

Investigation of phase separation in the $\text{Ge}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ system

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The spinel series $\text{Ge}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.0$ to 0.9) has been studied in detail by means of Mössbauer spectroscopy, X-ray diffraction and magnetization measurements at room temperature (298 K). Analysis of X-ray diffraction intensity data and Mössbauer intensity data suggest that this system remains in single phase up to $x = 0.4$ then it phase separates into two different phases for $x = 0.5$ to 0.9 . Lattice constants of this system deviate from Vegard's law. Mössbauer spectra for $x = 0.0$ to 0.4 suggest the existence of two hyperfine fields, one due to the Fe^{3+} tetrahedral ions (A-sites) and the other due to the Fe^{3+} octahedral ions (B-sites), while for $x = 0.5$ to 0.9 it gives Mössbauer patterns corresponding to two separate phases. The systematic composition dependence of quadrupole interactions and nuclear hyperfine fields of $^{57}\text{Fe}^{3+}$ ions also support the concept of phase separation for $x = 0.5$ to 0.9 . The observed variation of $^{57}\text{Fe}^{3+}$ hyperfine field on A- and B-sites with x for $x = 0.0$ to 0.4 can be explained qualitatively on the basis of supertransferred hyperfine interactions.

1. Introduction

In the solid solution of the spinel $\text{Ge}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$, the Ge^{4+} , Fe^{3+} , Fe^{2+} and Cu^{2+} cations are distributed among octahedral (B) and tetrahedral (A) interstitial sites. As GeFe_2O_4 ($x = 1.0$) is assumed to be "normal" spinel, Ge^{4+} ions have strong preference to the A sites, while CuFe_2O_4 ($x = 0.0$) has a predominantly inverse spinel structure with Cu^{2+} ions mainly on the B sites. Robbins [1] has suggested that in the $\text{Zn}_x\text{Ge}_{1-x}\text{Ni}_{2-2x}\text{Fe}_{2x}\text{O}_4$ system, Ge^{4+} has a lower A site preference than Zn^{2+} and Fe^{3+} .

The $\text{Ge}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ ferrite system is a substituted ferrimagnet. No measurements for this ferrite have been reported except for our recent Mössbauer study of this ferrite at 77 K [2]. The present paper reports X-ray diffraction, magnetization and Mössbauer study of Cu-Ge ferrites with different germanium concentrations ($x = 0.0$ to 0.9). The aim of this work is to investigate the magnetic properties of this ferrite at varying germanium concentrations at room temperature and to make clear the site

preference of Ge^{4+} ions in the mixed oxides spinel.

2. Experimental procedure

Analytical reagent grade powder mixes of GeO_2 (E. Merck), CuO (BDH), Fe_2O_3 (Robert and Johnson) and Fe in powder form (JMC) with appropriate ratios were well ground, fired at 1000°C for 50 h and slowly cooled to room temperature. Ten samples with $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and 0.9 were prepared by the usual ceramic method. Powder X-ray diffraction patterns were recorded on a Philips diffractometer using $\text{FeK}\alpha$ radiation to characterize the samples. The magnetization of each sample from $x = 0.0$ to 0.9 was carried out using the high field hysteresis loop techniques described elsewhere [3].

The absorbers were made using samples in the powdered form of thickness between 20 to 25 mg cm^{-2} . The Mössbauer spectra were obtained with a constant acceleration transducer and a 256 multichannel analyser operating in time mode. The spectrometer was calibrated

TABLE I X-ray analysis of $\text{Ge}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ system at 298 K

x	Phase I (fcc) Lattice constant (nm)	x	Phase II (fcc) Lattice constant (nm)	Phase III (bcc) Lattice constant (nm)
0.0	0.8225 ± 0.0002	0.5	0.8286 ± 0.0002	0.8637 ± 0.0002
0.1	0.8360 ± 0.0002	0.6	0.8296 ± 0.0002	0.8607 ± 0.0002
0.2	0.8356 ± 0.0002	0.7	0.8297 ± 0.0002	0.8607 ± 0.0002
0.3	0.8459 ± 0.0002	0.8	0.8300 ± 0.0002	0.8599 ± 0.0002
0.4	0.8380 ± 0.0002	0.9	0.8300 ± 0.0002	0.8589 ± 0.0002

using iron metal foil. A gamma source ^{57}Co (Cu) of a specific activity of 10 mCi was used. All spectra were obtained at room temperature (298 K) in transmission geometry and the 14.4 keV gamma rays were detected with NaI(Tl) detector specifically suitable for Mössbauer work.

3. Results and discussion

For all the samples of the system, the X-ray diffraction patterns showed sharp lines in the range of $2\theta = 5^\circ$ to 80° , corresponding to single phase for $x = 0.0$ to 0.4 and a mixture of two phases for $x = 0.5$ to 0.9. The intensity of X-ray diffraction for selected Bragg reflections as a function of germanium concentration (x) for each phase is shown in Fig. 1. It is apparent from Fig. 1 that the intensity of the (220) plane of phase I ($x = 0.0$ to 0.4) first increases, then decreases as x approaches 0.5 and from $x = 0.5$

to 0.9 the intensity of Bragg reflections (222) and (521) corresponding to phases II and III, respectively, increase as x increases. We have found that all phases possess cubic crystal structure and the lattice parameters obtained for each phase are listed in Table I. It should be noted that the lattice constants of the system deviate from Vigard's law. An interesting feature about phase III is that its molecular formula (Table V) is similar to that of a GeFe_2O_4 (fcc) the newly found phase III has bcc structure and its quadrupole splitting (QS) is about 2.3 times smaller than GeFe_2O_4 (fcc).

The saturation magnetizations of all samples have been estimated to within an accuracy of 5% and are listed in Table II. The magneton number, i.e. the saturation magnetization per formula unit in Bohr magneton, n_B , at 298 K, initially increases up to $x = 0.3$, then decreases as x is increased from 0.3 to 0.5 and it approaches zero at $x = 0.6$. We have also observed spin glass types of behaviour for $x = 0.1$ and 0.2 samples through the measurement of temperature dependence of low field a.c. susceptibility and the results of these measurements will be published elsewhere.

Mössbauer spectra obtained at 298 K are shown in Figs. 2, 3 and 4. For $x = 0.1, 0.2, 0.3$ and 0.4 the spectra exhibit two well defined Zeeman patterns, one due to the Fe^{3+} ions at the

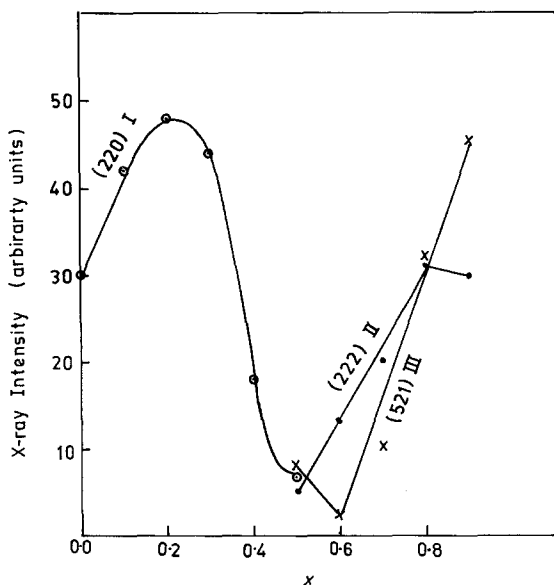


Figure 1 The variation of X-ray diffraction intensity with x for selected Bragg reflections corresponding to phases I(fcc), II(fcc) and III(bcc).

TABLE II Magnetization measurements of the Cu-Ge system at 298 K

x	Saturation magnetization, σ_s (emu g^{-1})	Bohr magneton, n_B
0.0	25.4	1.07
0.1	31.5	1.35
0.2	38.8	1.68
0.3	56.7	2.43
0.4	34.2	1.49
0.5	2.7	0.12
0.6	0.0	0.00

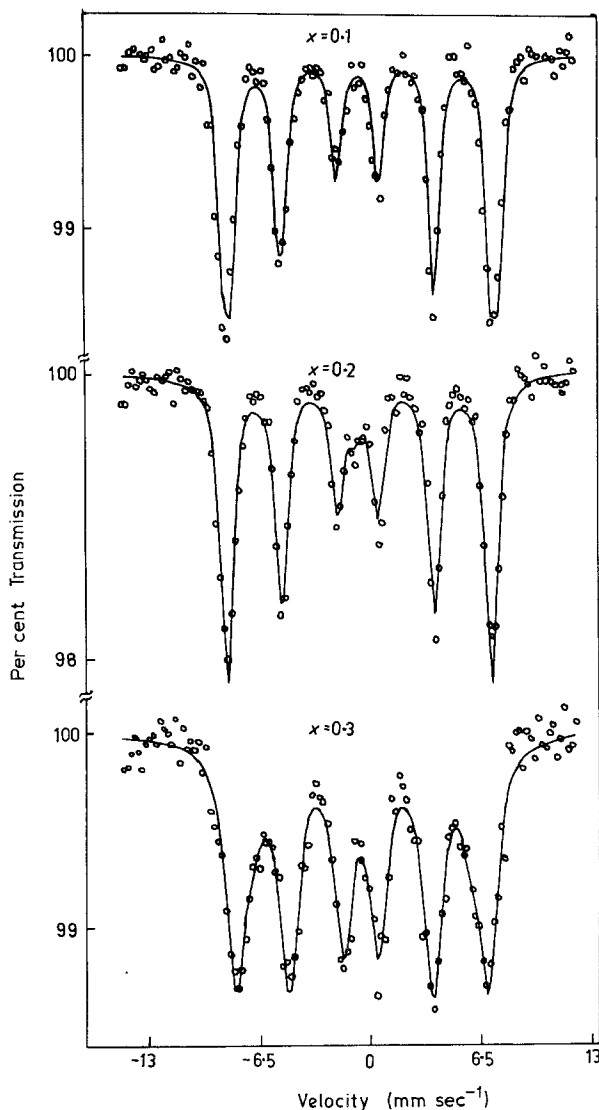


Figure 2 Mössbauer spectra of $x = 0.1, 0.2$ and 0.3 at 298 K for the Cu-Ge ferrite system. The solid lines are the least squares computer fits.

tetrahedral (A) site, the other due to the Fe^{3+} ions at the octahedral (B) site, which correspond to fcc phase I. The spectra for $x = 0.5, 0.7, 0.8$ and 0.9 shown in Figs. 3 and 4 consist of a doublet superimposed on a Zeeman split sextet. The Zeeman split sextet corresponds to fcc phase II and the doublet corresponds to bcc phase III, described above. Although we have observed the presence of both phases (II and III) for the $x = 0.6$ sample in X-ray data, the same has not been seen in the Mössbauer spectrum, possibly due to the very small intensity of phase III. The solid lines through the data points in Figs. 2, 3 and 4 are the results of least squares fits of the data obtained from IBM personal computer. The shapes of the lines were assumed to be Lorentzian. The intensities and widths of the

lines were allowed to vary freely subject only to the constraint that all sites were assumed to have the same width. The parameters derived from the least square fits are given in Tables III and IV.

In order to determine the cation distribution, we have taken into account both the X-ray intensity analysis and the Mössbauer integrated intensities. The most important feature of these Mössbauer spectra is that, in general, there are three types (I, II and III) of iron phases, that are populated in the composition range $0.0 \leq x \leq 0.9$. Fig. 5 gives a summary of the phase intensity variation. The curves labelled, II and III in Fig. 5 are associated with the different cation distributions listed in Table V. There are several new features of Fig. 5 which we will discuss in connection

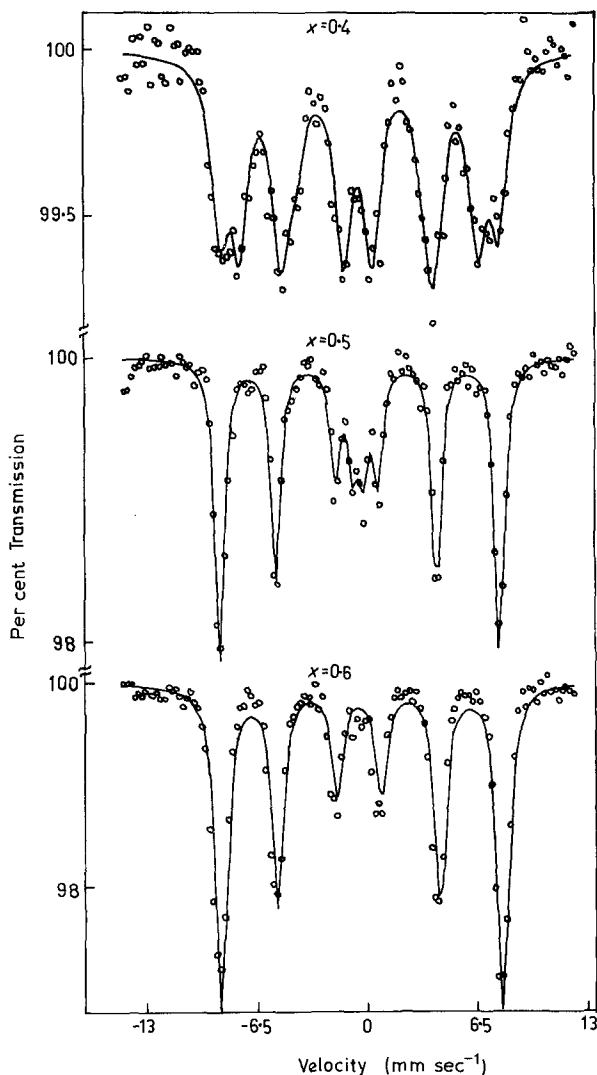


Figure 3 Mössbauer spectra of $\text{Ge}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ system for $x = 0.4, 0.5$ and 0.6 at 298 K . The solid lines are the least squares computer fits.

with quasi-equilibrium phase diagrams. These are: (a) at $x = 0.5$ the B site population reaches its maximum and the A site population nearly vanishes; (b) only two types of phase co-exist for most compositions for $0.5 \leq x \leq 0.9$. These observations of co-existence of phases II and III are in very good agreement with our

X-ray intensity data shown in Fig. 6 for $x = 0.6$ to 0.9 . We have observed two critical temperatures for the $x = 0.5$ sample by measuring the temperature dependence of a.c. susceptibility, as shown in Fig. 7, which confirm the co-existence of two separate phases in the sample.

Table V suggests that Ge^{4+} ions are present

TABLE III Mössbauer parameters of the Cu-Ge system at 298 K (phase I)

x	Isomer shift* (mm sec^{-1})		Quadrupole splitting (mm sec^{-1})		I_A/I_B expt.	I_A/I_B theo.
	IS(B)	IS(A)	QS(B)	QS(A)		
0.0	0.38 ± 0.02	0.24 ± 0.02	0.59 ± 0.06	0.00 ± 0.06		
0.1	0.53 ± 0.02	0.48 ± 0.02	0.13 ± 0.06	0.09 ± 0.06	0.94	1.00
0.2	0.52 ± 0.02	0.50 ± 0.02	0.13 ± 0.06	0.10 ± 0.06	0.69	0.77
0.3	0.52 ± 0.02	0.55 ± 0.02	0.10 ± 0.06	0.14 ± 0.06	0.50	0.55
0.4	0.46 ± 0.02	0.42 ± 0.02	0.22 ± 0.06	0.14 ± 0.06	0.82	0.72

*With respect to iron metal.

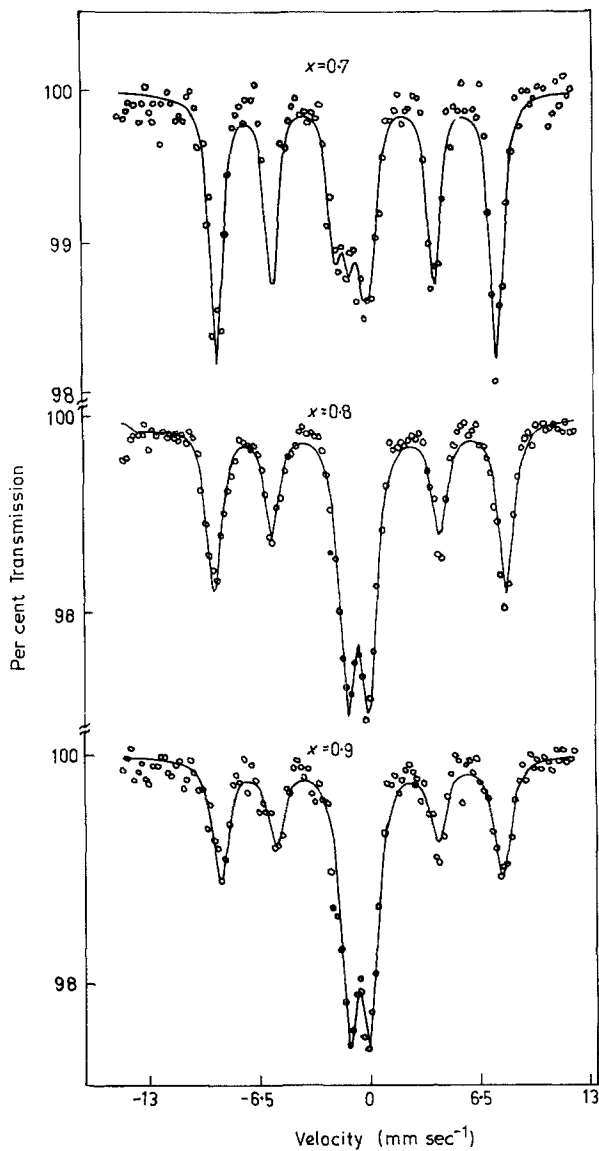


Figure 4 Room temperature (298 K) Mössbauer spectra of $x = 0.7, 0.8$ and 0.9 for Cu-Ge ferrite system. The solid lines are the least squares computer fits.

TABLE IV Mössbauer parameters of the Cu-Ge system at 298 K

x	Phase II			Phase III	
	Hyperfine field, H_{hf} (C) (kOe)	Isomer shift*, IS(C) (mm sec ⁻¹)	Quadrupole splitting, QS(C) (mm sec ⁻¹)	Isomer shift*, IS(D) (mm sec ⁻¹)	Quadrupole splitting, QS(D) (mm sec ⁻¹)
0.5	511 ± 3	0.56 ± 0.02	0.10 ± 0.06	0.55 ± 0.02	0.63 ± 0.06
0.6	515 ± 3	0.56 ± 0.02	0.09 ± 0.06		
0.7	507 ± 3	0.57 ± 0.02	0.11 ± 0.06	0.55 ± 0.02	0.79 ± 0.06
0.8	528 ± 3	0.55 ± 0.02	0.11 ± 0.06	0.53 ± 0.02	1.24 ± 0.06
0.9	511 ± 3	0.55 ± 0.02	0.13 ± 0.06	0.57 ± 0.02	1.22 ± 0.06

*With respect to iron metal.

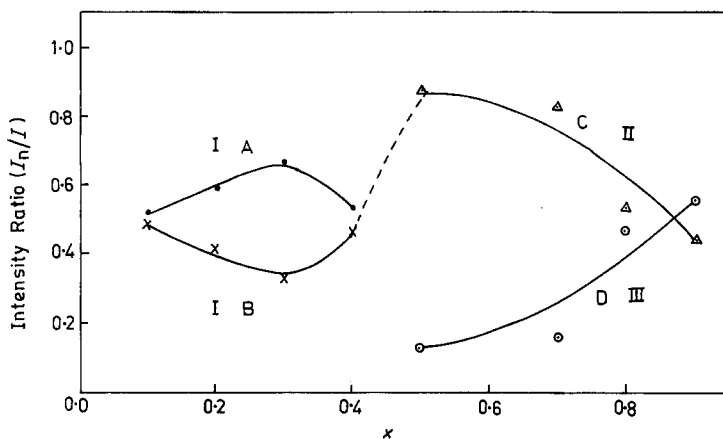


Figure 5 The variation of Mössbauer intensity ratio with x for phases I(A, B), II(C) and III(D).

on the B site for $x = 0.1$ to 0.4 , although they have a greater preference for the A site. On the other hand, Ge^{4+} ions occupy exclusively A sites for the composition $x = 0.5$ to 0.9 . Thus Ge^{4+} ions prefer B sites for phase I, whereas for phases II and III they prefer to be the A sites. Because of such site preference of Ge^{4+} ions no magnetization has been observed for this system between $x = 0.6$ to 0.9 .

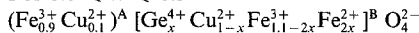
It is evident from the Tables III and IV that isomershifts show very little change with germanium content for $0.0 \leq x \leq 0.9$, indicating that s-electron distribution of the Fe^{3+} ions is practically not influenced by Ge^{4+} substitution. These results are in excellent agreement with our previous work [2].

The variation of quadrupole splitting (QS) with germanium concentration x is given in

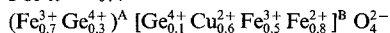
TABLE V Cation distribution in $\text{Ge}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$

Phase I

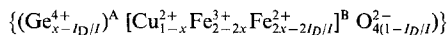
For $0.0 \leq x \leq 0.3$



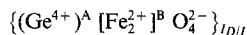
For $x = 0.4$



Phase II



Phase III



For	x	I_D/I
	0.5	0.13
	0.6	0.14
	0.7	0.16
	0.8	0.47
	0.9	0.55

Tables III and IV. It is apparent from Tables III and IV that there is a sudden change in QS at $x = 0.5$ and thereafter the QS values correspond to two separate phases II and III. It is also evident from Table IV and Fig. 8 that there is sudden change in the behaviour of hyperfine fields at $x = 0.5$.

All these observations, namely X-ray intensity data, Mössbauer intensity data, QS and nuclear hyperfine fields as a function of germanium concentration, confirm that there is phase transition at $x = 0.5$, which also corresponds to structural transition evident from lattice parameter data; thereafter phase separation takes place into II and III from $x = 0.5$ to 0.9 . The concept of phase separation is supported excellently by the present measurements shown in Figs. 5 and 6 as indicated by the magnitudes of I_C/I and I_D/I , which is qualitatively, similar to that found in oxide glasses [4].

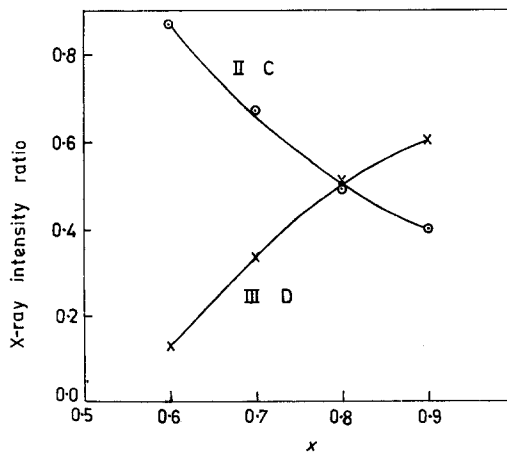


Figure 6 The variation of X-ray intensity ratio with x for phases II(C) and III(D) assuming $I = I_C + I_D$.

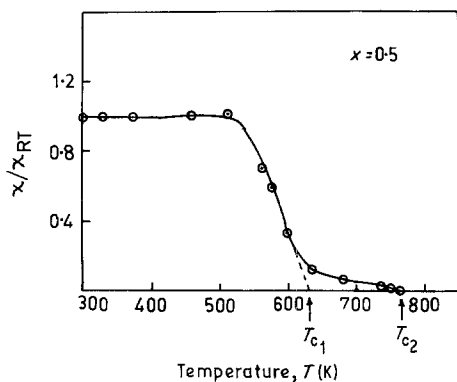


Figure 7 A.c. susceptibility of the $x = 0.5$ sample as a function of temperature.

The variation of the hyperfine fields H_A and H_B at the A- and B-sites as a function of germanium concentration is shown in Fig. 8 ($x \leq 0.4$) for phase I. It is evident from Fig. 8 that H_A decreases with increasing x and H_B is independent of x . These results are in very good agreement with our previous Mössbauer measurements of this system at 77 K [2]. Similar variations for H_A and H_B were observed in $\text{Ni}_{1-x}\text{Ge}_x\text{Fe}_{2-2x}\text{O}_4$ ferrite system ($x \leq 0.4$) at 80 K [5], which have been attributed to covalency. It was suggested earlier by us [2] that besides covalency, a significant contribution from supertransferred hyperfine interactions (STHIs) must be considered to understand the systematics of the magnetic hyperfine field at the A- and B-site iron ions. There is a striking resemblance between the observed variations of H_A and H_B and those in zinc-substituted ferrites

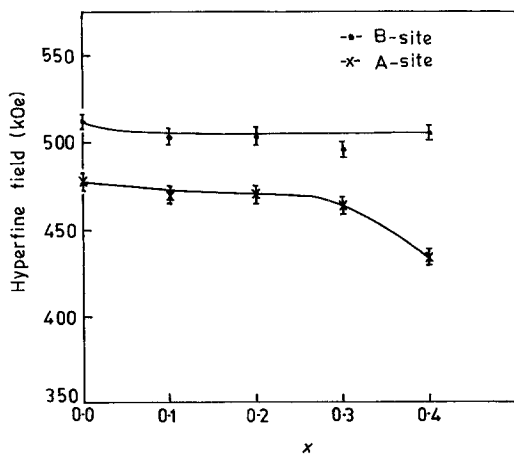


Figure 8 The variation of hyperfine fields H_A and H_B as a function of germanium concentration, for $x \leq 0.4$.

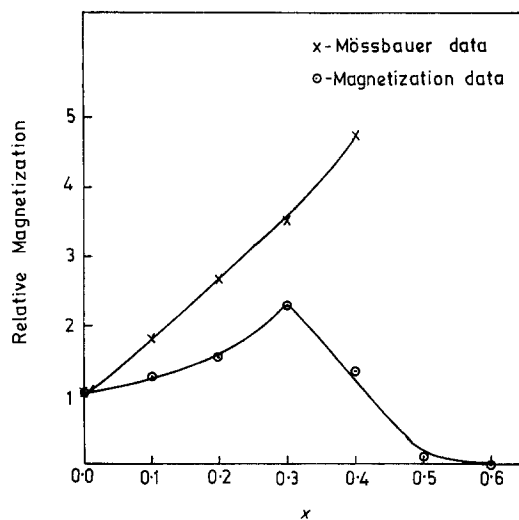


Figure 9 The relative magnetization obtained from (x) Mössbauer data and from (O) magnetization measurements.

such as Fe-Zn [6] and Cu-Zn [7], which have been explained on the basis of the canting of spins. This canting of spins gives rise to Yafet-Kittel (YK) angles, which suggest that the A-B and B-B superexchange interactions are comparable in strength.

In order to obtain an indirect check for the presence of canted spin structure, the comparison of relative magnetization obtained from Mössbauer data and from magnetization measurements shown in Fig. 9 exhibits a discrepancy. This discrepancy suggests an indirect indication of the presence of canted spins and hence of YK angles in Cu-Ge ferrites for $x \leq 0.4$. Therefore, the variations of the hyperfine fields with germanium concentration ($x \leq 0.4$) for $\text{Ge}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ can be approximately explained in terms of A-B and B-B supertransferred hyperfine interactions (STHIs) similar to that of Cu-Zn [7] ferrite system.

As has been mentioned earlier that spin glass type of behaviour was observed for $x = 0.1$ and 0.2 samples. Possibly, this is due to the magnetic inhomogeneity resulting in the formation of spin clusters.

It is evident from Fig. 9 that sample with $x = 0.3$ shows maximum magnetic moment. In this system, ion distribution is very important in connection with the origin of magnetization, since double exchange interaction between Fe^{2+} and Fe^{3+} on the B site can be the origin of the observed magnetization. The most important result is that about 64% of the A site of the

$x = 0.3$ samples is occupied by Fe^{3+} . The most probable ion distribution is $(\text{Fe}_{0.9}^{3+}\text{Cu}_{0.1}^{2+})^{\text{A}}[\text{Ge}_{0.3}^{4+}\text{Cu}_{0.6}^{2+}\text{Fe}_{0.5}^{3+}\text{Fe}_{0.6}^{2+}]^{\text{B}}\text{O}_4^{2-}$. The iron ions transferred from the A site to the B site will make various sizes of magnetic clusters through the strong A–B exchange interactions and compose an inhomogeneous spin system. Such an inhomogeneous ordering of spins is confirmed by the Mössbauer spectrum of $x = 0.4$ (Fig. 3). The obscure absorption lines indicate that the internal field at the iron ions is widely dispersed. As x increases beyond 0.4, the critical inhomogeneous ordering of spins changes into bigger molecular clusters, which transform into separate phases. This process leads to the phase separation as observed in the present work.

4. Conclusions

The spinel system $\text{Ge}_x\text{Cu}_{1-x}\text{Fe}_2\text{O}_4$ has been studied in detail by means of Mössbauer spectroscopy, X-ray diffraction and magnetization measurements at room temperature (298 K).

It has been found from X-ray intensity data and Mössbauer intensity data that this system remains in single phase I(fcc) for $x = 0.0$ to 0.4 then phase separates into two different phases II(fcc) and III(bcc) for $x = 0.5$ to 0.9. The systematic composition dependence of QS and hyperfine fields of $^{57}\text{Fe}^{3+}$ ions also support the concept of phase separation at $x = 0.5$.

The observed variation of the ^{57}Fe hyperfine field on A and B sites with germanium concentration for phase I ($x = 0.0$ to 0.4) is found to be similar in nature to that of zinc-substituted

ferrites. The variation of hyperfine fields with germanium concentration can be explained qualitatively on the basis of supertransferred hyperfine interactions.

Acknowledgements

This work was supported in part by the University Grants Commission, New Delhi. The authors are grateful to Professor P. Boolchand, Department of Physics, University of Cincinnati, Cincinnati, Ohio, USA for extending Mössbauer facilities. They are also thankful to RSIC, IIT, Bombay for providing X-ray diffractometric charts. One of the authors (GJB) wishes to thank the University Grants Commission, for providing financial support in the form of a fellowship.

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*Received 19 October
and accepted 22 November 1984*