

## COLLECTIVE ELECTRON STATES IN $Zn_xFe_{3-x}O_4$ AND $Cd_xFe_{3-x}O_4$ FOR $0 \leq x \leq 0.3$

B.J. EVANS and HANG NAM OK

*Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109, USA*

$^{57}Fe$  Mössbauer measurements of  $Zn_xFe_{3-x}O_4$  and  $Cd_xFe_{3-x}O_4$  have been made at 300 K in zero applied field and at 180 K in zero and 55 kG applied fields. The compositional dependence of the isomer shifts, B to A area ratios and hyperfine fields, which are sensitive to and diagnostic of the conduction mechanism, have been determined under all three experimental settings. The decreasing isomer shift difference between the A and B site, and increasing area ratio are in good agreement with the predictions of band conduction. The hyperfine field at the B site having no Zn or Cd A site neighbors is also observed to increase for small  $x$  values, again, in good accord with band conduction.

### 1. Introduction

In recent years, it has become apparent that significant insights into the mechanism of electron delocalization in binary transition metal oxides can be obtained from physical properties measurements on materials containing a second, substitutional metal ion [1-4]. In a previous  $^{57}Fe$  Mössbauer study of magnetite with Zn and Cd substitutions, i.e.,  $Cd_xFe_{3-x}O_4$  and  $Zn_xFe_{3-x}O_4$ , it was concluded that a band model for the conduction mechanism in  $Fe_3O_4$  is in best agreement with the critical Mössbauer parameters [5]. The Mössbauer spectra were obtained, however, in the absence of an applied magnetic field; and due to line broadening and decreased resolution of the A and B site patterns for  $x > 0.1$ , the conclusions reached depended heavily on least squares computer analyses of the spectra. Therefore, in the present study we have performed  $^{57}Fe$  Mössbauer measurements on  $Zn_xFe_{3-x}O_4$  and  $Cd_xFe_{3-x}O_4$  in an applied magnetic field of 55 kG at 180 K with improved spectral resolution. In addition to confirming the salient conclusions of the earlier study, some new spectral features were discovered which are interesting in terms of recent results of others regarding line broadening mechanisms in  $Fe_3O_4$  at 300 K [6].

### 2. Experimental

The  $M_xFe_{3-x}O_4$  ( $M = Zn, Cd$ ;  $x = 0.1, 0.2, \text{ and } 0.3$ ) are identical to those used previously and were prepared by standard ceramic [5] techniques. Precise stoichiometry was assured by firing intimate mixtures of spectroscopic grade ZnO, or CdO,  $Fe_2O_3$  and Fe metal in evacuated quartz tubes with small free volumes at 1273 and 1223 K for Zn and Cd doped  $Fe_3O_4$ , respec-

tively. X-ray powder diffraction patterns were obtained with a focused Guinier camera and indicated the presence of only a single phase spinel in every case. The lattice constants have been reported previously and show no unexpected variations [5]. The Mössbauer spectra were obtained with an electromechanical transducer operating in a constant-acceleration mode in conjunction with 1024 channel analyzer. A  $^{57}Co$  source in Pd metal was used for the 180 K applied field measurements and a  $^{57}Co/Rh$  source was used for the room temperature measurements. The absorber density was approximately  $10 \text{ mg/cm}^2$  of natural Fe.

### 3. Results

$^{57}Fe$  Mössbauer spectra were obtained at 300 K in zero applied magnetic field and at 180 K in a 0 and 55 kG external field. The  $Cd_xFe_{3-x}O_4$  spectra at 180 K and in a 55 kG field are shown in fig. 1. The  $Zn_xFe_{3-x}O_4$  spectra are quite similar except for somewhat narrower B site lines.

The solid line is the result of fitting to the spectra a local molecular field model in which the magnetic hyperfine field at a B site is determined by the number of A site Zn or Cd neighbors, with the hyperfine field experiencing a linear decrement,  $\Delta H$ , for each Zn or Cd neighbor. The intensity of each pattern is computed assuming a random intra-site distribution of Cd and Zn; neither Zn nor Cd occupies the B sites. The parameters in such a model are  $H_0$ , the field at a B site having no diamagnetic A site neighbor, and  $\Delta H$ , the decrement per A site diamagnetic neighbor. The A site hyperfine field,  $H(A)$ , and the isomer shifts of all patterns are completely free parameters. Completely satis-

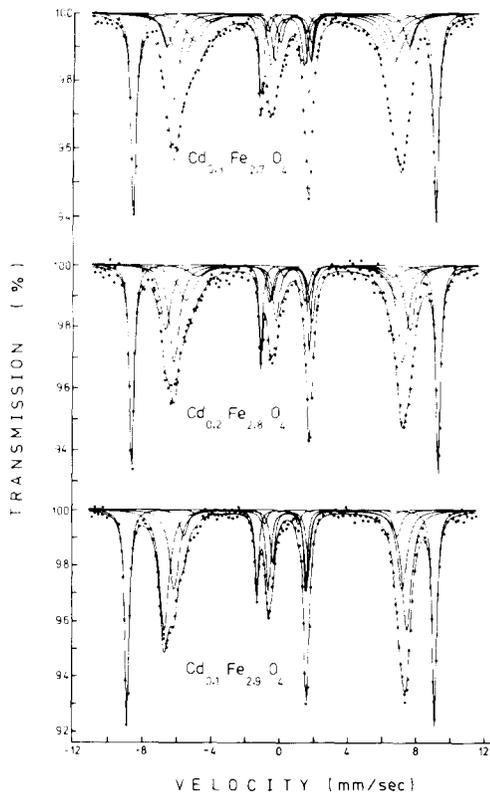


Fig. 1.  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{Cd}_x\text{Fe}_{3-x}\text{O}_4$  at 180 K in 55 kG field. The  $^{57}\text{Co}$  source temperature is 200 K. The more widely split pattern is from A site  $\text{Fe}^{3+}$  ions and the pattern with the smaller splitting and broader lines is due to B site Fe ions. The solid lines through the data points are the results of a least squares fit of several sets of 4-line (Lorentzian) patterns to the experimental data.

factory fits are obtained with the above model as indicated by the solid line in fig. 1. The relevant Mössbauer parameters resulting from the fits are shown in table I.

#### 4. Discussion

The area ratios of the A and composite B site subspectra, as fitted in this study, are in good agreement with the expectation that *all* B site Fe ions contribute *only* to the B site subspectrum, i.e. there is little or no tendency for the formation of localized B site  $\text{Fe}^{3+}$  ions which would contribute to the A site pattern. As shown in table I, the isomer shift difference between Fe(B) with no Zn or Cd neighbors and  $\text{Fe}^{3+}(\text{A})$  is proportional to the conduction electron concentration. This result is in agreement with that expected if the conduction electrons interact equally, more or less, with all B site ions as in the case of a band description of the electron itinerancy. This result is, however, inconsistent with a pair-wise, localized hopping model since the average charge state within  $\text{Fe}^{2+}\text{-Fe}^{3+}$  pairs would be independent of  $x$  and would result in a nearly constant isomer shift. It is to be noted that the isomer shifts variations in zero applied field at 300 K and in a 55 kG field at 180 K are in excellent accord.

Since the conduction electrons are polarized opposite to the  $\text{Fe}^{3+}(\text{B})$  3d electrons, the slight increase in  $H_0(\text{B})$  is in accord with the de-

Table I

Results obtained in least squares fits of 4 to 6 patterns to the Mössbauer spectra of  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  and  $\text{Cd}_x\text{Fe}_{3-x}\text{O}_4$  at 300 K in zero applied field and 180 K in a 55 kG field

$x$	$H^*(\text{A})$ (kG)	$H_0(\text{B})^a$ (kG)	$\Delta H^a$ (kG)	$\Delta H^b$ (kG)	$S_0(\text{B}) - S(\text{A})^a$ (mm/sec)	$S_0(\text{B}) - S(\text{A})^b$ (mm/sec)	$(A_B/A_A)^a$	$(A_B/A_A)^b$
$\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$								
0.1	557 <sub>1</sub> <sup>c</sup>	433 <sub>2</sub>	11 <sub>2</sub>	7.2 <sub>1</sub>	0.34 <sub>1</sub>	0.32 <sub>1</sub>	2.48 <sub>3</sub>	1.91 <sub>1</sub>
0.2	552 <sub>1</sub>	446 <sub>2</sub>	22 <sub>2</sub>	16.3 <sub>6</sub>	0.21 <sub>1</sub>	0.28 <sub>1</sub>	2.49 <sub>3</sub>	2.1 <sub>1</sub>
0.3	551 <sub>1</sub>	445 <sub>2</sub>	19 <sub>2</sub>	18.4 <sub>4</sub>	0.16 <sub>1</sub>	0.18 <sub>1</sub>	2.69 <sub>3</sub>	2.7 <sub>1</sub>
$\text{Cd}_x\text{Fe}_{3-x}\text{O}_4$								
0.1	554 <sub>2</sub>	437 <sub>2</sub>	26 <sub>2</sub>	18.6 <sub>1</sub>	0.32 <sub>1</sub>	0.35 <sub>1</sub>	2.39 <sub>3</sub>	1.91 <sub>1</sub>
0.2	552 <sub>2</sub>	441 <sub>2</sub>	29 <sub>2</sub>	22 <sub>1</sub>	0.19 <sub>1</sub>	0.26 <sub>1</sub>	2.78 <sub>3</sub>	2.5 <sub>1</sub>
0.3	545 <sub>2</sub>	434 <sub>2</sub>	27 <sub>2</sub>	27 <sub>1</sub>	0.15 <sub>1</sub>	0.20 <sub>4</sub>	2.84 <sub>3</sub>	3.1 <sub>2</sub>

<sup>a</sup> At 180 K in a 55 kG external field.

<sup>b</sup> At 300 K in no external field.

<sup>c</sup> Subscript below each number indicates estimated error in last digit.

creasing conduction electron concentration as  $x$  goes from 0.1 to 0.2 and provides further support for a band description of the conduction electrons.

It has also been noticed in the applied field spectra that the hyperfine fields and external fields are not rigorously additive and this discrepancy is believed to be related to a small anisotropy in the B site hyperfine field as discussed recently [6].

Thus, the good accord between the  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{Cd}_x\text{Fe}_{3-x}\text{O}_4$  and  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  at 300 K in zero applied field and at 180 K in a 55 kG field and the good agreement between the parameter values observed and those expected for band conduction indicate that despite a narrow bandwidth the collective electron state in  $\text{Fe}_3\text{O}_4$  is a rather stable one.

Support of this study by the National Science Foundation is gratefully acknowledged. It is also a pleasure to acknowledge the assistance of Dr. L. J. Swartzendruber in obtaining the applied field spectra.

### References

- [1] D.C. Dobson, J.W. Linnett and M.M. Rahman, *J. Phys. Chem. Solids* 32 (1970) 2727.
- [2] D.B. McWhan and J.P. Remeika, *Phys. Rev. B* 2 (1970) 3734.
- [3] D.B. McWhan, M. Marezio, J.P. Remeika, and P.D. Dernier, *Phys. Rev. B* 10 (1974) 490.
- [4] B.J. Evans, *AIP Conf. Proc.* 24 (1975) 73.
- [5] Hang Nam Ok and B.J. Evans, *Phys. Rev. B* 14 (1976) 2956.
- [6] A.M. van Diepen, *Phys. Letters* (1976), In press.