

MOSSBAUER EFFECT STUDY OF Cd Cu FERRITE SYSTEM

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ABSTRACT

The spinel ferrite system $Cd_x Cu_{1-x} Fe_2 O_4$ ($0.0 \leq x \leq 1.0$) has been prepared by ceramic sintering process. The X-ray diffraction spectra proved the formation of spinel phases. The Mossbauer effect measurements have been carried out at room temperature.

Results showed that samples having $0.0 \leq x \leq 0.6$ are in the ferrimagnetic state. while samples having higher values of cadmium cations are in the paramagnetic state. The data are interpreted on the basis of the structure and electronic properties.

INTRODUCTION

Solid solutions of the spinel $Cd_x Cu_{1-x} Fe_2 O_4$ may be prepared with values of x between 0 and 1. The Fe^{3+} , Cu^{2+} , and Cd^{2+} cation are distributed among octahedral (B) and tetrahedral (A) interstitial positions of the face - center - cubic oxygen lattice. Cd- ferrite ($x=1$) is generally assumed to be a " normal spinel" with all Fe^{3+} ions on B-sites and all Cd^{2+} ions on A- sites [1]. In Cu ferrite ($x = 0$), the site preferences lead to predominantly "inverse spinel " structure with Cu^{2+} ions mainly on B -sites and Fe^{3+} ions distributed almost equally between A and B - sites. The inversion is not complete in Cu - ferrite and the degree of inversion depends on previous heat treatment [2]. As cadmium replaces copper between $x = 0$ and $x = 1$, Cd^{2+} ions appear to preferentially enter tetrahedral positions, while the Fe^{3+} ions displaced from these tetrahedral sites to enter the octahedral sublattice.

EXPERIMENTAL PROCEDURE

Six samples were prepared by the usual ceramic sintering process [4] of the ferrite system $Cd_x Cu_{1-x} Fe_2 O_4$. Pure constituent oxides were mixed, pressed, prefixed at 950 °C for two days, then sintered at 1100 °C for two hours, followed by slow Cooling. X-ray powder diffraction patterns were measured using $Cu - K_{\alpha}$ radiation and indicated that all samples had spinel structure with no evidence of impurities or separate phases. The lattice constant, of the cubic unit cells ranges from $8.4016 \pm 0.011 \text{ \AA}$ to $8.676 \pm 0.017 \text{ \AA}$ as x increases, as shown in Fig 1. Mossbauer Effect spectrometer was of the constant acceleration type. The calibration was done with an iron foil of natural abundance and the source used was $10^9 Bq$ ^{57}Co in Rh-matrix. The evaluations of Mossbauer spectra were carried out by least-squares fitting of Lorentzians lines.

RESULTS AND DISCUSSION

1) Hyperfine magnetic field

The Mossbauer spectra of Cd - Cu ferrits system at room temperature are given in Fig.2; the variations of the magnetic field at ^{57}Fe nuclei for both A and B-sites, with x are shown in Fig. 3. The most distinctive property is that the field at the ^{57}Fe B- site nucleuse decreases with increasing Cd^{2+} ions at A- site as a nearest neighbors.

To interpret the obtained Mossbauer results, the different exchange interaction have to be considered. The Fe^{3+} (A) O^{2-} - Fe^{3+} (B) so called A -B interaction, is always the strongest one, the A-A and B - B interaction between iron via oxygen ions are weaker, where as other possible interactions are generally considered to be the weakest [5].

The analysis of the data showed that for samples with x equal zero up to

$x=0.6$, the magnetic field is considerably smaller for the A -site iron ions than for the B -site iron ions. This difference cannot be attributed only to the slight covalence of the tetrahedral iron ions [6] but also it is due to the nature of the intersublattice magnetic bonds. It is well known that in the spinel structure each A -site ion is surrounded by twelve nearest B -site and each B -site ion has six A -sites nearest neighbour. As an example in the case of the nearly inverse Cu -ferrite, each tetrahedral iron ion will have on the average half with Fe^{3+} ions, while every octahedral Fe^{3+} ion will have on the average $3/4$ of the magnetic bonds with iron and $1/4$ of Cu^{2+} [7].

The following ferrimagnetic interactions are expected to exist :

for A -site

$$Fe_A - O - 6 Cu_B \text{ or } Fe_B \quad (1)$$

$$Fe_A - O - 6 Fe_B \quad (2)$$

$$Cu_A - O - nFe_B \text{ or } m Cu_B \quad (3)$$

For B - site

$$Fe_B - O - 6 Fe_A \quad (4)$$

$$Fe_B - O - 3 Fe_A \quad (5)$$

$$Fe_B - O - 3 Cu_B \quad (6)$$

$$Cu_B - O - 6 Cu_B \quad (7)$$

The interaction number (3) is a result of the non complete inversion in the Cu - ferrite. Due to these interaction it can be deduced that the hyperfine magnetic field at B -site ^{57}Fe nuclei are functions of the six nearest A -site by Fe^{3+} , Cu^{2+} and Cd^{2+} ions. On the other hand, the hyperfine field may be caused by the overlap distortions of the central (B) cation s -orbitals by the ligand orbitals which have been unpaired by transfer into nonoccupied 3b - orbitals of the neighbouring (A) cations.

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2) Isomer shifts

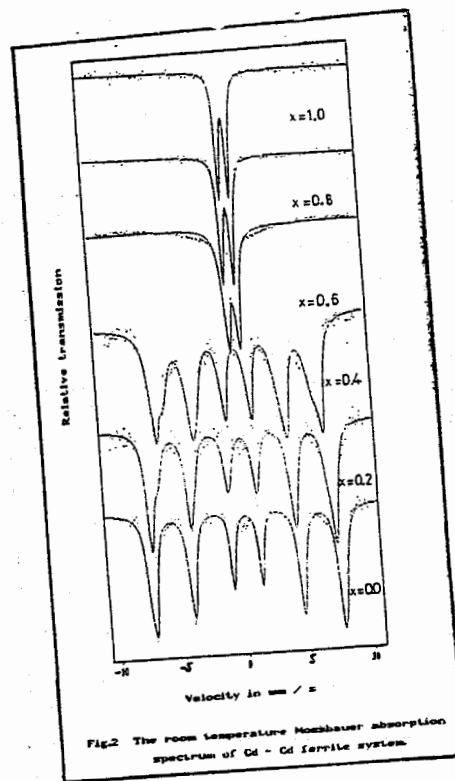
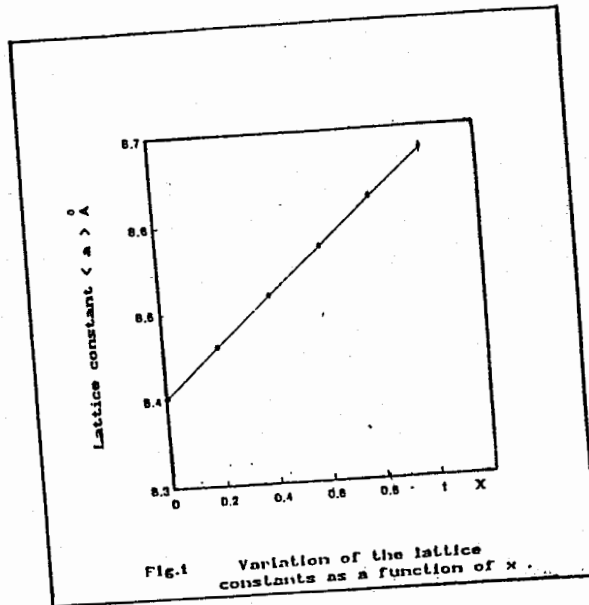
It was observed that there is no noticeable variation in isomer shift ΔE with x . Consequently the variations of s - electron charge density of Fe^{3+} ions is negligibly by Cd^{2+} substitution. The isomer shift values lie within the range of that characteristic of Fe^{3+} ions [8]. Nevertheless, there is a definite difference between the values of the isomer shift corresponding to each site $\Delta E_A - \Delta E_B = -0.01073$ mm/s (for Cu - ferrites). According to these values only Fe^{3+} ions are expected to be present, i.e. no Fe^{2+} ions exist. It was found also that the Fe^{3+} ions in A-site are more more covalent than those in the B-site.

3) The line width

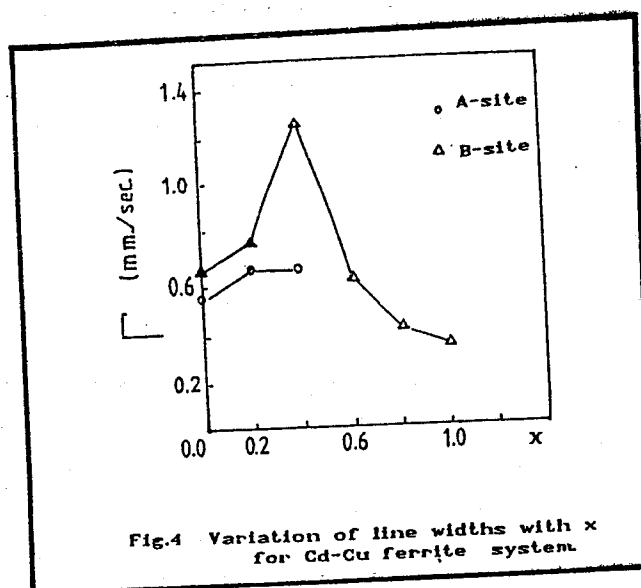
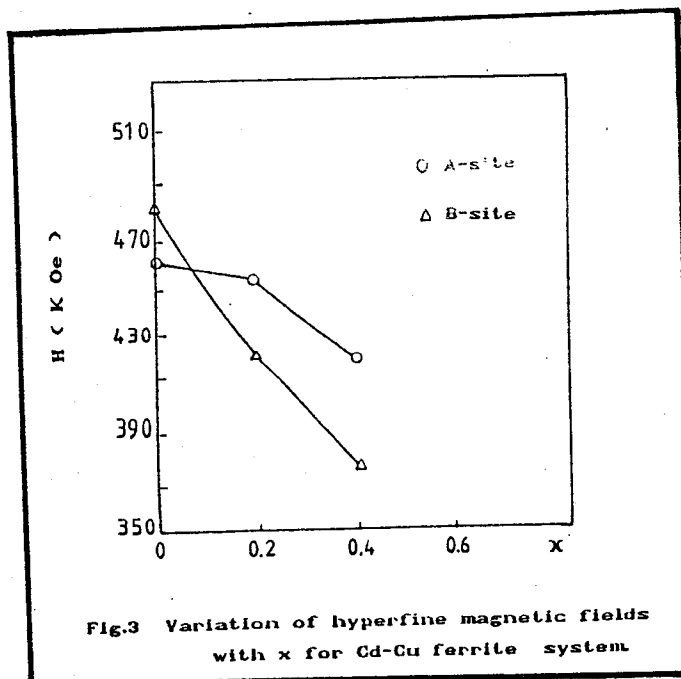
The line width of the Fe^{3+} Mossbauer spectra are useful for estimating the influence of cation disorder on both electric and magnetic interactions. The average line width for A and B-sites are plotted as a function of x as shown in Fig"4"

Generally the hyperfine magnetic field at the Fe^{3+} nucleus is proportional to the $\langle S \rangle$ total spine of the ion, and its time dependence τ . Where $1/\tau$ is defined as the transition or relaxation rate between the hyperfine states, providing the life time of the isomeric excited state $\tau = 1/\omega_L$ where ω_L is the Larmor frequency of the Fe^{3+} nuclear spin. Three possible situations may be considered : the magnetic region with a normal zeeman pattern for $\tau \gg 1/\omega_L$, the relaxation region with relaxation effects for $\tau \sim 1/\omega_L$ and the paramagnetic region for $\tau \ll 1/\omega_L$ with $\langle s_z \rangle = 0$. These regions are illustrated in Fig "4" The dramatic line broadening is due mainly to hyperfine magnetic field distributi. when paramagnetic region is reached i.e $\tau < 1/\omega_L$ the line widths quickly decreased I believe that the relaxation effects in Mossbauer line shapes are due to domain wall

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oscillations in accordance with panicker *et al.* [8], and Upadhay, *et al.* [9].

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دراسة مجموعة نريت الكاديوم - النحاس بواسطة تأثير الموسباور

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تم تحضير مجموعة من عينات الفريت $Cd_xCu_{1-x}Fe_2O_4$ حيث قيمة x فى المدى صفر $\geq x \geq 1$ ، بطريقة التحميص الحرارى الخزفى . وقد تم التأكد من صحة التركيب بواسطة حيود الأشعه السينيه . وأستخدمت طيف موسباور لدراسة هذه المجموعه عن درجة حرارة الغرفة .

وأوضحت النتائج العمليه والحسابات النظرية أن العينات التى تقع فى المدى من $x = 0$ إلى $x = 1$ مواد فيرى م ٧ مغناطيسييه ، بينما العينات التى تحتوى على نسبة أعلى من أكسيد الكاديوم وجد أنها مواد باءا مغناطيسية وقد تم تفسير النتائج تبعاً للتركيب البلورى والألكترونى لهذه المجموعه .