectra (298 K) for the slow cooled samples of ZnCuFeCrO system.

doublet superimposed on an unresolved broad magnetic hyperfine field distribution indicating the dominance of short range ordering (clustering) over the long range ferrimagnetic ordering as it is strongly suppressed. The Mössbauer parameters derived from the least square fits are given in Table 1. In both cases, quadrupole splitting (Q.S.) decreases with increasing Zn^{2+} concentration (Table 1). Therefore, the observed clustering in chosen composition may be attributed to the frustration and disorder which arise from the competing the next neighbour interaction J_{AB}, J_{BB} .

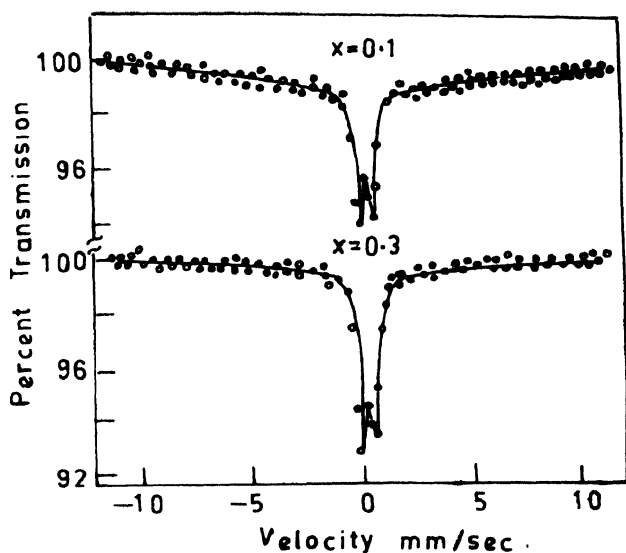


Figure 7. Typical Mössbauer spectra (298 K) for the slow cooled samples of ZnCuFeCrO system.

4. Conclusions

The above results on slow cooled and quenched samples of disordered spinel system $Zn_xCu_{1-x}FeCrO_4$ leads to the following conclusions :

- (i) the rate of cooling has highly influenced the structural and magnetic properties,
- (ii) it clearly establishes the existence of a cluster spin glass consisting of randomly ordered groups of spins for slow cooled ($x > 0.4$) and for quenched ($x > 0.1$) systems.

Acknowledgment

The authors are thankful to Dr. G J Baldha, Department of Physics, Saurashtra University, Rajkot for critical reading of manuscript and valuable guidance.

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