MÖSSBAUER EFFECT AND NMR STUDIES OF COPPER-CADMIUM FERRITES

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Hyperfine magnetic field distributions have been observed at room temperature in $Cd_xCu_{1-x}Fe_2O_4$ ($O \leqslant x \leqslant 0.5$) ferrites by the Mössbauer and NMR methods and are explained by statistical distributions of metallic ions separately within A and within B crystal sublattices.

1. Introduction

The copper ferrite $(Cu_zFe_{1-z})[Cu_{1-z}Fe_{1+z}]O_4$ is a non-completely inverted spinel for which the cation distribution ($0 < z < 0.15$) over non-equivalent tetrahedral (A) and octahedral [B] sites is dependent on the preparation technology and on the temperature. By cooling the specimen slowly from about 1030 K to room temperature the tetragonal phase is obtained, while a fast quenching process, or substitution of Cd ions for Cu ones, leads to the cubic form. The cadmium substituted copper ferrites $Cd_xCu_{1-x}Fe_2O_4$ ($0 < x < 1$) have all Cd ions at A sites and, for $x \geqslant z$, they have all copper ions at B sites.

Previous ^{57}Fe Mössbauer investigations of the above-mentioned ferrites [1–4] have indicated hyperfine magnetic fields both at A and B sites. Apart from two ^{57}Fe nuclear magnetic resonances, a broad resonance in copper nuclei was also registered in the reported NMR studies [5].

The purpose of this work was to study the influence of Cu and Cd ions on hyperfine magnetic fields acting on ^{57}Fe nuclei in the $Cd_xCu_{1-x}Fe_2O_4$ ($0 \leqslant x \leqslant 0.5$) ferrites at room temperature. The Mössbauer effect and spin echo NMR methods were used.

2. Experimental

Polycrystalline samples of $Cd_xCu_{1-x}Fe_2O_4$ ($O \leqslant x \leqslant 0.50$) ferrites were prepared using 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 an X-ray analysis, which shows that samples for $x < 0.10$ have tetragonal symmetry and for $x \geqslant 0.10$ cubic symmetry.

The ^{57}Fe Mössbauer absorption spectra were recorded for powdered samples at room temperature using a ^{57}Co(Cr) source and a constant acceleration Mössbauer spectrometer of Polon type. 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 of 20 to 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 spin-echo signal as a function of frequency point-by-point in the range of 40 to 80 MHz.

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

3. Results and discussion

In the spinel crystal lattice each cationic configuration most closely neighbouring A-site (B-site) consists of twelve B-site (six A-site) cations. The occurence of more than one type of cations at the given type of lattice sites leads to a set of different nearest-neighbour cationic configurations of the other type of crystal sites. This results in distributions of hyperfine interaction parameters at each type of crystal sites, especially at octahedral sites.

A line broadening, observed in our Mössbauer and NMR spectra (figs. 1 and 2), can be interpreted as due to distributions in hyperfine magnetic fields caused by the distribution of the nearest neighbours of A sites and mainly by distribution of nearest Fe, Cu and/or Cd neighbours of B sites. In our numerical analysis of the spectra a separate subspectrum was ascribed to each nearest-neighbour cationic configuration. Its intensity was supposed to be proportional to the probability of formation of the corresponding configuration. Positions and intensities of the subspectra lines are shown by the stick diagrams in figs. 1 and 2. The lines corresponding to ^{57}Fe at A and B sites are denoted by letters A and B (or B_i, i-number of nearest Fe neighbours), respectively. Configurations containing Cu and Fe cations are marked by the superscript ($'$) while those containing Cu, Cd and Fe cations by the superscript ($''$). This was done in order to distinguish them from the configurations which consist of Fe and Cd cations. The lines indicating ^{63}Cu and ^{65}Cu nuclear magnetic resonances at A and at B sites are not marked individually. They are denoted by symbols Cu(A) and Cu(B), respectively.

The occurrence of Cu or Cd cations as the nearest neighbour of the given site reduces the hyperfine magnetic field at this site. The value of this reduction at a given site was assumed, in our spectra fitting procedure, to be proportional to the

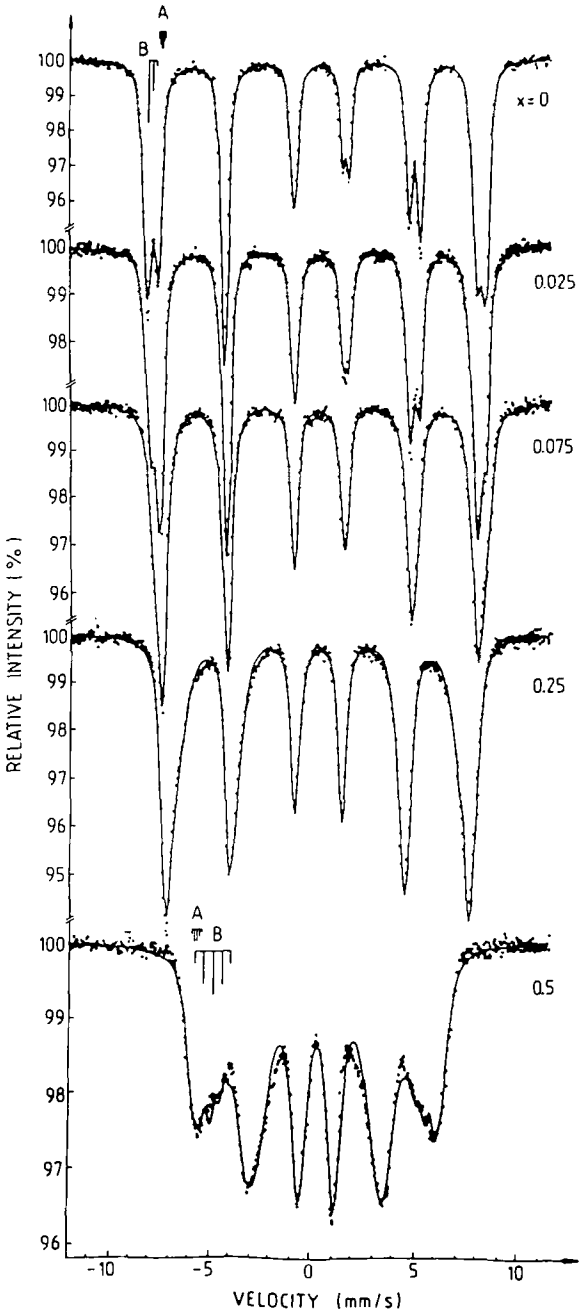

Fig. 1. The selected Mössbauer absorption spectra of $Cd_xCu_{1-x}Fe_2O_4$ ferrites recorded at room temperature.

number of Cu (or Cd) cations as the nearest neighbours of this site. It was found that the proportionality parameter increases with the increase of the x value and that the one ascribed to magnetic Cu cations is about 3 times smaller than that

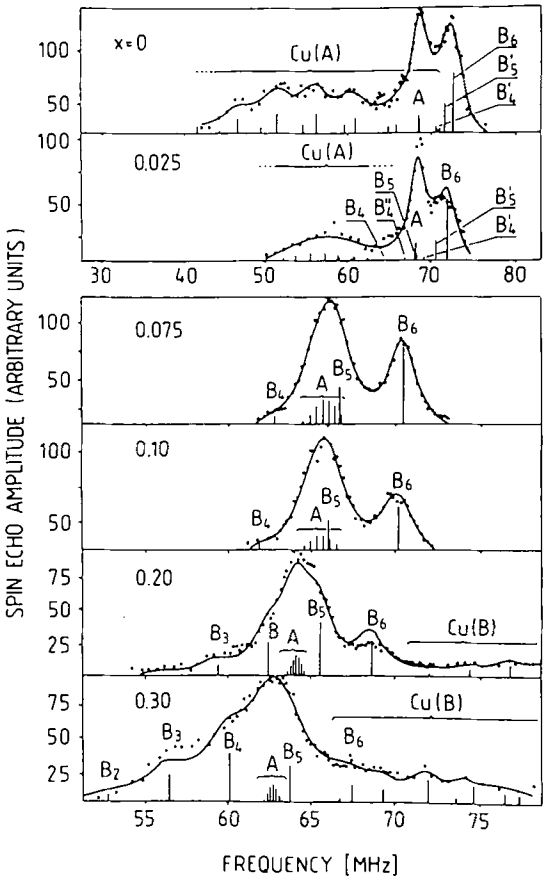

Fig. 2. The selected spin echo NMR spectra of $Cd_xCu_{1-x}Fe_2O_4$ ferrites recorded at room temperature. Details are in the text. Notice the frequency scale different for $x = 0$ and 0.025 samples than for the other ones.

associated with non-magnetic Cd cations, which should be expected. Moreover, the reduction in the averaged hyperfine magnetic field value observed with the increase of the x value is more pronounced in B than in A sublattice, as is shown in fig. 3.

The NMR signals from copper nuclei at A sites gradually disappear with the increase in cadmium content in ferrites since Cd cations substitute firstly for Cu cations at A sites and only after repleacing all of them do Cd cations dislodged Fe cations from A to B sites. Cu(A) signals are not observed for samples with $x \geqslant 0.075$. Only for two samples, $x = 0.20$ and 0.30, were the NMR spectra recorded for frequencies high enough to observe the lower part of copper resonances at B sites.

In conclusion, the hyperfine magnetic field distributions, observed at room temperature at A and B sites of the $Cd_xCu_{1-x}Fe_2O_4$ ($0 \leqslant x \leqslant 0.5$) ferrites by the

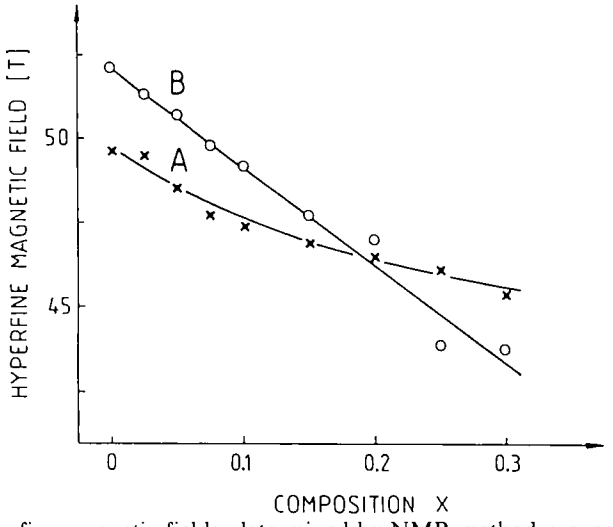

Fig. 3. Averaged hyperfine magnetic fields, determined by NMR method, v.s. composition parameter x.

Mössbauer and NMR methods, can be well described assuming statistical distribution of Fe, Cu and/or Cd cations at A sites as well as that of Fe and Cu cations at B sites. The Mössbauer effect data and the NMR data are in agreement with each other.

Partial financial support of Project 01.09 under Central Research Programme is acknowledged.

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