

ELECTRICAL CONDUCTIVITY AND HYPERFINE INTERACTIONS IN  
 $M_xFe_{3-x}O_4$  ABOVE AND BELOW  $T_N$

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ABSTRACT

For  $T < T_N$ , the results of the present study of the  $^{57}Fe$  Mössbauer spectra of Zn- and Ni-substituted  $Fe_3O_4$  are in qualitative agreement with those of recent investigations, supporting a band model for the conduction mechanism in  $Fe_3O_4$ . Asymmetric line shapes are observed, however, for the B site pattern of the substituted samples. Attempts to simulate the asymmetry using a binomial probability distribution and linear hyperfine field perturbations are only marginally successful. The effects of Cd substitution are considerably greater than those of Ni and Zn. A localized conduction mechanism appears to set in at lower x values for Cd. These results are consistent with existing ideas concerning conduction mechanisms in transition metal oxides. The band-like character of the conduction electrons does not appear to be diminished above  $T_N$ , and the isomer shifts indicate a close approach to the +3 oxidation state for all Fe ions. A quadrupole doublet and a singlet pattern with similar isomer shifts may account for the spectra above  $T_N$ .

INTRODUCTION

Recently, there have been several  $^{57}Fe$  Mössbauer studies of substituted  $Fe_3O_4$  below  $T_N$ .<sup>1-3</sup> Similar conclusions supporting a band model for the conduction mechanism in pure and substituted  $Fe_3O_4$  were reached in each case. No measurements have been reported for  $T > T_N$ . It has been suggested that the delocalization of the conduction electrons should be enhanced by the  $Fe^{2+}(B)-Fe^{3+}(B)$  double-exchange interaction.<sup>4,5</sup> Measurements above  $T_N$  are therefore of some significance, and here we report the results of such measurements for  $Ni_xFe_{3-x}O_4$ ,  $0 < x < 0.4$ , and  $Zn_xFe_{3-x}O_4$ ,  $x = 0.2$  and  $0.8$ . As the transition from the collective to the localized electron state is expected to depend upon the Fe-Fe separation and the covalence of the Fe-O bonds,<sup>5</sup> measurements have also been made on  $Cd_xFe_{3-x}O_4$ , which differs from  $Zn_xFe_{3-x}O_4$  mainly in these two respects. In each of these systems the substituted ions have strong site preferences, with the Cd and Zn ions occupying the tetrahedral(A) sites and the Ni ions occupying the octahedral(B) sites. Hence, only Fe ions occupy the B sites in  $Cd_xFe_{3-x}O_4$  and  $Zn_xFe_{3-x}O_4$  with nominal  $Fe^{2+}(B)/Fe^{3+}(B)$  and  $Fe(B)/Fe(A)$  ratios of  $(1-x)/(1+x)$  and  $(1-x)/2$ , respectively. In  $Ni_xFe_{3-x}O_4$ , the values for  $Fe^{2+}(B)/Fe^{3+}(B)$  and  $Fe(B)/Fe(A)$  are  $(1-x)$  and  $1/(2-x)$ , respectively. Because of the different modes of substitution,  $T_N$  increases with increasing x for  $Ni_xFe_{3-x}O_4$  and decreases with increasing x for Zn and Cd substitution.

In the main, our results and conclusions for  $T < T_N$  agree with

those of the previous studies. However, consideration of the B site linewidths and line shapes reveals differences in the influence of the different ions. The effect of Cd is considerably greater than that of either Zn or Ni in agreement with the ideas of Goodenough on conduction mechanisms in transition metal oxides.<sup>5</sup> For  $T > T_N$  the A and B site patterns are not resolved and isomer shifts are quite similar, tending toward a value characteristic of the +3 oxidation state. In keeping with the larger perturbation of Cd for  $T < T_N$ , a weak absorption, due possibly to incipient  $Fe^{2+}$ , is observed for  $Cd_{.4}Fe_{2.6}O_4$ .

#### EXPERIMENTAL

The samples were prepared by mixing previously characterized  $Fe_3O_4$ ,<sup>7</sup>  $ZnFe_2O_4$ ,  $CdFe_2O_4$ ,<sup>6</sup> spectroscopic grade NiO, and  $Fe_2O_3$  in the desired proportions and repeatedly grinding and firing in evacuated silica tubes at 1300 K until a single phase spinel was obtained. The spectra were obtained with an electromechanical transducer and a 1024 channel analyzer. A vacuum furnace ( $10^{-5}$  torr) was used for the high temperature measurements. 99.999% pure Al foil was used for the radiation shields, and no spectra were obtained from materials in the path of the  $\gamma$ -ray other than the sample. The  $Co^{57}/Cu$  source was at 298 K for all measurements.

#### RESULTS

The  $^{57}Fe$  Mössbauer spectra of  $Cd_{.2}Fe_{2.8}O_4$  at 298 K and of  $Fe_3O_4$  at 900 K are given in Figs. 1 and 2; the spectra of the other materials studied were similar to these, especially for  $T > T_N$ . The results of fitting two six line patterns to the spectra at 298 K and a single line pattern to the spectra above  $T_N$ , using Lorentzian lines in each case, are given in Tables I and II. Each of these fits led to a  $\chi^2$  of  $\sim 2$  per data point. The asymmetric lines in the spectrum of Fig. 1 are reminiscent of those observed in partially inverse, insulating spinel ferrites,<sup>8</sup> and the spectra obtained below  $T_N$  were also fitted assuming a binomial probability distribution and a linear relation between the change in  $H_{eff}(B)$  and the number of non-Fe neighbors. The fits improved and the asymmetry in the lines was qualitatively reproduced; the weak structure in the experimental data was more diffuse, however, than that resulting from the fits to the model. The decrease in  $H_{eff}(B)$  was 12 kOe per Zn and 32 kOe per Cd A site neighbor. As shown in Fig. 2 and also from the large  $\chi^2$  values, the single line fit is inadequate in accounting for the details of the spectra above  $T_N$ . A symmetric (quadrupole) doublet and a single line pattern may be used to fit these data. For such fits  $\chi^2$  decreased to  $\sim 1$  per data point. The parameters of the single line pattern were nearly the same as those in Table II. The isomer shift and splitting of the doublet for  $Fe_3O_4$  were +0.1 mm/s and 0.29 mm/s, respectively; the values of these parameters for the other samples differed only slightly from those of  $Fe_3O_4$ . An additional, weak absorption at  $\sim 1.5$  mm/s was observed in  $Cd_{.4}Fe_{2.6}O_4$ .

TABLE I

Parameters obtained in least squares fits of two six line patterns to the  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{M}_x\text{Fe}_{3-x}\text{O}_4$  at 298 K.  $a_B/a_A$  is the area ratio of the B to A site patterns.

Sample	$H_{\text{eff}}(\text{A})$ kOe ( $\pm 2$ ) <sup>a</sup>	$H_{\text{eff}}(\text{B})$ kOe ( $\pm 2$ )	$\delta_B - \delta_A$ mm/s ( $\pm 8$ )	$a_B/a_A$ ( $\pm 5$ )	$\Gamma_1(\text{B})$ mm/s ( $\pm 3$ )	$\Gamma_1(\text{A})$ mm/s ( $\pm 3$ )
$\text{Fe}_3\text{O}_4$	493	461	0.391	1.85	0.37	0.30
$\text{Ni}_{.1}\text{Fe}_{2.9}\text{O}_4$	490	458	0.373	1.70	0.72	0.33
$\text{Ni}_{.2}\text{Fe}_{2.8}\text{O}_4$	490	461	0.371	1.43	0.88	0.38
$\text{Ni}_{.4}\text{Fe}_{2.6}\text{O}_4$	492	470	0.393	1.24	1.25	0.50
$\text{Zn}_{.2}\text{Fe}_{2.8}\text{O}_4$	488	454	0.393	2.69	0.76	0.30
$\text{Cd}_{.2}\text{Fe}_{2.8}\text{O}_4$	481	430	0.337	3.00	1.37	0.36
$\text{Cd}_{.4}\text{Fe}_{2.6}\text{O}_4$	478	425	0.367	3.74	1.63	0.43

<sup>a</sup>Indicates error in last digit of tabulated values

TABLE II

Parameters obtained in least squares fits of a single line pattern to the  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{M}_x\text{Fe}_{3-x}\text{O}_4$  at 900 K. Line positions are uncorrected for the second-order Doppler shift and are given with respect to an Fe absorber at 298 K.

Sample	Line Position mm/s ( $\pm 6$ ) <sup>a</sup>	Linewidth( $\Gamma$ ) mm/s ( $\pm 1$ )
$\text{Fe}_3\text{O}_4$	0.124	0.56
$\text{Ni}_{.1}\text{Fe}_{2.9}\text{O}_4$	0.123	0.61
$\text{Ni}_{.2}\text{Fe}_{2.8}\text{O}_4$	0.109	0.69
$\text{Ni}_{.4}\text{Fe}_{2.6}\text{O}_4$	0.069	0.64
$\text{Zn}_{.2}\text{Fe}_{2.8}\text{O}_4$	0.134	0.62
$\text{Zn}_{.8}\text{Fe}_{2.2}\text{O}_4$	0.068	0.63
$\text{Cd}_{.2}\text{Fe}_{2.8}\text{O}_4$	0.124	0.89
$\text{Cd}_{.4}\text{Fe}_{2.6}\text{O}_4$	0.105	0.73

<sup>a</sup>Indicates error in last digit of tabulated values

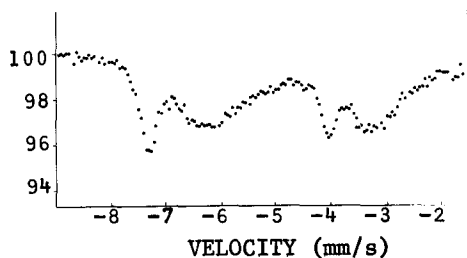


Fig. 1. Lines 1A, 1B, 2A, and 2B of the  $^{57}\text{Fe}$  Mössbauer spectrum of  $\text{Cd}_{.2}\text{Fe}_{2.8}\text{O}_4$  at 298 K.

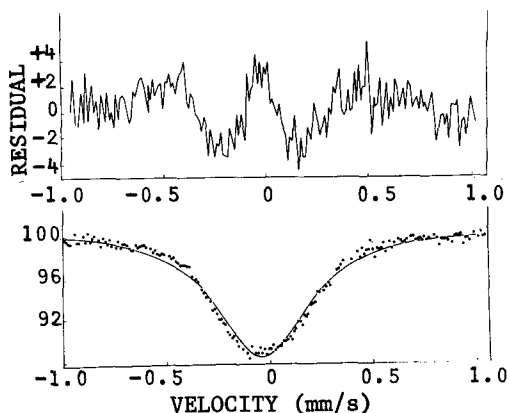


Fig. 2.  $^{57}\text{Fe}$  Mössbauer spectrum of  $\text{Fe}_3\text{O}_4$  at 900 K. Bottom: Least squares fit (solid line) of a single line pattern to experimental data (dots). Top: Residual of single line fit showing presence of doublet pattern.

## DISCUSSION

Qualitatively, the results of the present study agree with previous measurements on  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  and  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  and support a band model for the conduction mechanism in pure and slightly impure  $\text{Fe}_3\text{O}_4$ . In addition, the relative covalence of the substituted ion is found to be an important factor in determining the strength of its perturbation on the conduction mechanism. The deviations of the B/A area ratios in Table I from the site occupancy ratios are mainly artifacts of fitting Lorentzian line shapes to the B pattern; these deviations, however, provide us with the clues to the differences in the influences of the different substituted ions. For  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  and for  $x > .1$ , the experimental area ratios are less than the site occupancy ratios, with the difference resulting from changes in the magnetic exchange interactions and charge transfer processes which tends to increase  $H_{\text{eff}}(\text{B})$ . The B site pattern is asymmetric and overlaps strongly the A site pattern; the fitting of a single Lorentzian line about the apparent center of gravity of the B pattern results in a low estimate of the its total area. A detailed interpretation of very similar data for  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  has been reported.<sup>3</sup> The differences between the B/A area ratios and the site occupancy ratios are evidence for incipient  $\text{Fe}^{3+}$  ions and the onset of localized hopping conduction for  $.4 < x < .6$ . The B/A area ratios of

$Zn_xFe_{3-x}O_4$  and  $Cd_xFe_{3-x}O_4$ , in contrast to  $Ni_xFe_{3-x}O_4$ , are greater than the site occupancy ratios. Again, the lines of the B pattern are inhomogeneously broadened but in a manner opposite to that in  $Ni_xFe_{3-x}O_4$ , resulting in an overestimate of the contribution of the tails of the lines of the B pattern to the A pattern. There is no evidence for  $Fe^{3+}(B)$  ion in these systems, incipient or otherwise, for x values up to 0.4 and possibly as high as 0.6.<sup>1</sup> Both the simple six-line pattern and local-molecular-field-like fit (which leads to inhomogeneously broadened line envelopes) indicate a weak influence of Zn on the conduction mechanism. Similarly, either fitting technique leads to the conclusion that Cd perturbs the B pattern to a much greater extent than in insulating ferrites.<sup>6</sup> The stronger perturbations by Cd arise from its greater influence on the electrical conduction mechanism. The increase in the Fe(B)-Fe(B) and Fe(B)-O internuclear separations and the attendant increase in the ionicity of the Fe(B) bonds occasioned by Cd substitution<sup>6</sup> is expected to lead to a greater tendency toward localized hopping conduction, as observed. No evidence for pair-wise hopping conduction is found for either  $Zn_xFe_{3-x}O_4$  or  $Cd_xFe_{3-x}O_4$ .

While double-exchange interactions below  $T_N$  may enhance the band character of the conduction electrons, the spectra above  $T_N$  indicate that facile electron transfer is also possible in its absence. Indeed, the isomer shifts above  $T_N$  are consistent with an increase in the delocalization of the conduction electrons: At 900 K the isomer shifts of an A and a B site  $Fe^{3+}$  ion and a B site  $Fe^{2+}$  ion are expected to be  $\sim 0$  mm/s,  $\sim 0.1$  mm/s, and  $\sim 1$  mm/s, respectively.<sup>6,9</sup> The measured value of  $\sim 0.1$  mm/s is somewhat less than the expected value of  $\sim 0.4$  mm/s for a +2.5 oxidation state. The fitting of the spectra above  $T_N$  to the singlet and doublet patterns is perhaps non-unique, and other combinations of patterns and line shapes are possible. Nonetheless, the conclusions of this study as to the degree of electron delocalization above and below  $T_N$  and the influence of different kinds of substituted ions are not expected to be altered significantly by other modes of fitting the data.

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