

Mössbauer Spectra of Copper Nickel Ferrites

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Mössbauer spectra of the compositions $\text{Cu}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1$) have been studied. For $x \leq 0.2$, the compounds are tetragonal and the rest are cubic spinels. Cation distribution obtained from the split lines of the Mössbauer spectra does not agree with that obtained from magnetisation data. The spectra seem to be complicated due to the presence of more than one hyperfine field at the B site Fe^{3+} owing to the distorting effect of the Cu^{2+} ion on the A sites. This leads to non-Lorentzian line shapes and excludes straight-forward calculation of cation distribution from relative areas under resonances.

MAGNETIC properties of spinel ferrites are strongly dependent on the nature of the cations and their distribution between the tetrahedral (A) and octahedral (B) sites in the cubic close packed oxygen lattice. CuFe_2O_4 is particularly interesting in this respect because the distribution of Cu^{2+} ions between the nonequivalent sites is temperature sensitive. Moreover, the presence of Cu^{2+} ions leads to severe Jahn-Teller distortion making the nonequivalent sites more distinct than in other spinels¹.

Nickel ferrite is an inverse spinel. It is interesting to see how the distribution of Cu^{2+} ions in the A and B sites are affected in the presence of Ni^{2+} ion which has a strong octahedral site preference. This prompted us to determine the cation distribution in the $\text{Cu}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ system ($0 < x < 1$) by magnetisation measurements (Kiran *et al.*²). Several reports have appeared in the literature on the Mössbauer spectra of CuFe_2O_4 and NiFe_2O_4 (Evans and Hafner³, Yamadaya *et al.*⁴, Evans *et al.*⁵, Sawatzky *et al.*⁶, Morel⁷), but no report has been made on the Mössbauer study of the mixed ferrite system $\text{Cu}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$. This is being reported in this paper.

Experimental

The compounds were prepared by mixing appropriate quantities of CuO , NiO and $\alpha\text{-Fe}_2\text{O}_3$ (all AR grade) and firing at 1320 K for 24 hr. The samples were then cooled slowly to 1020 K, annealed at this temperature for 48 hr and cooled to room temperature at 60°/hr. All the samples were characterised as monophasic solid solutions by X-ray diffraction (XRD).

Mössbauer spectra were recorded on a multi-channel analyser (MCA 38A of ECIL) in the constant acceleration mode. The source used was ^{57}Co in rhodium matrix. The spectrometer was checked for velocity calibration by comparing the line positions of various standard absorbers (SS 310,

pure iron foil and $\alpha\text{-Fe}_2\text{O}_3$). The spectra were analysed using a computer program which performs a least mean square fit of the Lorentzian lines to the experimental points.

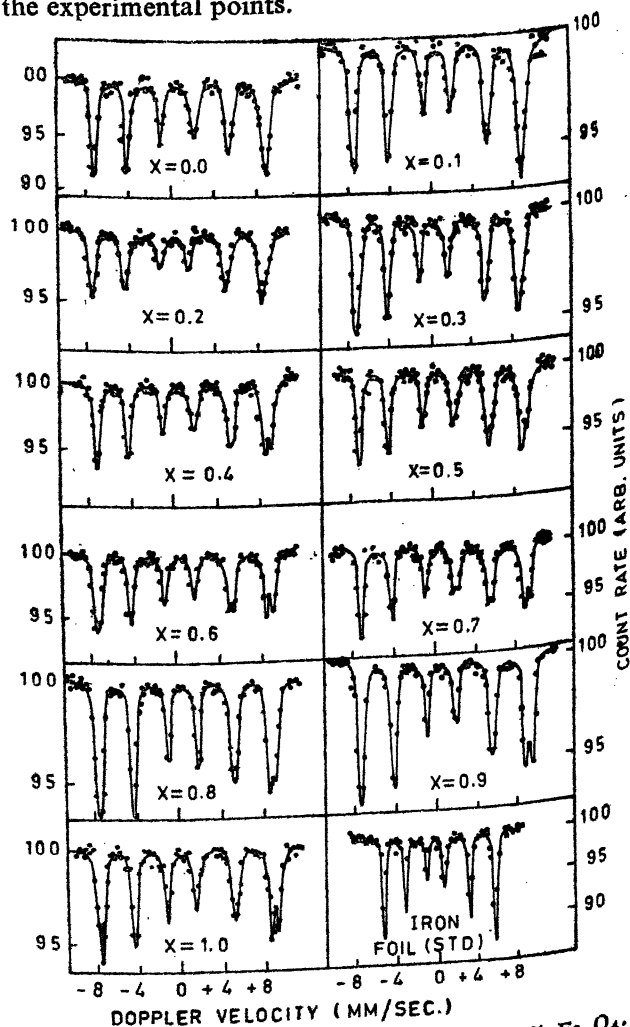


Fig. 1. Mössbauer spectra of the system $\text{Cu}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$.

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TABLE 1—MÖSSBAUER SPECTRAL PARAMETERS*
 OF $\text{Cu}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$

Composition x	Lattice parameter a (Å)		Hyperfine field $H_{eff} \pm 5\text{kOe}$		Isomer shifts IS(mm/sec)		Quadrupole splittings QS (mm/sec)		Intensity ratio I_B/I_A	$[\frac{\text{Fe}^{3+}_B}{\text{Fe}^{3+}_A}]^\dagger$	
			A	B	A	B	A	B			
0.0	$a=8.268$ $c=8.607$	T							—	1.103	
0.1	$a=8.270$ $c=8.584$	T							—	1.059	
0.2	$a=8.340$ $c=8.468$	T							—	1.111	
0.3	8.362	C							—	1.125 [†]	
0.4	8.353		484	498	0.54		0.67	0.10	0.21	0.860	1.134
0.5	8.356		484	498	0.55		0.66	0.08	0.20	0.930	1.105
0.6	8.344		484	502	0.38		0.52	0.04	0.19	0.877	1.083
0.7	8.342		491	509	0.55		0.69	0.10	0.14	0.743	1.057
0.8	8.333		488	506	0.41		0.55	0.06	0.20	0.792	1.030
0.9	8.331		491	511	0.54		0.71	0.06	0.22	0.967	1.010
1.0	8.320		491	510	0.33		0.48	0.08	0.23	1.010	1.000

+—all values at 300 K; T—Tetragonal; C—Cubic; †—from magnetisation data.

Results and Discussion

XRD patterns showed all the compositions as monophasic spinels. The compounds with $x=0.0-0.3$ were tetragonal and all other compositions were found to be cubic spinels, with lattice parameter decreasing linearly with increasing x .

Mössbauer spectra are given in Fig. 1 and the relevant parameters in Table 1. The spectra for the compositions $x=0-0.3$ are of simple six-line type. Although the lines are broad, they fitted well into six Lorentzians. The large line width seems to suggest that the spectra may be due to superposition of two six-line patterns whose envelope is also Lorentzians. For $0.4 \leq x \leq 1$, the spectra no longer correspond to a single six-line pattern; the extreme line (in some cases, the last two or all the lines) on the positive velocity are split. This is due to the superposition of two six-line patterns arising from Fe^{3+} ions at the two nonequivalent sites in the spinel structure. This was first proposed by Evans *et al.*⁸ for CuFe_2O_4 who assigned the pattern with larger hyperfine splitting to the B site Fe^{3+} and that with the smaller hyperfine split to Fe^{3+} at A sites. The same assignment may be accepted in the present case in view of the fact that isomer shift (IS) and quadrupole splitting (QS) of the latter are smaller. It is possible to resolve the Lorentzians corresponding to Fe^{3+} at A and B sites and compute the relative concentrations of Fe^{3+} in the two sites. The ratios of the areas under resonance I_B/I_A are given in Table 1 along with the ratio $[\text{Fe}^{3+}]_B/[\text{Fe}^{3+}]_A$ obtained from magnetisation values (Kiran *et al.*⁶). It may be observed that the agreement between the two ratios is poor except for the compositions $x=0.9$ and 1.0 . Such discrepancy has also been reported by Evans and Hafner¹ who observed that for CuFe_2O_4 the intensity ratio was 0.6 and 0.7 for single crystal and ceramic samples, respectively, whereas expected cation ratio was between 1.22-1.33. Since the difference in recoilless fraction of Fe^{3+} at A and B sites is less than 10%, such large differences are unexpected. Since the assignment

of the A and B sites appears to be correct, we along with Evans and Hafner¹ are forced to conclude that the discrepancy in the I_B/I_A values are due to anomalous line shapes brought about by different QS, IS and magnetic hyperfine fields (H_{eff}) at apparently equivalent sites. Local symmetry at the $[\text{Fe}^{3+}]_B$ sites may be different depending upon the type and number of neighbouring cations. Distortions at these sites may be particularly important in copper containing ferrites because Cu^{2+} ions distort their environment severely. Symmetry of the iron site will then depend on the number of neighbouring Cu^{2+} ions which are randomly distributed. Overall absorption lines may become non-Lorentzian in shape or may even split into a number of lines¹. The large line width may be

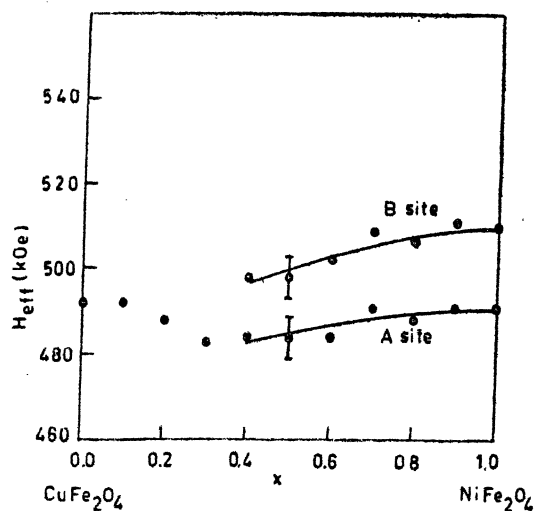


Fig. 2. Variation of hyperfine field (H_{eff}) with x in the system $\text{Cu}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$.

suggestive of the presence of B site Fe^{3+} with different symmetry, although the overall spectra of B site iron fits into a set of Lorentzians.

The isomer shifts are all in the range 0.3-0.7 mm/sec with respect to $^{57}\text{Co}/\text{Fe}$ and this corresponds to iron in the trivalent state only. There is no regular variation of IS as well as of QS with composition.

The variation of the hyperfine fields at the A and B sites (H_{eff} average in case of $0 < x < 0.3$) with composition is given in Fig. 2. The hyperfine fields at both the sites increase with x . The relatively higher value of $H_{eff}(B)$ may be understood as follows. The average field for all the ions in a given sublattice is proportional to the average magnetisation of that sublattice. In an inverse ferrite, an Fe^{3+} ion at the B site will have all its nearest neighbouring A sites occupied by Fe^{3+} ions whereas the A site Fe^{3+} ion will have inter-sublattice bonds with Cu^{2+} , Fe^{3+} and Ni^{2+} . Since $\text{Fe}_A^{3+}-\text{O}^{2-}-\text{Fe}_B^{3+}$ is the strongest superexchange interaction, the H_{eff} of an Fe^{3+} ion surrounded in part by cations other than Fe^{3+} will be smaller than when surrounded by all Fe^{3+} ions only. The

increase in H_{eff} at A sites as x increases could be due to the fact that the interaction $\text{Fe}_A^{3+}-\text{O}^{2-}-\text{Ni}_B^{2+}$ is stronger than $\text{Fe}_A^{3+}-\text{O}^{2-}-\text{Cu}_B^{2+}$. The increase in $H_{eff}(B)$ with x is due to the fact that as x increases from 0.4 onwards, the fraction of A sites occupied by the Fe^{3+} ions also increases as shown by the magnetisation data, and hence the number of Cu^{2+} ions on A sites decreases in these compositions⁶.

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