Mossbauer Effect Study of the Cations Distribution and its Influence on the Electric Field Gradient of the Cd_x Co_{1-x} Ferrite System

by

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ABSTRACT

In the ferrite system Cd_xCo_{1-x} Fe_2 O_4 (X=0.0, 0.1, 0.2, ... , 1.0), it was found that the introduction of Co^{2+} decrease the EFG at the octahedral B-site. This was attributed to the distributions of the different cations among the tetrahedral A and the octahedral B-sites. These distributions were completely calculated and found to follow four different formulas along the whole series of the system.

Introduction

The properties of some mixed ferrites with spinel type crystal structure have been studied lately by the ME technique. However, a contradiction in the behaviour of the quadrupole splitting was observed between results obtained by Daniels and Rosencwaig [1] for Zn_xNi_{1-x} ferrite system and that obtained by Bayukov, et al [2] for Cd_xNi_{1-x} and Cd_xCo_{1-x} ferrites, on increasing the concentration of the diamagnetic Z_n^{2+} or Cd^{2+} in the system. So, in a previous paper [3] we studied the quadrupole interaction in the Cd_xNi_{1-x} Fe_2O_4 system and the present work includes the exact distribution of the different kinds of cations on both tetrahedral (A) and octahedral (B) sites of the series $Cd_xCo_{1-x}Fe_2O_4$ and the influence of these distributions on the electric field gradients at both sites.

Experimental Procedure

Eleven samples for the ferrite system $Cd_xCo_{1-x}Fe_2O_4$, where $0 \leq x \leq 1$, were prepared by the usual ceramic sintering process [4] in steps of 0.1. Pure constituent oxides were mixed, pressed, prefired at 900C for 30 hours, then sintered at 1100°C for 6 hours and were annealed in air. The ferrite formations were proved by X-ray diffraction. The lattice constant for each member was calculated and found to vary from 8.365 $\pm$ 0.019 A for x = 0.0 to 8.676 $\pm$ 0.017 Å for x = 1.0. The cation distribution between the (A) and (B) sites was calculated by :

i) comparing the corresponding ME peak areas due to Fe^{3+} ions,
ii) making use of the fact that in spinel ferrites all cations existing are distributed in the ratio 1:2 among A — and B — sites respectively,
iii) taking into account the site preference for each of Co^{2+} and Cd^{2+} ions.

TABLE 1

X	% of Total Iron		Y
	A — site	B — site	
0.0	38.5	61.5	0.23
0.1	42.0	58.0	0.06
0.2	37.5	62.5	0.05
0.3	32.5	67.5	0.05
0.4	30.0	70.0	0.00
0.7	18.1	81.9	0.06
0.8	13.5	86.5	0.07
0.9	5.0	95.0	0.00
1.0	0.0	100.0	0.00

Results and Discussion

The results in the table assure the incomplete inversion of cobalt ferrite [5 & 6], x = 0.0 where 0.23 of Co^{2+} ions occupy the A — sites. These cation distributions can be described by the formula $(Fe_{1-y}Co_y)$ $[Co_{1-y}\ Fe_{1+y}]$ 0_4. On the other hand the spectrum of Cd $Fe_2 0_4$, x = 1.0, (Fig. 1) shows only a single doublet characteristic of the normal spine [7] Decreasing x leads to the appearance of a second doublet, corresponding to the Fe^{3+} ions in the A — sites (Fig. 1) and for x = 0.7 the Fe^{3} ions in the B — site decreased to 82%. Magnetic ordering (Fig. 1) started to appear, when x was decresed to 0.6, which made it difficult to analyse the spectra for x = 0.6 and 0.5 to calculate the cation distribution for these two concentrations, and thus we proposed for 0.7 ≤ x ≤ 0.9 the formula $(Cd_{x-y}\ Fe_{1-x+y})$ $[Fe_{1+x-y}$

$Cd_yCo_{1+x}]$ O_4. For $0.1 \leq x \leq 0.4$, we applied the formula $(Cd_xCo_yFe_{1-x-y})$ $[Fe_{1+x+y}]$ O_4, which was proved [6] to be valid in the case of $Zn_xCo_{1-x}Fe_2O_4$. These distributions affect the electric field gradients (EFG) at the A — and B — sites, where it can be seen (Fig. 2), that pure Cd Fe_2O_4 has the highest value of a quadrupole splitting. EFG at the octahedral sites arises not only from the metal cations, but also from the oxygen anions, because the size of the ions in the tetrahedral sites causes an outward displacement of the four surrounding oxygen anions along the III direction [2] . When some Co^{2+}ions were introduced to the system, we observed that some Fe^{3+} ions started to migrate to the A — site and the EFG of the B — site decreased. This can be interpreted on the basis of the ionic radii, causing distortion of the local symmetry of the EFG, where the radius of Fe^{3} ions is smaller than that of Cd^{2+} . So it can be concluded, that the EFG is more dependant on the ionic radii than on the oxygen parameters.

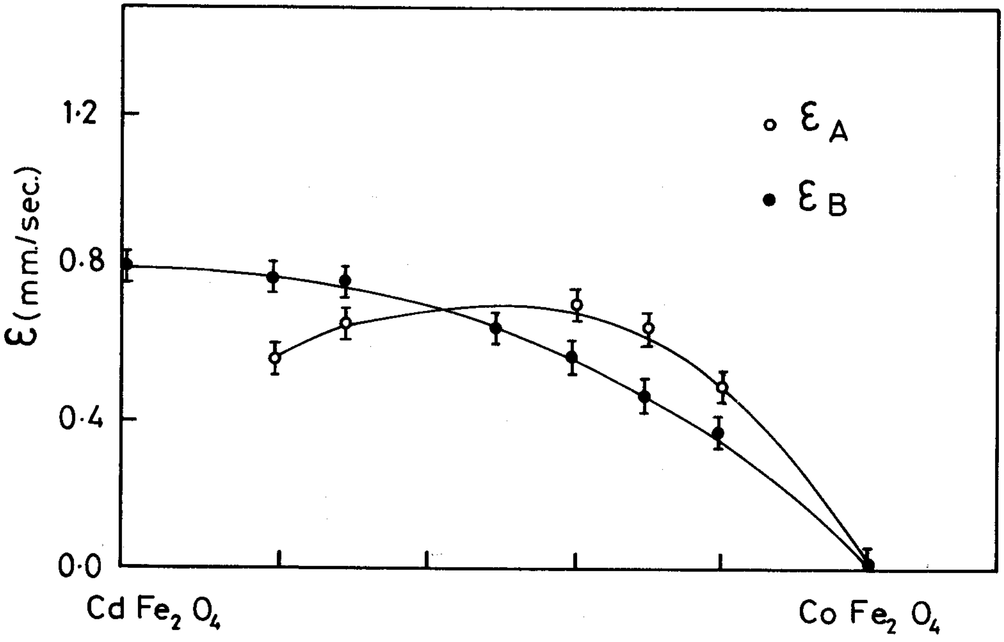

Fig. 2: The values of quadrupole splitting as a function of Cd - concentration for A and B sites.

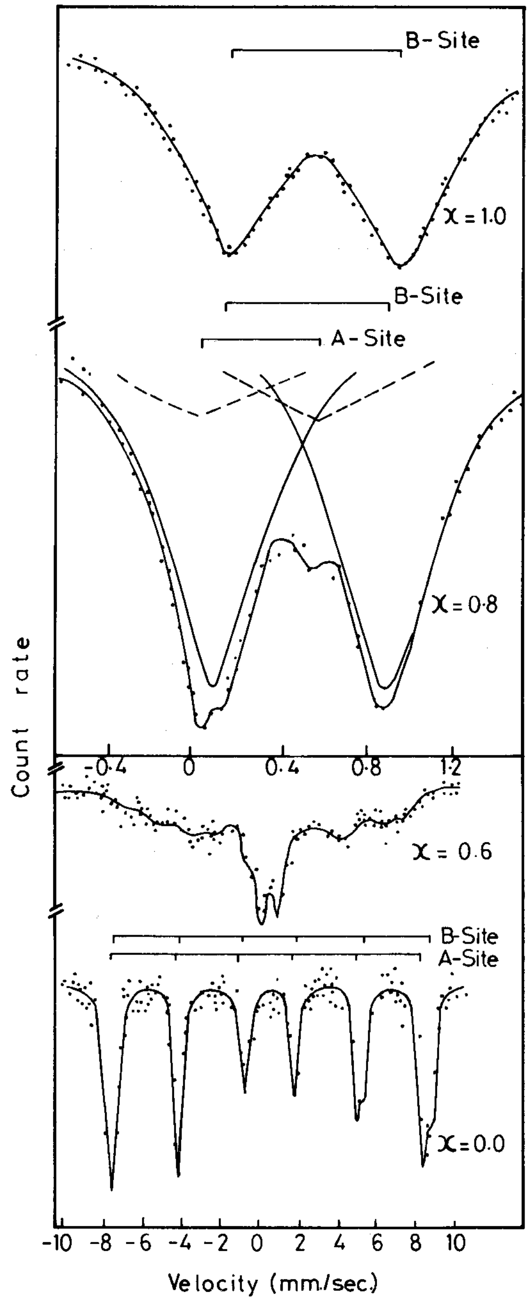

Fig. 1: The room temperature ME spectra of Cd-Co ferrite system.

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استـــــخدام ظاهرة موسباور لدراسة توزيع الايونات الموجبــة في مجموعة الفريت كدس كو١-س ح٢ أ٤ وتأثير هذا التوزيع على ميل المجال الكهربي حول نواة ذرة الحديد

نبيـــل عيســـى - هنـــاء ســـلام

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ملخــــــــــــــص

استخدمت في هذا البحث ظاهرة موسباور لدراسة التوزيع الكامل للأنواع المختلفة من الأيونات الموجبة لمجموعة فريت الأسبنل كدس كو١-س ح٢ أ٤ كيفيا وكميا داخل التجويف رباعي التآزر (أ) والتجويف ثماني التآزر (ب) ووجد أن هذا التوزيع يتبع أربعة قوانين مختلفة كل واحد منها يمكن تطبيقه على بعض أعضاء المجموعة طبقا لنسبة وجود الكادميوم في الفريت .

ولقد ثبت من دراسة ميل المجال الكهربي حول نواة الحديد لكل فريت من المجموعة ، أي عند تغيير تركيز الكادميوم بالنسبة إلى الكوبالت ، ثبت أن ميل المجال الكهربى يقل عند التجويف ثماني التآزر بزيادة نسبة وجود الكوبالت .

هذا ولقد تم توضيح سبب هذا التأثير على ضوء التوزيع الكامل للايونات الموجبة .