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Cation distribution of the system $CuAl_xFe_{2-x}O_4$ by X-rays and Mossbauer studies

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The structural and Mossbauer spectroscopy studies have been performed on the spinel solid solution series $CuAl_xFe_{2-x}O_4$ ($0.0 \le x \le 1.0$). All the compounds with $0.0 \le x \le 1.0$ crystallised with cubic spinel structure. Lattice constant values calculated from XRD analysis were found to decrease on increasing x, linearly obeying Vegard's law. The X-ray intensity calculations indicated that Cu^{2+} prefers to occupy octahedral (B) site, where as Al^{3+} ions replace Fe^{3+} ions from both tetrahedral (A) and octahedral (B) sites. Mossbauer spectra at room temperature display magnetic sextets corresponding to A and B-sites superimposed on each other. The data shows that Al-possesses greater preference for B-site compared to A-site, and iron exists in high spin ferric Fe^{3+} state. The hyperfine fields for both A and B-sites decrease with increasing x. The cation distribution calculated from X-ray intensity data agrees with the Mossbauer results. © *2000 Kluwer Academic Publishers*

1. Introduction

Diamagnetic substitution in single and mixed ferrites have received a lot of attention over the past years. The preference of non magnetic ions in spinels is found to alter their magnetic and electrical properties, and studies have revealed useful information on the nature of the exchange interaction, direction of magnetization, cation distribution, spin canting etc.. The introduction of diamagnetic ions in spinels is expected to weaken the magnetic coupling which may be reflected in a decrease of the magnetic hyperfine field and Curie temperature as a function of diamagnetic substitution.

There have been numerous investigations on the substitution of diamagnetic Al^{3+} in spinels. In our recent study [1] on $CuAl_xFe_{2-x}O_4$ ($0.0 \le x \le 1.6$) system through magnetization, Mossbauer effect and a.c. susceptibility, we have obtained cation distribution for this system. We report here structural and Mossbauer spectroscopy studies on $CuAl_xFe_{2-x}O_4$ ($0.0 \le x \le 1.0$) to clarify the site occupancy of Al and more appropriate cation distribution. We report cation distribution for quenched samples.

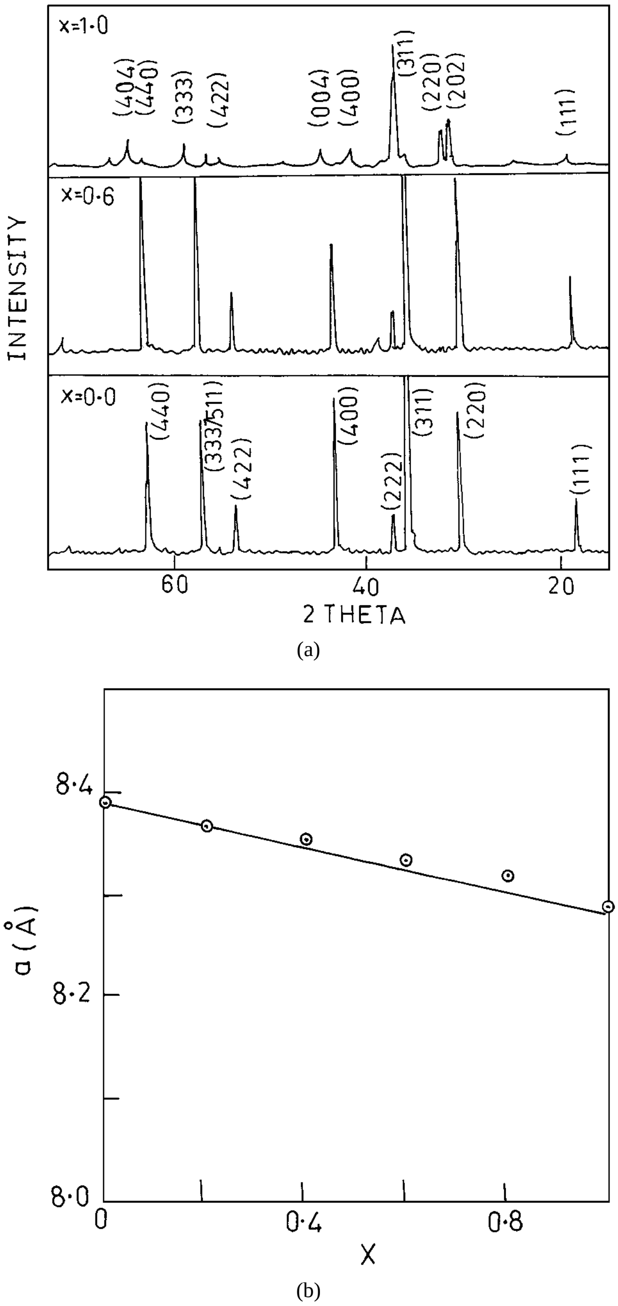
2. Experimental

The polycrystalline samples of $CuAl_xFe_{2-x}O_4$ ($0.0 \le x \le 1.0$) with a step of $x = 0.2$ were prepared by the usual double sintering ceramic method. The starting materials were Fe_2O_3, CuO and Al_2O_3, all 99.9% pure supplied by E.Merck. The oxides were thoroughly mixed, pelletized and sintered at 1000°C for 24 hours and slowly cooled to room temperature. The samples were again powdered, pressed into pellets, refired in air at 1000°C for 24 hours and then quenched at liquid nitrogen temperature. The X-ray diffraction (XRD) patterns indicated the presence of only the spinel structure with no impurity phases. Slight tetragonality was observed for the sample $x \ge 0.8$. The Mossbauer spectra were obtained at room temperature in transmission geometry with a source of 20 mCi ^{57}Co(Rh) and a constant acceleration transducer. Magnetization measurements on each sample were carried out using the high field hysteresis loop technique [2] at 300 K.

3. Results and discussion

Typical X-ray diffractograms of the system $CuAl_x Fe_{2-x}O_4$ ($x = 0.0$, 0.6 and 1.0) are shown in Fig. 1a. The X-ray diffractograms for $x = 0.0$ to 0.6 show sharp lines corresponding to single phase cubic spinel, while for $x \ge 0.8$ display slight cubic tetragonal distortion with axial ratio $c/a \approx 1.06$–1.01. The values of the lattice constant 'a' determined from XRD data with an accuracy of ±0.002 Å are shown in Fig. 1b, as a function of x. The lattice constant exhibits a very slow linear decrease with increasing x from $x = 0.0$ to 1.0 there by obeying Vegard's law [3].

In order to determine the cation distribution, XRD intensities were calculated using the formula suggested by Buerger [4].



(a)

(b)

Figure 1 (a) Typical X-ray diffractograms of $CuAl_xFe_{2-x}O_4$ at 300 K for $x = 0.0$, 0.6 and 1.0; (b) Variation of the lattice parameter '*a*' with Al concentration (x) in $CuAl_xFe_{2-x}O_4$.

The integrated XRD intensity is given by

$$I_{hkl} = F_{hkl}{}^2 P L_\mathrm{P} \tag{1}$$

where F_{hkl} is the structure factor, P is the multiplication factor and L_p Lorentz Polarization factor. The ionic configurations based on its preference energy values proposed by Miller [5] for individual cations in $CuAl_xFe_{2-x}O_4$ suggests that Cu^{2+} prefers to occupy B-sites and Al^{3+} and Fe^{3+} ions can occupy both A and B sites. Accepting the cation distribution of $CuFe_2O_4$ [6–8] an approximate cation distribution for the $CuAl_xFe_{2-x}O_4$ system can be written as,

$$\left(Cu^{2+}_{0.15}Fe^{3+}_{0.85-0.3x}Al^{3+}_{0.3x}\right)^{A}\left[Cu^{2+}_{0.85}Fe^{3+}_{1.15-0.7x}Al^{3+}_{0.7x}\right]^{B}O^{2-}_{4} \tag{2}$$

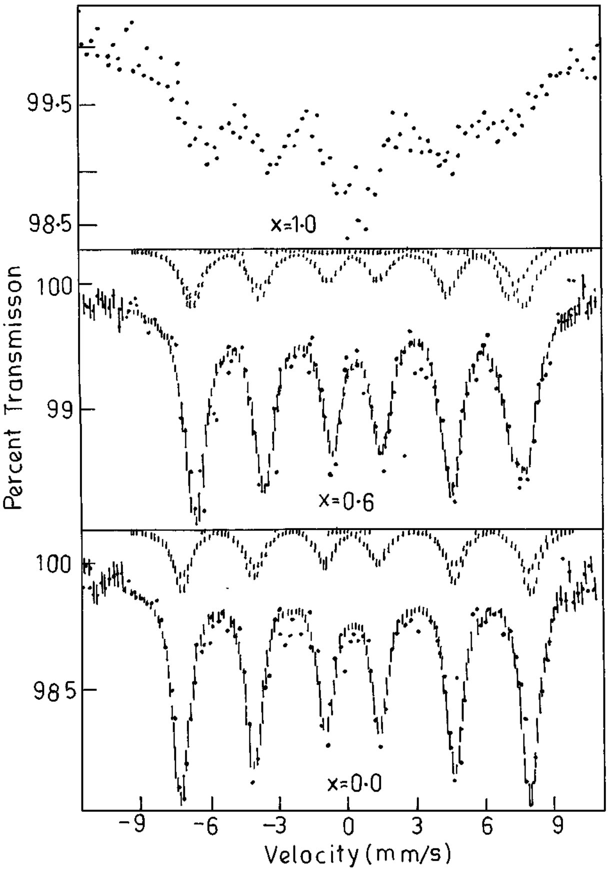


Figure 2 Typical Mossbauer spectra of $CuAl_xFe_{2-x}O_4$ at 300 K for $x = 0.0$, 0.6 and 1.0.

In Table I the results of X-ray intensity calculations for various possible models which agree with the observed intensity data are given. It is clear from Table I that observed and calculated intensity ratios are in good agreement with each other for $0.0 \leq x \leq 0.6$, while for $x \geq 0.8$ they slightly differ from each other which may be due to slight tetragonality in the structure. From this Table I, it is evident that the Cu^{2+} ions occupy more preferentially B-sites than A-sites, and Al^{3+} ions replace Fe^{3+} from both sites.

Typical Mossbauer spectra recorded at 300 K are shown in Fig. 2. The spectra for $x = 0.0$ to 0.8 exhibit magnetic sextets corresponding to A and B sites superimposed on each other, while for $x = 1.0$ displays the presence of central quadrupole doublet superimposed on an unresolved broad magnetic sextets, which indicates ferrimagnetic behaviour of samples in confirmity with magnetization data (Table II). The solid lines through the data points in Fig. 2 are the results of computer fits of spectra obtained assuming equal line widths for A and B sites.

The Mossbauer data for the system under investigation ($CuAl_xFe_{2-x}O_4$) have shown that Al^{3+} can occupy both A and B sites. We have used the intensities calculated from the tetrahedral (I_A) and octahedral (I_B) magnetic sextets measured at 300 K and the cation distribution of copper ferrite $(Cu_{0.15}Fe_{0.85})^A\,[Cu_{0.85}Fe_{1.15}]^BO_4$ as reference material. Using the intensities of the Fe^{3+} magnetic sites in $CuAl_{0.2}Fe_{1.8}O_4$ measured at 300 K, we find that 1.01 Fe^{3+} enters B-site, while 0.79 Fe^{3+} enters the A-site. This suggests that a maximum of 0.21 of

TABLE I Comparision of X-ray intensity ratios for $CuAl_xFe_{2-x}O_4$

	Cation distribution		I_{220}/I_{440}		I_{220}/I_{400}		I_{400}/I_{422}	
x	A-site	B-site	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
0.0	$(Cu_{0.2}Fe_{0.8})$	$[Cu_{0.8}Fe_{1.2}]$		0.61		1.27		2.27
	$(Cu_{0.15}Fe_{0.85})$	$[Cu_{0.85}Fe_{1.15}]$	0.57	0.60	1.45	1.24	2.34	2.33
	$(Cu_{0.15}Fe_{0.85})$	$[Cu_{0.85}Fe_{1.15}]$		0.60		1.24		2.33
0.2	$(Cu_{0.2}Al_{0.04}Fe_{0.76})$	$[Cu_{0.8}Al_{0.16}Fe_{1.04}]$		0.61		1.28		2.23
	$(Cu_{0.15}Al_{0.06}Fe_{0.79})$	$[Cu_{0.85}Al_{0.14}Fe_{1.01}]$	0.63	0.59	1.41	1.20	2.18	2.38
	$(Cu_{0.15}Al_{0.04}Fe_{0.81})$	$[Cu_{0.85}Al_{0.16}Fe_{0.99}]$		0.60		1.25		2.29
0.4	$(Cu_{0.2}Al_{0.08}Fe_{0.72})$	$[Cu_{0.8}Al_{0.32}Fe_{0.88}]$		0.62		1.32		2.19
	$(Cu_{0.15}Al_{0.12}Fe_{0.73})$	$[Cu_{0.85}Al_{0.28}Fe_{0.87}]$	0.57	0.59	1.23	1.18	2.58	2.44
	$(Cu_{0.15}Al_{0.08}Fe_{0.77})$	$[Cu_{0.85}Al_{0.32}Fe_{0.83}]$		0.61		1.28		2.25
0.6	$(Cu_{0.2}Al_{0.12}Fe_{0.68})$	$[Cu_{0.8}Al_{0.48}Fe_{0.72}]$		0.63		1.34		2.14
	$(Cu_{0.15}Al_{0.18}Fe_{0.67})$	$[Cu_{0.85}Al_{0.42}Fe_{0.73}]$	0.66	0.58	1.07	1.14	2.70	2.50
	$(Cu_{0.15}Al_{0.12}Fe_{0.73})$	$[Cu_{0.85}Al_{0.48}Fe_{0.67}]$		0.62		1.30		2.21
0.8	$(Cu_{0.2}Al_{0.16}Fe_{0.64})$	$[Cu_{0.8}Al_{0.64}Fe_{0.56}]$		0.64		1.37		2.10
	$(Cu_{0.15}Al_{0.24}Fe_{0.61})$	$[Cu_{0.85}Al_{0.56}Fe_{0.59}]$	0.75	0.57	1.06	1.11	1.78	2.56
	$(Cu_{0.15}Al_{0.16}Fe_{0.69})$	$[Cu_{0.85}Al_{0.64}Fe_{0.51}]$		0.63		1.33		2.16
1.0	$(Cu_{0.2}Al_{0.20}Fe_{0.60})$	$[Cu_{0.8}Al_{0.80}Fe_{0.40}]$		0.64		1.39		2.50
	$(Cu_{0.15}Al_{0.30}Fe_{0.55})$	$[Cu_{0.85}Al_{0.70}Fe_{0.45}]$	0.75	0.56	1.07	1.07	0.99	3.20
	$(Cu_{0.15}Al_{0.20}Fe_{0.65})$	$[Cu_{0.85}Al_{0.80}Fe_{0.35}]$		0.63		1.35		2.58

TABLE II Saturation magnetization per formula unit (η_B) obtained at 300 K and by Neel's model

x	Magnetization 300 K $\eta_B(\mu_B)$	Neel's Model $\eta_B(\mu_B)$
0.0	2.17	2.2
0.2	1.69	1.8
0.4	1.22	1.4
0.6	0.86	1.0
0.8	0.48	0.6
1.0	0.27	0.2

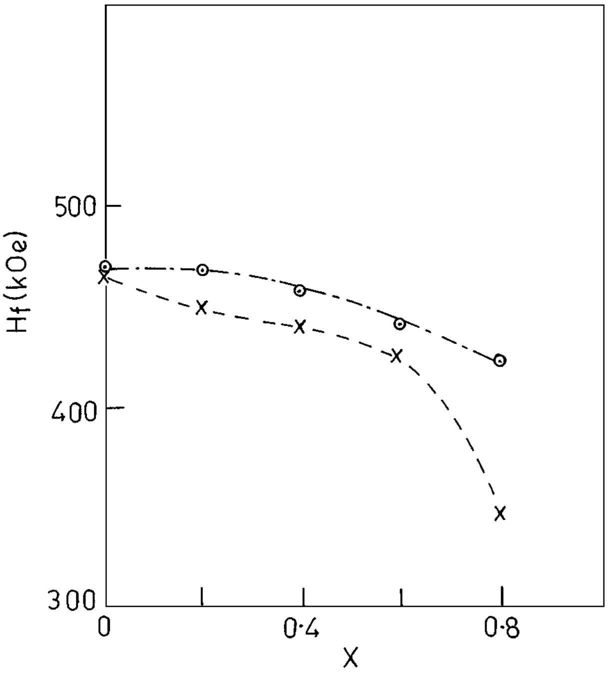


Figure 3 Variation of the hyperfine field (H_f) with Al concentration (x).

$(Cu^{2+} + Al^{3+})$ enters the A-site. The fractions of Al^{3+} and Cu^{2+} ions at A and B sites are estimated on the basis of magnetization data (Table II). From that we find that Al^{3+} cations replace Fe^{3+} cations in A and B sites linearly with the probability ratio 3 : 7 without any exchange of copper cations between A and B sites. We recall that all of our compounds have been prepared under similar conditions and that the degree of inversion is assumed to be the same. With the above distribution of Cu^{2+}, the site occupancy of Al^{3+} in the concentration range $0 \leq x \leq 1.0$ have been calculated and presented in Table III.

The experimental integrated intensity ratios of the A and B sites ^{57}Fe spectra and those calculated on the basis of cation distribution obtained from X-ray intensity data given in Table I are in very good agreement with each other (Table III) for $x = 0.0$ to 0.8. This confirms the cation distribution formula given above as it agrees with Mossbauer and X-ray intensity data satisfactorily.

Fig. 3 shows the variation of hyperfine fields with the Al^{3+} concentration x. Assuming that the hyperfine field

TABLE III Intensities of Fe^{3+} and calculated Al^{3+} and Cu^{2+} site occupancy from Mossbauer spectra at 300 K

X	I_A(%)	I_B(%)	A-site Occupancy $(Cu^{2+}+Al^{3+})_A$	B-site Occupancy $(Cu^{2+}+Al^{3+})_B$	Mossbauer $\frac{I_B(Fe^{3+})}{I_A(Fe^{3+})}$	XRD Intensity ratio $\frac{I_B(Fe^{3+})}{I_A(Fe^{3+})}$
0.0	42.5	57.5	$(0.15 + 0.00)$	$(0.85 + 0.00)$	1.35	1.35
0.2	44.0	56.0	$(0.15 + 0.06)$	$(0.85 + 0.14)$	1.27	1.28
0.4	45.2	54.8	$(0.15 + 0.12)$	$(0.85 + 0.28)$	1.21	1.19
0.6	46.5	43.5	$(0.15 + 0.18)$	$(0.85 + 0.42)$	1.15	1.10
0.8	30.8	66.4	$(0.15 + 0.24)$	$(0.85 + 0.56)$	2.15	0.97
1.0	—	—	$(0.15 + 0.30)$	$(0.85 + 0.70)$	—	0.82

at a site is proportional to the local magnetic moment i.e. $M_A \alpha H_A$ and $M_B \alpha H_B$, it is evident from Fig. 3 that the decrease in hyperfine field at both sites (H_A and H_B) with increasing x demonstrates a reduction in ferrimagnetic behaviour with increasing x in agreement with magnetization data (Table II).

The magnetization data can be explained in terms of Neel's two sublattice model satisfactorily. The Neel's magnetic moments in μB obtained from

$$\eta_B^N(x) = M_B(x) - M_A(x) \tag{3}$$

Where M_B and M_A represent sublattice moments calculated using the cation distribution are listed in Table II. These η_B^N (μ_B) values agree very well with the measured $\eta_B(\mu_B)$ values indicating collinear spin ordering.

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