The hyperfine field distribution in copper–cadmium ferrites studied by Mössbauer and NMR spectroscopies

J.J. Bara[a], B.F. Bogacz[a], J. Hankiewicz[b], Z. Pająk[b]

[a]*Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Cracow, Poland*
[b]*Institute of Physics, A. Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland*

Abstract

Hyperfine fields have been studied at liquid nitrogen temperature in $Cd_xCu_{1-x}Fe_2O_4$ ($0 \leq x \leq 0.5$) ferrites by Mössbauer and NMR spectroscopies. The distributions of the hyperfine fields at iron sites, caused by substitution of cadmium for copper, are observed both in the tetrahedral and octahedral crystal sublattices. In both sublattices the values of the averaged hyperfine field decrease with increasing cadmium concentration. The hyperfine field distributions and size reductions are more pronounced in the octahedral sublattice than in the tetrahedral one. They are explained by different statistical distributions of the metallic cations within the tetrahedral and octahedral crystal sublattices. The Mössbauer effect and NMR data are in a good agreement each with other.

Keywords: Copper–cadmium ferrites; NMR; Mössbauer spectroscopy

1. Introduction

The copper–cadmium ferrites, $Cd_xCu_{1-x}Fe_2O_4$ ($0 < x < 1$), belong to a large class of compounds having the general formula $A^{2+}B_2^{3+}O_4$ and crystallising in the spinel structure. In this structure metal cations are in two types of positions: the A sites which are tetrahedrally coordinated and the B sites which are octahedrally coordinated by the surrounding oxygen ions. There are 64 tetrahedral and 32 octahedral positions in the unit cell. However, not all of them are accessible to metal cations. Only eight tetrahedral and 16 octahedral sites are occupied, which means that in all spinels the B sites are more accessible for metallic cations than the A sites, independent of whether cations of either one kind or two kinds are in a given crystal position. The magnetic properties of the spinels are very sensitive to the nature of the metallic cations present in the compound and to their distribution among the A and B sites.

The antiferromagnetic A–B superexchange interaction is the main cause of the cooperative behaviour of the magnetic dipole moments, known as ferrimagnetism, which is observed in the copper–cadmium ferrites below their Néel temperatures. The magnetic moments of the cations located in the same type of crystal position are coupled parallel to one another and at the same time are coupled antiparallel to the magnetic moments of the cations occupying another type of crystal position. The A–B magnetic coupling is considerably stronger than that between the cations located in the same type of crystal site.

The basic compound for the investigated series, the copper ferrite $(Cu_zFe_{1-z})[Cu_{1-z}Fe_{1+z}]O_4$, is an incompletely inverted spinel, since not all Cu^{2+} cations are located at the octahedral sites. Its cation distribution ($0 < z < 0.15$) over non-equivalent tetrahedral (A) and octahedral [B] sites and its crystal structure depend on the manner of preparation. The tetragonal phase is obtained when a sample is cooled slowly from about 1030 K to room temperature. The fast quenching process, or substitution of Cd cations for Cu ones, leads to the cubic form.

The cadmium cations strongly prefer the tetrahedral positions. Thus, the cadmium substituted copper ferrites $Cd_xCu_{1-x}Fe_2O_4$ ($0 < x < 1$) have all Cd cations at A sites and, for $x \geq z$, they have copper cations at B sites only.

Previous [57]Fe Mössbauer investigations of the $Cd_xCu_{1-x}Fe_2O_4$ ferrites [1–4] have indicated hyper-

fine fields both at A and B sites and pronounced field distributions [5]. Apart from two ^{57}Fe nuclear magnetic resonances, broadened in ^{63}Cu and ^{65}Cu resonances were also registered in NMR studies [5,6].

The purpose of this investigation is to extend to low temperatures our preliminary room-temperature studies [5] of the influence of Cu and Cd ions on hyperfine magnetic fields acting on ^{57}Fe nuclei in the $Cd_xCu_{1-x}Fe_2O_4$ ($0 \le x \le 0.5$) ferrites. The Mössbauer effect and spin echo NMR methods will be used.

2. Experimental

Polycrystalline samples of $Cd_xCu_{1-x}Fe_2O_4$ ($0 \le x \le 0.5$) ferrites were prepared using a standard sintering process. The products were ground to a fine powder and pressed to form samples. The composition and purity of the samples was controlled by X-ray analysis which showed that samples with $x < 0.10$ have tetragonal symmetry and for $x \ge 0.10$ they have cubic symmetry.

The ^{57}Fe Mössbauer absorption spectra were recorded for powdered samples at liquid nitrogen temperature using a $^{57}Co(Cr)$ source, placed at room temperature, and a constant acceleration Mössbauer spectrometer. High purity metallic iron foil was used for the calibration of the velocity scale.

The NMR spectra were recorded using a home-made spectrometer operating in the frequency range 20-100 MHz. The spectrometer was equipped with a microcomputer system for controlling the experiment, data acquisition and data processing. The sample was placed inside the coil of a series resonant tank circuit. Inhomogeneously broadened NMR spectra in copper-cadmium ferrites were obtained by measuring the amplitude of the spin-echo signal as a function of frequency point-by-point in the range 40-80 MHz. All samples were measured at liquid nitrogen temperature.

The least squares computer program was used to derive the discrete values of the hyperfine interaction parameters from both Mössbauer effect and NMR spectra.

3. Results and discussion

Selected Mössbauer and NMR spectra recorded for $Cd_xCu_{1-x}Fe_2O_4$ ($0 \le x \le 0.5$) ferrites are shown in Figs. 1, 2 and 3,. The values of the hyperfine interaction parameters, derived from the spectra, are compiled in Table 1. Both methods used have energy resolution good enough to resolve the tetrahedral and octahedral ^{57}Fe subspectra. Moreover, the ^{63}Cu and ^{65}Cu nuclear magnetic resonances are partially shown
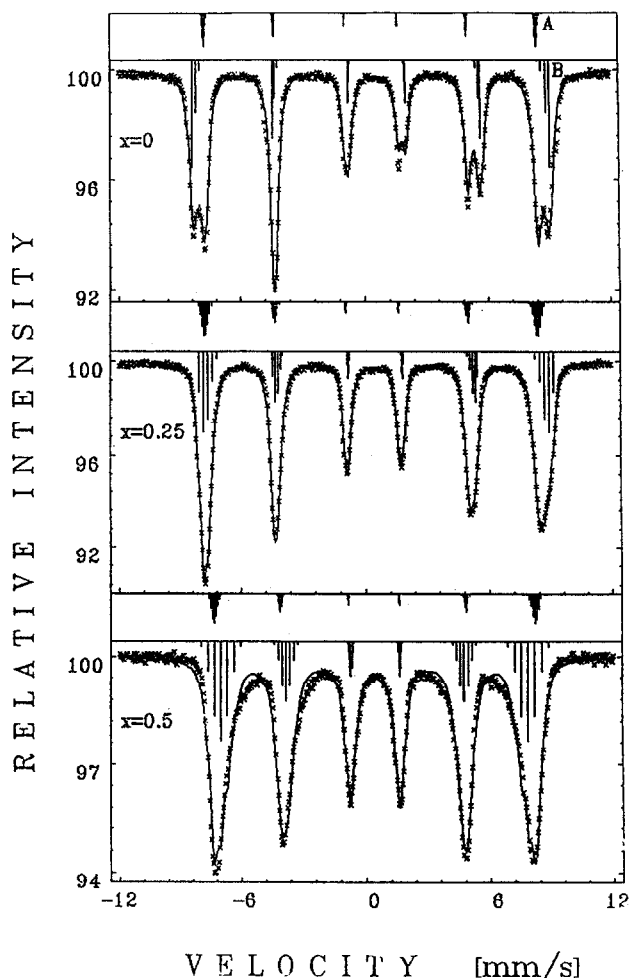

Fig. 1. The selected Mössbauer absorption spectra of $Cd_xCu_{1-x}Fe_2O_4$ ferrites recorded at liquid nitrogen temperature.

in Figs. 2 and 3 although they were not studied in detail.

The NMR signals from copper nuclei at A sites gradually disappear with the increase in cadmium content in the ferrites since Cu cations are first substituted by Cd cations at A sites, and only after having replaced all of them ($x \ge 0.075$) do the Cd cations dislodge the Fe cations from A to B sites. Cu(A) signals are not observed for samples with $x \ge 0.075$. The low frequency parts of the Cu(B) signals are seen for samples with $x \ge 0.15$.

The decrease in the magnitude of Zeeman splitting and the broadening of the spectra lines, caused by substitution of copper by cadmium, are clearly shown by both methods used. The line broadening is much larger for the octahedral subspectrum than for the tetrahedral one.

The line broadening observed in our Mössbauer and NMR ^{57}Fe spectra (Figs. 1-3) can be interpreted as being due to distributions in hyperfine fields caused by the distribution of the nearest Fe and Cu neighbours
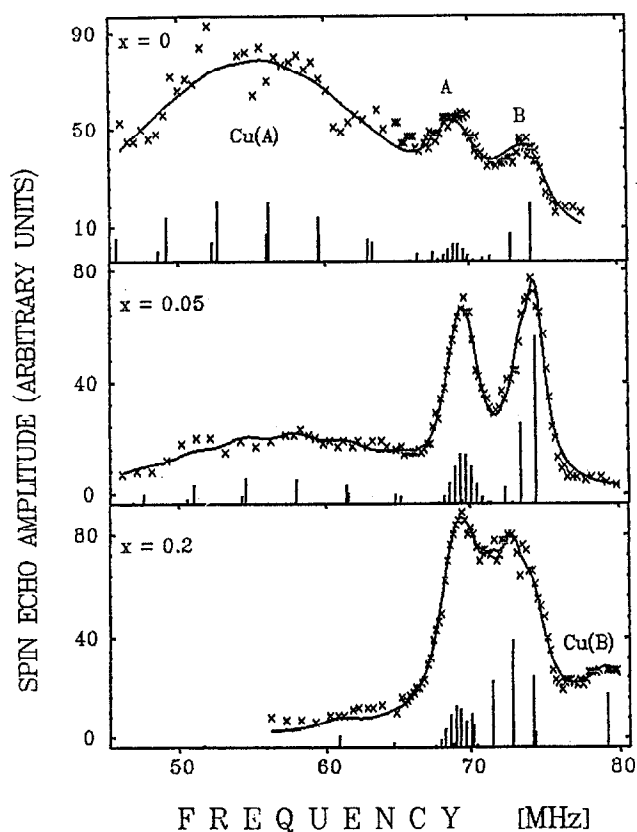
Fig. 2. The selected spin echo NMR spectra of $Cd_xCu_{1-x}Fe_2O_4$ ferrites recorded at liquid nitrogen temperature. Details are given in the text. Note that the frequency scale is different from that of the spectra shown in Fig. 3.

Fig. 3. The selected spin echo NMR spectra of $Cd_xCu_{1-x}Fe_2O_4$ ferrites recorded at liquid nitrogen temperature. Details are given in the text. Note that the frequency scale is different from that of the spectra shown in Fig. 2.

of A sites and mainly by distribution of nearest Fe, Cu and / or Cd neighbours of B sites. In the spinel crystal lattice each cationic near-neighbour configuration of the A-site (B-site) consists of twelve B-site (six A-site) cations. The occurrence of more than one type of cation at the given type of lattice site leads to a set of different nearest-neighbour cationic configurations of the other type of crystal site. This results in distributions of hyperfine interaction parameters for each type of crystal site, especially for octahedral sites.

In our numerical analysis of the spectra a separate subspectrum (see the vertical bar diagrams in Figs. 1–3) was ascribed to each nearest-neighbour cationic configuration. Its intensity was supposed to be proportional to the probability of formation of the corresponding configuration. All subspectra belonging to the given type of site (A-sites or B-sites) were supposed to have common isomer shifts and quadrupole interactions. Positions and relative intensities of the subspectra lines are shown by the bar diagrams in Figs. 1–3. The sets of subspectra corresponding to ^{57}Fe at tetrahedral and octahedral sites are denoted by the letters A and B, respectively, while the lines indicating
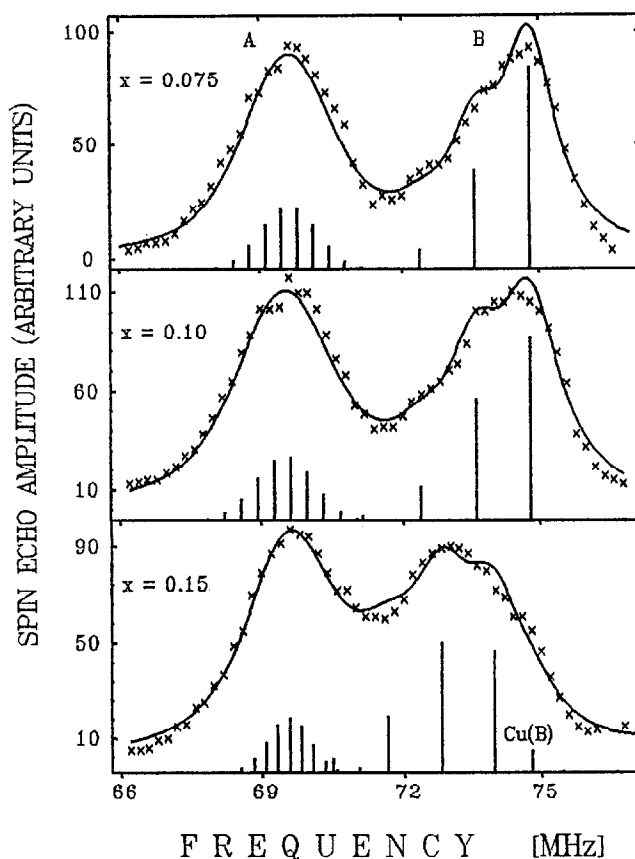
^{63}Cu and ^{65}Cu nuclear magnetic resonances at A and at B sites are denoted by symbols Cu(A) and Cu(B), respectively.

The occurrence of Cu or Cd cations as the nearest neighbour of a given site reduces the hyperfine field at that site. The value of this reduction at a given site was assumed, in our spectra fitting procedure, to be proportional to the number of Cu (or Cd) cation nearest neighbours of this site. It was found that at 78 K the proportionality parameter ascribed to non-magnetic Cd cations is similar to that associated with magnetic Cu cations, contrary to the situation at room temperature where it was three times larger [5]. The reduction in the averaged hyperfine field value observed with increasing x is much more pronounced in the B than in the A sublattice, as is shown in Fig. 4.

In the spinel type lattice a B-site cation is magnetically coupled to each of its six A-site neighbours by magnetic interaction transferred through a separate oxygen anion, while an A-site cation is coupled through a separate oxygen anion to every three of its twelve B-site neighbours. Thus, the magnetic dilution

Table 1
The ^{57}Fe hyperfine interaction parameters of $Cd_xCu_{1-x}Fe_2O_4$ ferrites[a]

Sample x	Method	A-sublattice			B-sublattice		
		$\langle H \rangle$ (T)	IS (mm s^{-1})	QS (mm s^{-1})	$\langle H \rangle$ (T)	IS (mm s^{-1})	QS (mm s^{-1})
0	MS	50.1	0.344	−0.005	53.3	0.475	−0.147
	NMR	50.0			53.3		
0.025	MS	49.9	0.343	−0.011	53.1	0.463	−0.138
	NMR	50.3			53.5		
0.05	MS	50.0	0.343	−0.010	53.0	0.469	−0.115
	NMR	50.3			53.6		
0.075	MS	50.1	0.346	−0.009	53.2	0.469	−0.038
	NMR	50.4			53.8		
0.10	MS	50.0	0.347	−0.006	52.9	0.466	−0.005
	NMR	50.3			53.6		
0.15	NMR	50.4			52.8		
0.20	MS	49.9	0.333	−0.011	51.8	0.475	0.010
	NMR	50.0			52.6		
0.25	MS	49.9	0.308	−0.015	51.1	0.492	0.020
	NMR	50.1			51.9		
	NMR	49.7			50.9		
0.50	MS	48.0	0.396	0.025	46.0	0.421	−0.012

[a] MS, the Mössbauer spectroscopy method; NMR, the nuclear magnetic resonance method; $\langle H \rangle$, the averaged hyperfine magnetic field; IS, the isomer shift relative to metallic iron at room temperature; QS, the quadrupole shift of subspectra lines $[(V_6 - V_5) - (V_2 - V_1)]/2$. Errors: $\langle H \rangle$ (± 0.4 T), IS (± 0.002 mm s^{-1}), QS (± 0.003 ms s^{-1}).
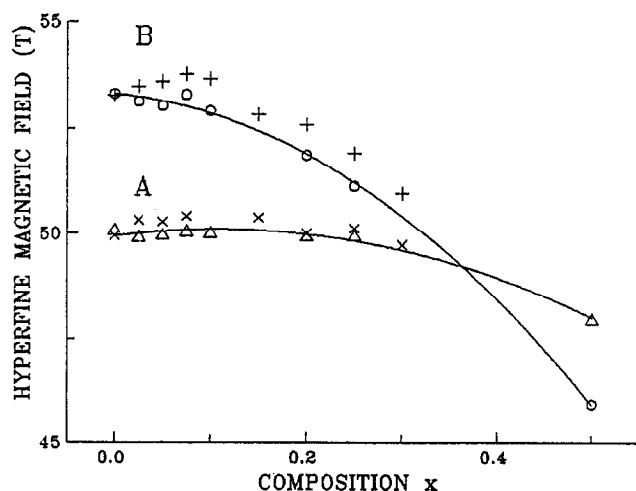

Fig. 4. Averaged hyperfine magnetic fields at octahedral ($\bigcirc$,+) and tetrahedral ($\triangle$,×) sublattices, determined by the Mössbauer effect method ($\bigcirc$,$\triangle$) and by the NMR method (+,×), vs. composition parameter x. The solid lines guide the eye through the Mösbauer effect data.

process within the A-sublattice has a greater influence on the magnetic interaction transferred towards a B-site cation from its A-site neighbours than vice versa. Substitution of only one non-magnetic cation for a magnetic one within the A-sublattice results in the disappearance of the magnetic interaction transmitted through one oxygen anion towards a B-site cation. A similar result for an A-site cation can be obtained only by simultaneous substitution of non-magnetic cations for all three magnetic B-site cations coupled to the given A-site cation through the same oxygen anion. The probability of such a process is very small.

In $Cd_xCu_{1-x}Fe_2O_4$ ferrites magnetic dilution takes place in the A-sublattice since the non-magnetic cadmium cations occupy this sublattice exclusively. Thus, in the B-sublattice a large distribution of the hyperfine fields and a large reduction in the value of the averaged hyperfine field should be observed. This is indeed seen in Figs. 1–3 and 4, respectively. After all A-site copper cations have been replaced by cadmium cations ($x > z$) the number of iron cations in the B-sublattice increases when the dilution process in the A-sublattice is continued. As a result of this, the number of iron-rich nearest-neighbour configurations of A-sites, composed of the B-sites cations, increases. This is an additional reason for a smaller distribution of the hyperfine fields in the A-sublattice than in B-sublattice, as well as for a smaller reduction in its averaged value when x increases. We could not find an explanation for the somewhat larger values of the hyperfine fields determined by the NMR method as compared with those derived from the Mössbauer spectra.

In conclusion, the distributions of the hyperfine fields and reduction of the average values, observed at liquid nitrogen temperature at A and B sites of the $Cd_xCu_{1-x}Fe_2O_4$ ($0 \leqslant x \leqslant 0.5$) ferrites by Mössbauer spectroscopy and NMR, can be well described assuming a statistical distribution of Fe, Cu and / or Cd cations at A sites as well as of Fe and Cu cations at B sites. The Mössbauer effect data and NMR data are generally in good agreement with each other.

References

[1] B.J. Evans and S.S. Hafner, *J. Phys. Chem. Solids, 29* (1968) 1573.

[2] A. Nagarajan and N. Fgajanian, *J. Appl. Phys., 41* (1970) 1642.

[3] J. Janicki, J. Pietrzak, A. Porębska and J. Suwalski, *Phys. Status Solidi (a), 72* (1982) 95.

[4] J. Janicki, I. Onyszkiewicz and J. Suwalski, *Acta Phys. Polonica, A72* (1987) 315.

[5] J.J. Bara, B.F. Bogacz, J. Hankiewicz, Z. Pająk and J. Radomski, *Hyperfine Interactions, 54* (1990) 453.

[6] Le Dang Khoi, *Compt. Rend. Acad. SC. Paris, 256* (1967) 705.