JOURNAL OF MATERIALS SCIENCE 19 (1984) 1622–1628

Magnetic properties of Cu–Cd ferrite investigated by Mössbauer spectroscopy

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Samples of the copper–cadmium ferrite series $Cd_xCu_{1-x}Fe_2O_4$ ($x = 0$ to 1) have been investigated by means of Mössbauer spectroscopy at 77 K. Mössbauer spectra for $x = 0.0$ to 0.7 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 $x = 0.8$ it shows relaxation behaviour and for $x \geqslant 0.9$ it exhibits a paramagnetic quadrupole doublet. The systematic dependence of the isomer shifts, line widths, quadrupole interactions and nuclear magnetic fields of $^{57}Fe^{3+}$ ions in both A and B sites has been determined as a function of cadmium content. The variation of nuclear magnetic fields at the A and B sites is explained on the basis of the A–B and B–B supertransferred hyperfine interactions. Analysis of the average Mössbauer line widths as a function of cadmium concentration suggests that the relaxation spectrum observed at $x = 0.8$ (77 K) is possibly due to domain wall oscillations. It has been found here that QS (B) increases from $CuFe_2O_4$ to $CdFe_2O_4$ as the cadmium concentration is increased.

1. Introduction

The Cu–Cd ferrite system has the cubic spinel configuration with the unit cell consisting of 8 formula units of the form $(Cd_x^{2+}Fe_{1-x}^{3+})^A[Cu_{1-x}^{2+}Fe_{1+x}^{3+}]^BO_4^{2-}$. The spinel structure is characterized by a close packed oxygen sublattice with the cations on octahedral (B) and tetrahedral (A) sites. The distribution of ferric ions can be determined by Mössbauer experiments because tetrahedral and octahedral sites have different hyperfine magnetic fields.

The $Cd_xCu_{1-x}Fe_2O_4$ ferrite system is a substituted ferrimagnet. Recently, our group has reported [1] the Mössbauer study of this ferrite at room temperature. The aim of the present work is to investigate by the Mössbauer effect the magnetic properties of the Cu–Cd ferrite for varying cadmium concentrations at a liquid nitrogen temperature of 77 K and to study the effect of temperature on the relaxation behaviour up to 4.2 K.

2. Experimental details

Eight samples with $x = 0.0, 0.2, 0.4, 0.6, 0.7, 0.8, 0.9$ and 1.0 were prepared by the ceramic method. The starting materials were analytical reagent grade Fe_2O_3 (Robert Johnson), CdO (USSR) and CuO (BDH). The oxides were mixed in proper proportions to yield the desired compositions, fired at 1100° C for 50 h and slowly cooled to room temperature. All the samples were found to be single-phase spinel by X-ray powder diffractometry.

The Mössbauer absorbers were made using samples in the powdered form of thickness between 20 to 30 mg cm^{-2}. The Mössbauer spectra were obtained with a constant acceleration transducer and a 512 multichannel analyser, operating in the time mode. The spectrometer was calibrated using enriched iron metal foil. A gamma source of ^{57}Co (Rh) of a specific activity of 30 mCi was used. All spectra were obtained at 77 K in transmission geometry and the 14.4 keV gamma-rays were detected with a high count-rate argon–methane filled proportional counter.

The Mössbauer spectra obtained at 77 K are shown in Figs. 1 and 2. For $x = 0.0, 0.2, 0.4$ and 0.6, the spectra exhibit two well defined Zeeman patterns, one due to the Fe^{3+} ions at the tetrahedral (A) site, the other due to the Fe^{3+} ions at

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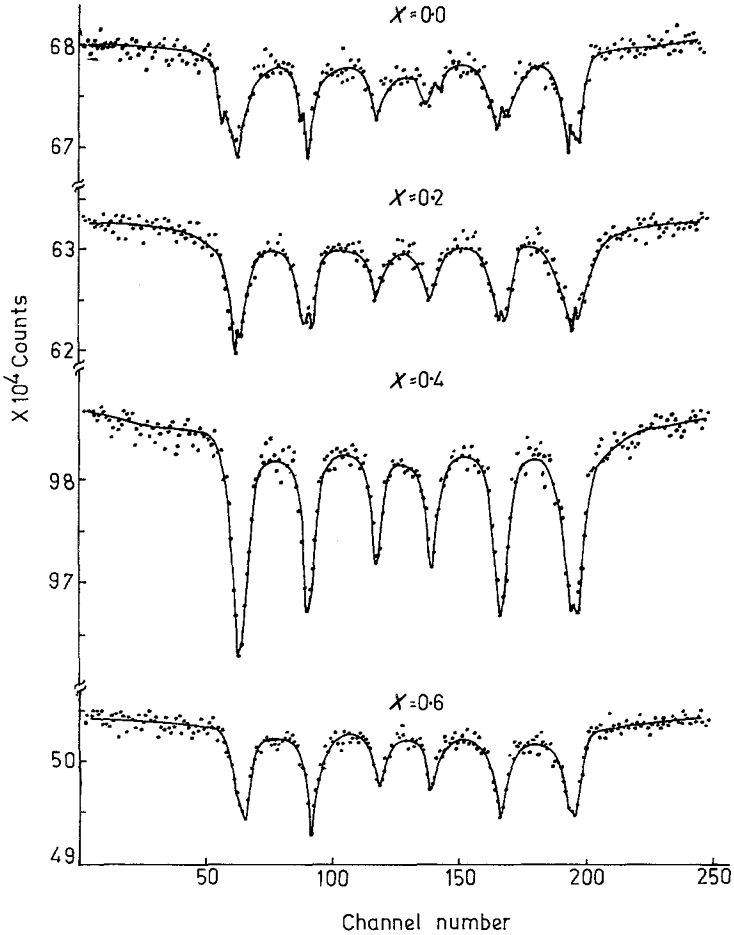

Figure 1 Liquid nitrogen temperature (77 K) Mössbauer spectra of $x = 0.0$, 0.2, 0.4 and 0.6 samples of Cu–Cd ferrite. The solid lines are the least squares computer fits.

the octahedral (B) site. The spectrum for $x = 0.8$ is shown in Fig. 3b and exhibits relaxation behaviour. All the samples with $x \geqslant 0.9$ exhibit very similar paramagnetic spectra (Fig. 2). The solid lines through the data points in Figs. 1 and 2 are the results of computer fits of the spectra.

3. Results and discussion

The parameters derived from the least squares fits are given in Table I. It is evident from the table that both the absolute and the relative values, i.e. [IS(B)–IS(A)] of the isomer shifts (IS) are insensitive to the cadmium content. This indicates that the s electron distribution of the Fe^{3+} ions is not greatly influenced by cadmium substitution.

The variation of the hyperfine fields, H_A and H_B, as a function of cadmium concentration is shown in Fig. 4 ($x \leqslant 0.7$). It is clear that H_B decreases faster than H_A at 77 K. Similar variations for H_A and H_B were observed in zinc substi-

TABLE I.

x	Isomer shift* (mm sec^{-1})		Quadrupole splitting (mm sec^{-1})	
	IS(B)	IS(A)	QS(B)	QS(A)
0.0	0.15 ± 0.02	0.19 ± 0.02	−0.37 ± 0.06	0.06 ± 0.06
0.2	0.22 ± 0.02	0.26 ± 0.02	+0.06 ± 0.06	0.06 ± 0.06
0.4	0.24 ± 0.02	0.27 ± 0.02	0.25 ± 0.06	−0.12 ± 0.06
0.6	0.27 ± 0.02	0.27 ± 0.02	0.37 ± 0.06	−0.12 ± 0.06.
0.7	0.24 ± 0.02	0.27 ± 0.02	0.25 ± 0.06	−0.37 ± 0.06
0.8		Relaxation spectrum		
0.9	0.18 ± 0.02	–	0.99 ± 0.06	–
1.0	0.15 ± 0.02	–	0.87 ± 0.06	–

*With respect to iron metal.

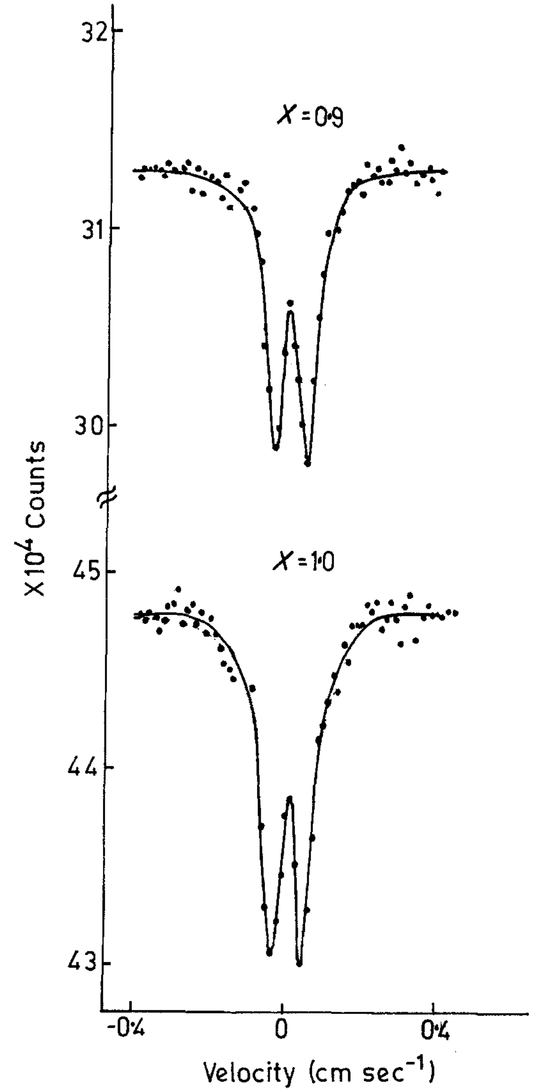

Figure 2 Mössbauer spectra of $x = 0.9$ and 1.0 samples at 77 K for Cu–Cd ferrite. The solid lines are the least squares computer fits.

tuted ferrites like Ni–Zn [2], Fe–Zn [3], Cu–Zn [4] and Mn–Zn [5]. Recently, Patil and Kulkarni [4] and Srivastava *et al.* [3] have given a satisfactory explanation for the variation of H_A and H_B with x. They have shown that the canting of the spins gives rise to Yafet–Kittel angles (YK), which suggest that A–B and B–B super-exchange interactions are comparable in strength.

It has been shown in our previous paper [1] that the comparison of the relative magnetization and Mössbauer data (300 K) for these samples shows a discrepancy. This suggests an indirect indication of the presence of canted spins and hence of YK angles in Cu–Cd ferrites. By considering A–B and B–B supertransferred hyperfine interactions (STHIS), the variation of the hyperfine field with cadmium concentration for $\mathrm{Cd}_x\mathrm{Cu}_{1-x}\mathrm{Fe}_2\mathrm{O}_4$ can be expressed approximately by the following relations:

$$\begin{aligned}\langle H(x)\rangle_{\mathrm{A}} &= H_{\mathrm{OA}} + \sum_{n=0}^{12} \eta_{\mathrm{AB}}(n,x)^{\Lambda}\mathrm{AB}^{(n)} \quad f_n(\theta_{\mathrm{AB}})\\ \langle H(x)\rangle_{\mathrm{B}} &= H_{\mathrm{OB}} + \sum_{n=0}^{6} \eta_{\mathrm{BA}}(n,x)^{\Lambda}\mathrm{AB}^{(n)}\\ &\qquad f_n(\theta_{\mathrm{AB}}) - \sum_{n=0}^{3} \eta_{\mathrm{BB}}(n,x)^{\Lambda}\mathrm{BB}^{(n)}\\ &\qquad [1+g_n(\theta_{\mathrm{BB}})]. \end{aligned} \tag{1}$$

Here H_{OA} and H_{OB} are the hyperfine fileds in the absence of STHIS, $^{\Lambda}\mathrm{AB}^{(n)}$ and $^{\Lambda}\mathrm{BB}^{(n)}$ are strengths of the A–B and B–B STHIS, respectively, with $n(\mathrm{Fe}^{3+} - \mathrm{Fe}^{3+})$ near neighbours. $f_n(\theta_{\mathrm{AB}})$ and $g_n(\theta_{\mathrm{BB}})$ are the functions denoting the dependence of STHIS on the angles between the spins of the Fe^{3+} ions on different sublattices. η_{AB} denotes the relative frequency of occurrence of an A-site Fe^{3+} ion having n B-site Fe^{3+} neighbours. Similarly, $\eta_{\mathrm{BA}}(n,x)$ and $\eta_{\mathrm{BB}}(n,x)$ are the relative frequencies of occurrence of a B-site Fe^{3+} ion having n A-site and n B-site Fe^{3+} neighbours respectively. The explicit expressions for η_{AB}, η_{BA} and η_{BB} are given in our earlier papers [1, 4].

The variation of the hyperfine field with cadmium concentration is explained qualitatively using Equation 1. Consider the hyperfine field at the A-site. As x increases the magnetic Fe^{3+} ions on the A-site are replaced by nonmagnetic Cd^{2+} ions, to this effect $\eta_{\mathrm{AB}}(n,x)$ increases and $f_n(\theta_{\mathrm{AB}})$ decreases due to YK angles on the B-sublattice. Since the presence of YK angles is more predominant for $x > 0.2$, the H_{B} remains practically constant up to $x = 0.2$ and it decreases for $x > 0.2$ (Fig. 4). It seems that the decrease in $f_n(\theta_{\mathrm{AB}})$ is faster than the increase in $\eta_{\mathrm{AB}}(n,x)$ for $x > 0.2$. The H_{B} decreases with increasing x because both $\eta_{\mathrm{BA}}(n,x)$ and $f_n(\theta_{\mathrm{AB}})$ decrease and $\eta_{\mathrm{BB}}(n,x)$ increases with respect to x. The factor $g_n(\theta_{\mathrm{BB}})$ has negligible dependence of H_{A} and H_{B} on x (Fig. 4), and this clearly suggests that a significant contribution from STHIS must be invoked to understand the systematics of the magnetic hyperfine field at A and B site iron ions.

The line widths of the $^{57}\mathrm{Fe}$ Mössbauer spectra are useful for estimating the influence of cation disorder on both electric and magnetic interactions. In Fig. 5, the average line widths of the

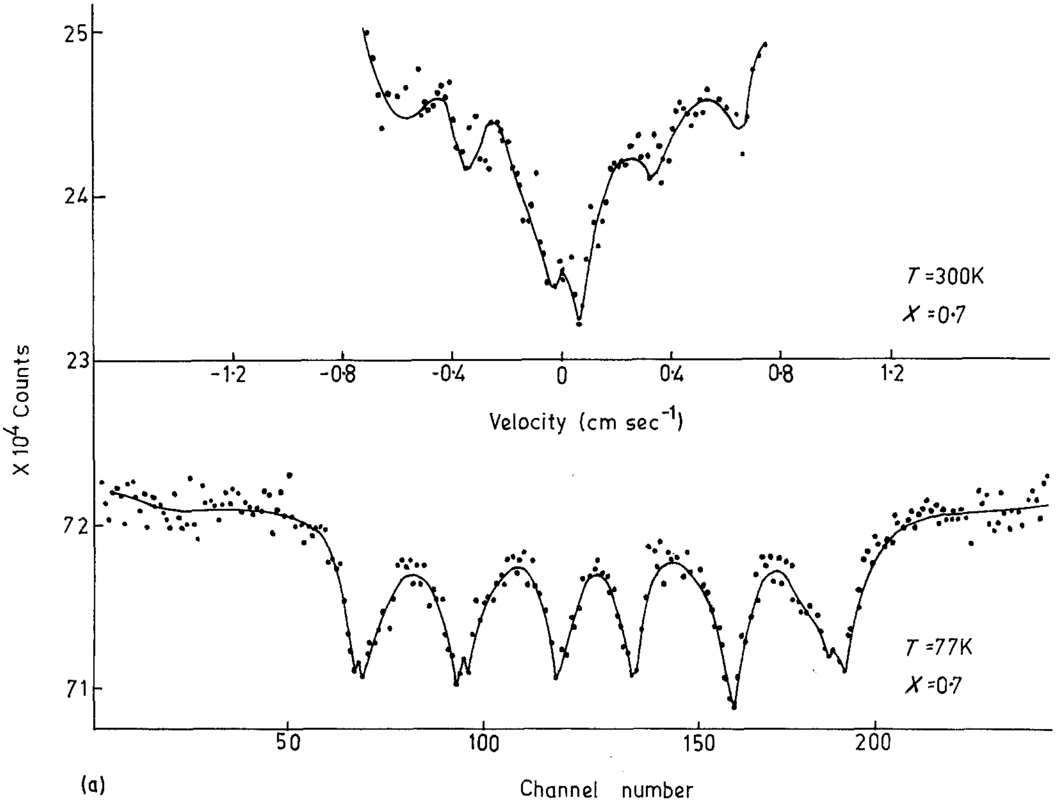

Figure 3 (a) Mössbauer spectra of $x = 0.7$ samples at 300 and 77 K for Cu–Cd ferrites. The solid lines are the least squares computer fits. (b) Liquid nitrogen temperature (77 K) and liquid helium temperature (4.2 K) Mössbauer spectra of $x = 0.8$ samples for Cu–Cd ferrites. The solid lines are the least squares computer fits.

tetrahedral hyperfine pattern $\bar{\Gamma}_A$, and that of the octahedral pattern $\bar{\Gamma}_B$, are plotted as a function of x at 77 K. In the magnetic region ($x \leqslant 0.7$) $\bar{\Gamma}_B$ remains nearly constant up to $x = 0.6$, and then it increases monotonically with increasing x. While $\bar{\Gamma}_A$, which is initially greater than $\bar{\Gamma}_B$ ($x = 0$), decreases slowly up to $x = 0.6$ and then follows the same trend as $\bar{\Gamma}_B$.

The nuclear magnetic field at the ^{57}Fe nucleus is proportional to the $\langle S_z \rangle$ of the ion and its time dependence of $\langle S_z \rangle$. If we define $1/\tau$ as the transition or relaxation rate between the hyperfine states, then provided the lifetime of the isomeric excited state $\tau_N > 1/\omega_L$ where ω_L is the Larmor frequency of the ^{57}Fe nuclear spin, we shall have three possible situations.

1. If $\tau \gg 1/\omega_L$ we are in the "magnetic region" and a normal Zeeman pattern will result.
2. If $\tau \sim 1/\omega_L$ we have relaxation effects and are in the "relaxation region".
3. If $\tau \ll 1/\omega_L$ then $\langle S_z \rangle = 0$, we are in "paramagnetic region" and thus a paramagnetic pattern will result.

These three regions of relaxation time are all illustrated in Fig. 5, which shows that the Mössbauer line widths vary within these regions.

In order to observe the effect of low temperature on relaxation, the Mössbauer spectra in the relaxation region were obtained between 300 and 4.2 K. The Mössbauer spectra of the $x = 0.7$ sample at 300 and 77 K are displayed in Fig. 3a. Similarly, the Mössbauer spectra of an $x = 0.8$ sample at 77 and 4.2 K are shown in Fig. 3b. The 300 K spectrum of the $x = 0.7$ sample and 77 K spectrum of the $x = 0.8$ sample show relaxation behaviour, while the spectra of the $x = 0.7$ sample at 77 K and $x = 0.8$ sample at 4.2 K, respectively, show well defined hyperfine fields. The primary features of a relaxation spectrum for a magnetically ordered system are a significant broadening of Zeeman lines, and a growth of the inner lines of the Zeeman patterns at the expense of the outer lines. Both these effects are evident in the spectra obtained with $x = 0.7$ at 300 K (Fig. 3a) and $x = 0.8$ at 77 K (Fig. 3b). The dramatic line broadening in the relaxation region is clearly

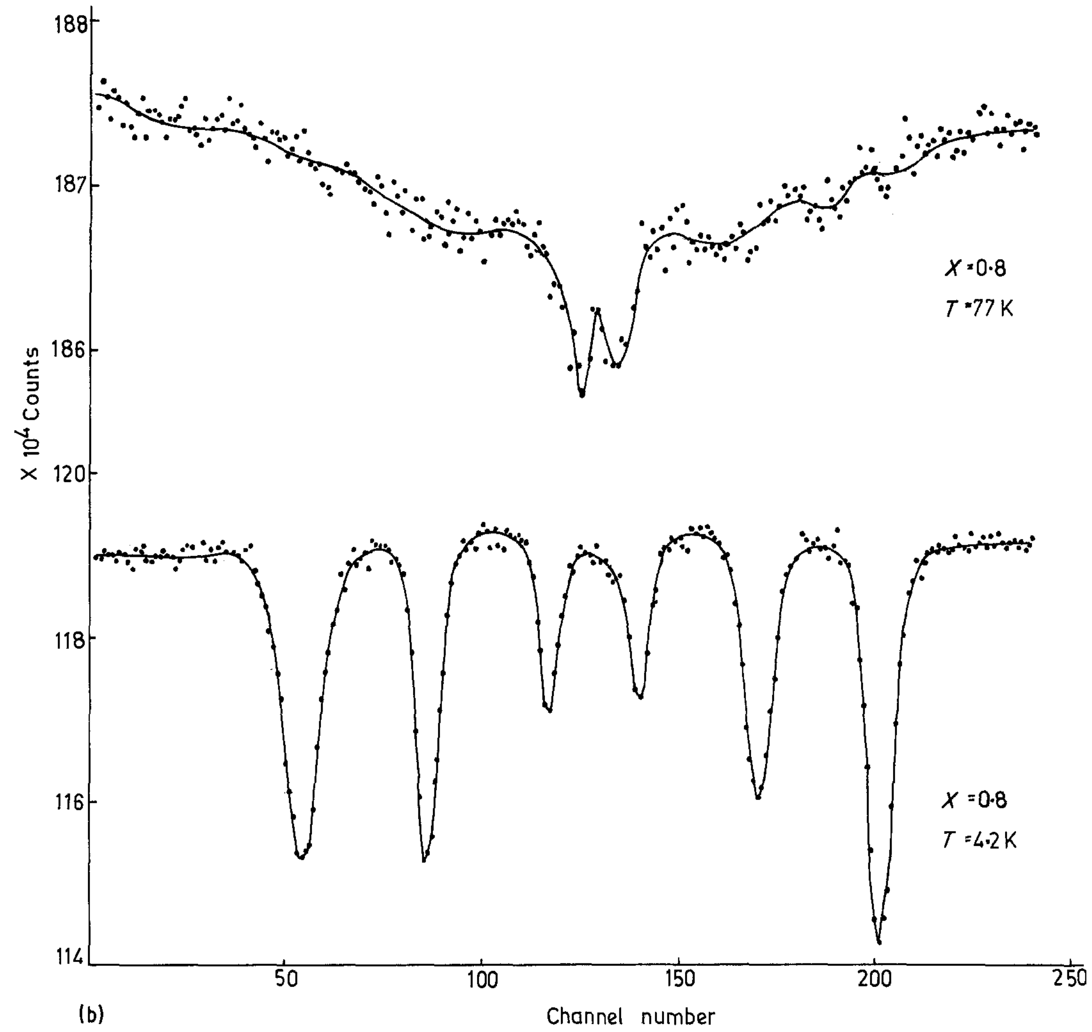

Figure 3 Continued.

demonstrated in Fig. 5. When the paramagnetic region is reached, i.e. $\tau < 1/\omega_L$, the line widths decrease quickly to non-relaxation levels as shown in Fig. 5. It is evident from Fig. 3 that the relaxation effect is temperature dependent and vanishes as T approaches 0 K. It is also a function of cadmium content.

As relaxations occur at temperatures ($T = 300$ K for $x = 0.7$ and $T = 77$ K for $x = 0.8$) much lower than the Néel temperatures ($T_n = 353 \pm 10$ K and $T_N = 160 \pm 10$ K) they cannot be accounted for by critical point fluctuations. We believe that the relaxation effects in the Mössbauer line shapes are due to domain wall oscillations in accordance with Srivastava *et al.* [3] and Patil and Kulkarni [4].

It is well known that the electric field gradient (EFG) at a ^{57}Fe nucleus arises from a non-spherical distribution of the 3d electrons of the ion itself, and from the charges on neighbouring ions. Since the Fe^{3+} ion has a half-filled 3d shell, the EFG can arise only from neighbouring ions and thus exist only at those sites having non-cubic point symmetry. In a system exhibiting no chemical disorder, the tetrahedral (A) sites have cubic point symmetry and thus experience no EFG. The octahedral (B) sites, however, have trigonal symmetry and thus an EFG exists with a principal axis along the [1 1 1] direction.

It is evident from Table I that quadrupole splitting, QS(B) increases from $CuFe_2O_4$ to $CdFe_2O_4$ as the cadmium content increases, while QS(A) decreases from $x = 0.2$ to $x = 0.7$ as the cadmium content increases. The present results at 77 K are in good agreement with those of room temperature (300 K) measurements [1]. In

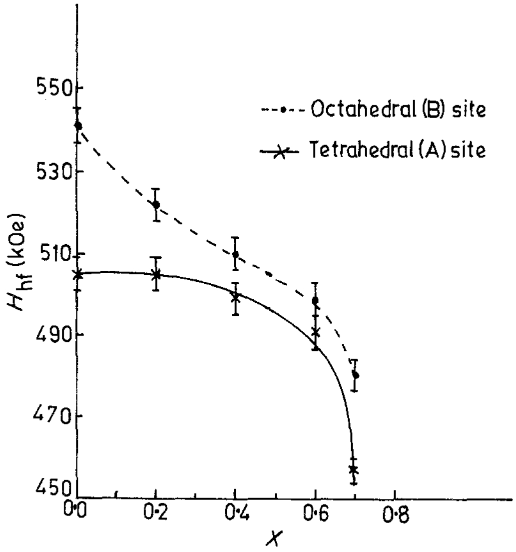

Figure 4 The average magnitude of the hyperfine fields $|H|$ at the ^{57}Fe nuclei at octahedral (B) and tetrahedral (A) sites against cadmium content (x) at 77 K.

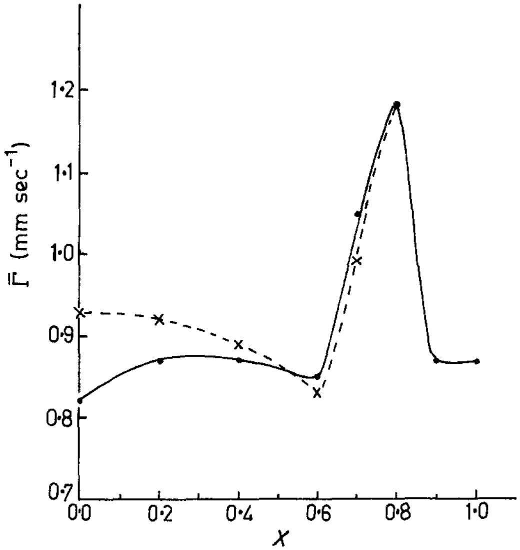

Figure 5 The average Mössbauer line widths for the tetrahedral pattern, $\bar{\Gamma}_A$, and for the octahedral pattern $\bar{\Gamma}_B$, as a function of x at 77 K. The dots represent the line widths for octahedral (B) sites while the cross represents the line widths for tetrahedral (A) sites.

$Cd_xCd_{1-x}Fe_2O_4$ system, the A-sites are occupied by Cd^{2+} and Fe^{3+} ions and the B-sites by Cu^{2+} and Fe^{3+} ions. As we go from $CuFe_2O_4$ ($x = 0$) to $CdFe_2O_4$ ($x = 1$) A-sites Fe^{3+} ions are gradually replaced by Cd^{2+} ions. The replacement of small Fe^{3+} ions (0.06 nm) by large Cd^{2+} ions (0.097 nm) at the tetrahedral sites distort the oxygen octahedron mostly around the B-site, thereby increasing the field gradient at the B-site considerably. The displacement of oxygen ions around the A-site caused by the replacement of Fe^{3+} by Cd^{2+} is such that the cubic symmetry of this site is retained till $x = 0.2$, and becomes disturbed for $0.2 \leqslant x \leqslant 0.7$. To this effect QS(A) remains almost constant up to $x = 0.2$ and then it decreases for higher values of x. Similar type behaviour has also been observed for H_A against x. (Fig. 4). The distortion in the B-site octahedron is evidenced by the change in the oxygen parameter U from $CuFe_2O_4$ to $CdFe_2O_4$. The reported values of U are 0.380 [6] and 0.389 [7] for $CuFe_2O_4$ and $CdFe_2O_4$ respectively. Therefore, it is proposed that the increase of quadrupole splitting (QS(B)) from $CuFe_2O_4$ is ascribed to the increase in the U value. Such a monotonic increase in the magnitude of QS with increasing U values has been observed by Yagnik and Mathur [8] in their study of the solid solutions of $ZnFe_2O_4$ and $CdFe_2O_4$. The U values for $ZnFe_2O_4$ and $CdFe_2O_4$ are 0.385 and 0.389 respectively. Recently, Mathukumarasamy *et al.* [9] observed an increase in QS from $NiFe_2O_4$ to $CdFe_2O_4$ as the cadmium concentration was increased. They also suggested that this increase in QS is due to the increase in U values. It is, therefore, concluded that in our $Cd_xCu_{1-x}Fe_2O_4$ system, the observed increase of QS with cadmium concentration is attributable to the increase in the U parameter of the compositions.

4. Conclusions

The Cu–Cd ferrite system has been studied in detail by means of the Mössbauer effect at 77 K.

The observed variation of the ^{57}Fe hyperfine field on A- and B-sites with cadmium concentration is found to be similar in nature to that of zinc substituted ferrites. The variation of hyperfine fields with cadmium concentration can be explained qualitatively on the basis of supertransferred hyperfine interactions.

The line widths of the octahedral and tetrahedral Mössbauer patterns and their variation with cadmium content within the "magnetic region" were accounted for partly on the hypothesis that the chemical disorder which is present in the Cu–Cd ferrite system results in a distribution of $\langle S_z \rangle$ values, a distribution which is a function of both the temperature and the cadmium content. In the "relaxation region" the spectra displayed typically large increases in line widths associated with the relaxation phenomenon.

It has been found here that the QS(B) increases from $CuFe_2O_4$ to $CdFe_2O_4$ as the cadmium concentration is increased. This change in QS is attributed to the change in the oxygen parameter U.

Acknowledgements

The authors are grateful to Professor J. C. Walker, Johns Hopkins University, Baltimore, MD, USA, for extending low-temperature facilities. One of the authors (RVU) is thankful to the Department of Atomic Energy, CSM Marg, Bombay, for providing financial support in the form of a fellowship.

References

1. V. G. PANIKER, S. N. RAO and R. G. KULKARNI, *Solid State Commun.* **43** (1982) 647.
2. L. K. LEUNG, B. J. EVANS and A. H. MORRISH, *Phys. Rev.* **B8** (1973) 29.
3. C. M. SRIVASTAVA, S. N. SHRINGI and R. G. SRIVASTAVA, *ibid.* **B14** (1976) 2041.
4. V. U. PATIL and R. G. KULKARNI, *Solid State Commun.* **31** (1979) 551.
5. B. J. EVANS and S. S. HAFNER, *J. Phys. Chem. Solids* **29** (1978) 1573.
6. J. SMIT and H. P. J. WIJN, "Ferrites" (John Wiley, New York, 1959).
7. B. J. EVANS, S. S. HAFNER and H. P. WEBER, *J. Chem. Phys.* **55** (1971) 5282.
8. C. M. YAGNIK and H. B. MATHUR, *Mol. Phys.* **16** (1969) 625.
9. P. MUTHUKUMARASAMY, T. NAGARJAN and A. NARAYANASAMY, *Phys. Status Solidi (a)* **64** (1981) 747.

Received 19 August
and accepted 13 September 1983