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MOSSBAUER EFFECT AND NMR STUDIES OF COPPER-CADMIUM FERRITES

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Hyperfine magnetic field distributions have been observed at room temperature in Cd$_x$Cu$_{1-x}$Fe$_2$O$_4$ (0 $\leq$ $x$ $\leq$ 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$_{1-x}$Fe$_{1+x}$)[Cu$_{1-x}$Fe$_{1+y}$]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$_x$Cu$_{1-x}$Fe$_2$O$_4$ (0 $<$ $x$ $<$ 1) have all Cd ions at A sites and, for $x$ $\geq$ $z$, 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$_x$Cu$_{1-x}$Fe$_2$O$_4$ (0 $\leq$ $x$ $\leq$ 0.5) ferrites at room temperature. The Mössbauer effect and spin echo NMR methods were used.

2. Experimental

Polycrystalline samples of Cd$_x$Cu$_{1-x}$Fe$_2$O$_4$ (0 $\leq$ $x$ $\leq$ 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

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was controlled by an X-ray analysis, which shows that samples for $x < 0.10$ have
tetragonal symmetry and for $x \geq 0.10$ 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 neighbour-
ing A-site (B-site) consists of twelve B-site (six A-site) cations. The occurrence 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 distribu-
tion 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 inten-
sities 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