

THE INFLUENCE OF MAGNETIC ORDER ON CHARGE DELOCALIZATION IN PURE AND Zn-DOPED Fe_3O_4

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ABSTRACT

The unexpected simplicity of the ^{57}Fe Mössbauer spectrum of Fe_3O_4 above its Néel temperature has been confirmed for pure Fe_3O_4 and $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$, $x = .01, 0.1,$ and 0.2 . The abrupt change in the isomer shifts of the A and B site patterns is observed to take place near the Neel temperature for all samples, despite a 90 K variation in Neel temperatures. The abrupt change in isomer shifts is caused by electron delocalization from the B site to the A site as the spins on these two sites lose their antiparallel arrangement near T_N . This facile electron exchange between the A and B sites is possible because of the high thermal energies available at T_N and the delocalization mechanism is believed to be hopping in between localized sites.

INTRODUCTION

Even though the low temperature structural/electronic transition in Fe_3O_4 is well known, an adequate understanding of the mechanism and phenomenology of this transition has not been achieved [1]. Previously, we have

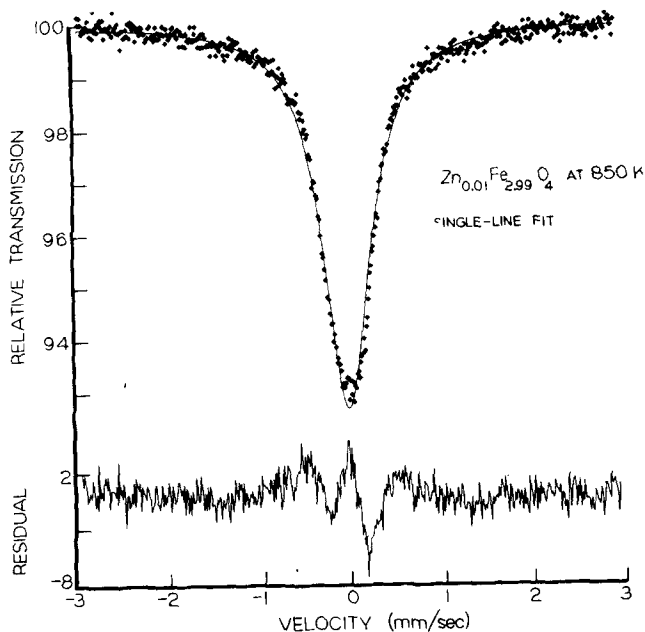


Fig. 1. ^{57}Fe Mössbauer spectrum for $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$ with $x = .01$ fitted with a single line. The strong structure in the residual and its magnitude demonstrates the inadequacy of this fit.

reported on the unexpected similarity of the electronic structure of A and B site Fe ions in Fe_3O_4 as revealed by their isomer shifts and on the fact that the substantial difference 0.4 mm s^{-1} between the A and B site isomer shifts and their electronic structures is reduced rather abruptly in the vicinity of the Néel temperature [2]. In this earlier study, it could not be determined if the similarity in temperatures at which magnetic ordering is lost and at which the isomer shifts changed was accidental or whether there was a relationship between the two phenomena.

Because of the changes of the Néel temperature associated with Zn doping, we have been able to answer this question in the investigation reported. Further, we have arrived at a satisfactory understanding of the interactions responsible for the observed phenomena in contrast to the current state of affairs surrounding the Verwey transition.

EXPERIMENTAL

Pure and Zn-doped Fe_3O_4 samples were prepared as previously described by making intimate mixtures of Fe metal powder and Fe_2O_3 and ZnO in proportions such that stoichiometric magnetites result when pressed ceramic compacts are fired in evacuated, small free-volume silica tubes [3]. All specimens were characterized by means of

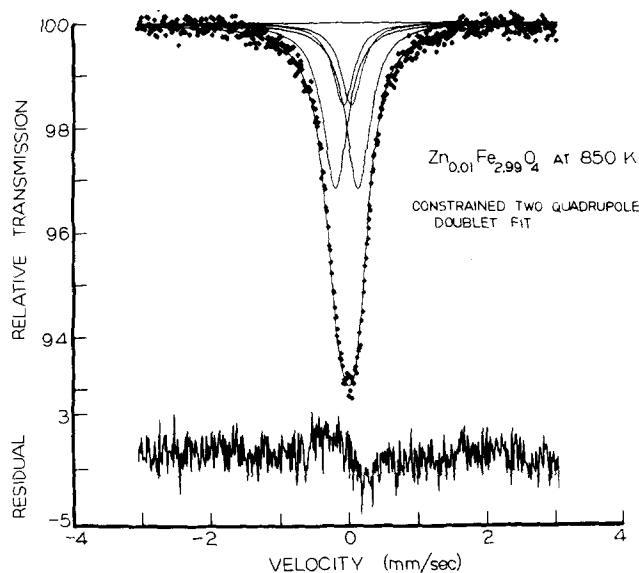


Fig. 2. The same spectrum as in Fig. 1 to which two quadrupole doublets have been fitted with their integrated intensities constrained to a B/A ratio of 2.02.

wet chemical analysis and X-ray diffraction. The results of these characterization measurements were reported earlier [3]. The samples were single phase and of the desired composition. The samples reported on here have the compositions $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$, with $x = 0.01, 0.10,$ and 0.20 .

^{57}Fe Mössbauer measurements were performed with an electromechanical velocity drive operating synchronously with a 1024 multichannel analyzer operated in the multi-scaling mode. The source was a 50 mCi $^{57}\text{Co}/\text{Rh}$ foil and was at 298 K for all measurements. The high temperature measurements were made in a commercially available vacuum furnace. The heater block consisted of boron nitride as did also the absorber holder. Two thermocouples were used: one as the transducer for the proportional temperature controller and the second one which was in contact with that absorber holder for monitoring the temperature. The temperature stability was $\pm 2 \text{ K}$ at 800 K. The absorber thickness was 6 mg/cm^2 . The spectra were analyzed by means of least-mean-squares fitting techniques assuming Lorentzian-shaped lines.

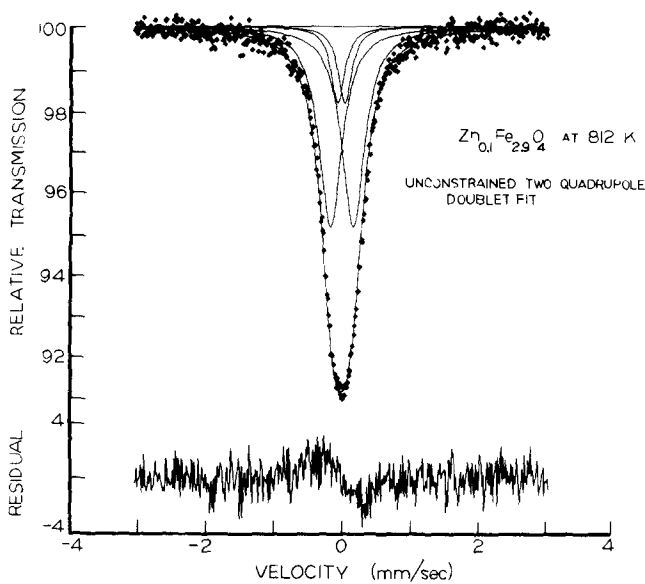


Fig. 3. Two quadrupole doublet fit to the ^{57}Fe Mössbauer spectrum of the $x = 0.1$ sample at 812 K. The integrated intensities of the A and B site patterns are free variables. Parameters resulting from the constrained fit are given in Table 1.

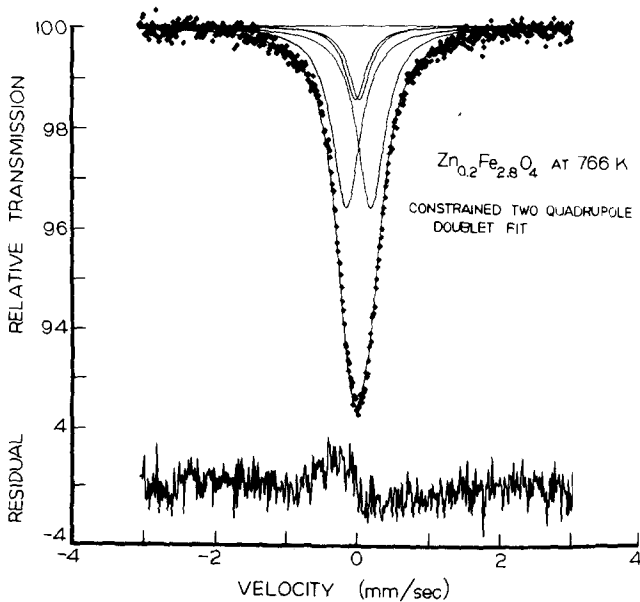


Fig. 4. Constrained two quadrupole doublet fit to the spectrum of the $x = 0.2$ sample at 766 K. Parameters for the unconstrained fit are given in Table 1.

RESULTS

^{57}Fe Mössbauer spectra for $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$, $x = 0.01, 0.10$ and 0.20 , above their respective Néel temperatures are shown in Figs. 1-4. The absence of any structure in the apparently simple absorption is obvious. However, as seen in Fig. 1 and as noted previously [2], a single Lorentzian-shaped line does not describe the absorption profile adequately. A simple two-line fit results in an improved calculated absorption envelope but is not entirely satisfactory since it eliminates out-of-hand the possibility of small quadrupole splittings. We have, therefore, fitted the spectrum under the assumption that there are two quadrupole doublets.

Initially, the intensities of the two doublets are constrained to have relative values consistent with the known cation distributions, as shown in Fig. 2. The hyperfine parameters resulting from this stage of the fitting are then used as the initial parameters for another cycle in which the intensity constrain is relaxed. The parameters obtained by the two different methods are in very good agreement as shown in Table 1.

In addition to the measurements above the Néel temperatures, thermal scanning techniques was also employed in determinations of the Néel temperatures which are also given in Table 1. In order to determine the range of

HIGH TEMPERATURE MOSSBAUER DATA OF $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$

COMPOSITION	$\frac{\Delta\beta}{\Delta\alpha}$	$\Delta E_0(B) - \Delta E_0(A)$	$\delta(B) - \delta(A)$	$\frac{\Gamma(B)}{\Gamma(A)}$	Néel TEMP.
X = 0.01 constrained intensity ratio	2.02	0.11	-0.0121	1.15	850 K
X = 0.01 unconstrained intensity ratio	1.91	0.11	-0.0163	0.95	
X = 0.10 constrained intensity ratio	2.22	0.13	0.0070	1.23	812 K
X = 0.10 unconstrained intensity ratio	2.41	0.12	0.0067	1.34	
X = 0.20 constrained intensity ratio	2.50	0.15	0.0191	1.29	765 K
X = 0.20 unconstrained intensity	2.62	0.14	0.0199	1.30	

temperatures in which the A and B site isomer shifts began their abrupt approach toward similar values, detailed spectra were also taken below the Néel temperatures. The temperature dependence of the isomer shifts obtained from fitting these spectra is shown in Figs. 5-7. The isomer shift variation for the $x = 0.01$ sample is similar to those in Figs. 5-7, except for the temperature at which $(\delta_B - \delta_A)$ decreases abruptly which is near 850 K for this sample.

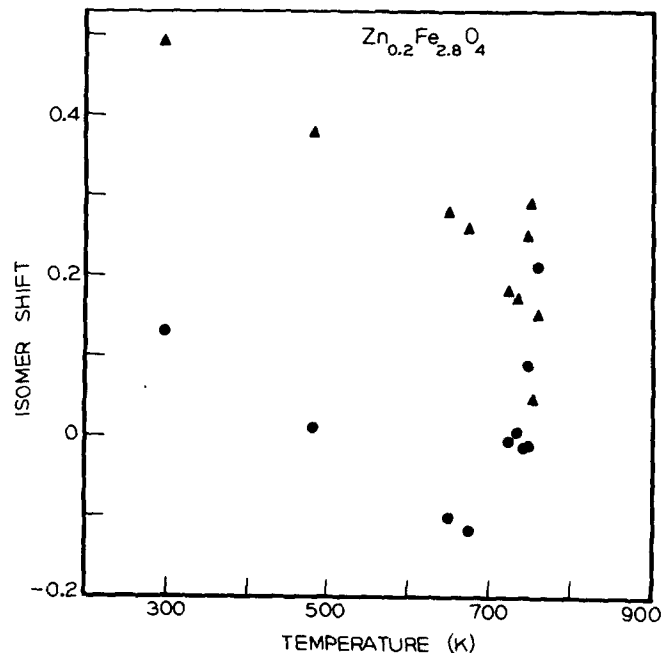


Fig. 5. Temperature dependence of the A and B site isomer shifts for the $x = 0.2$ sample. The Néel temperature of this sample is 765 K.

DISCUSSION

It is shown in Table 1 and Figs. 5-7 that there is a change in the electronic structure of Fe_3O_4 that is strongly correlated with magnetic ordering. As the Néel temperature is approached, the A site Fe ions assume more of an Fe^{2+} like character while the B site Fe ions assume more of an Fe^{3+} character. A consistent explanation of these data requires that the number of d electrons increases at the A sites and decreases at the B sites.

These changes in d electron density are caused by electron hopping between the A and B sites. Below the Néel temperatures, electron hopping between the A and B sites is not possible since the spins of the electrons on the two sites have opposite directions. The small differences in the isomer shifts indicates a significant degree of B-to-A electron delocalization which is possible because of the large thermal energies available at these high Néel temperatures. Recent measurements by other investigators on superparamagnetic, small-particle Fe_3O_4 show a partial resolution of the A and B site patterns at 298 K. In this case, the number of electrons involved in the activated B-to-A hopping is less than for the samples investigated in this study because of the lower thermal energy available [4].

The magnitudes of the B site quadrupole splittings above the Néel temperature are in good agreement with that deduced for pure Fe_3O_4 derived from ^{57}Fe Mössbauer measurements on single crystals at 298 K [5].

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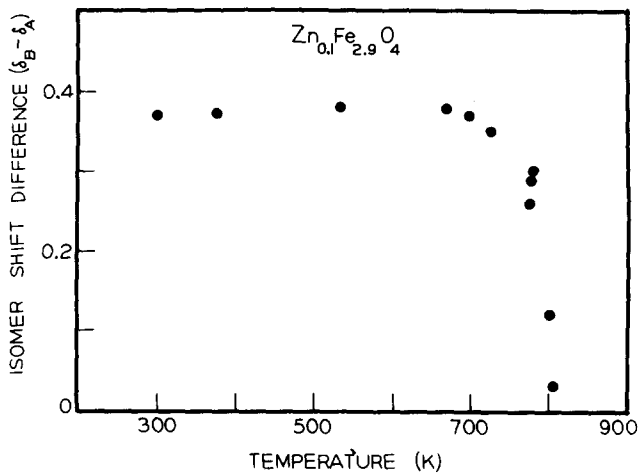


Fig. 6. Temperature dependence of the difference in the B and A site isomer shifts, $(\delta_B - \delta_A)$, for $x = 0.1$.

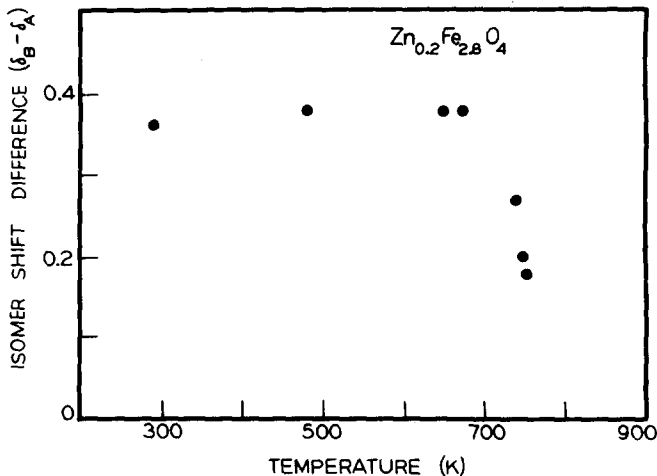


Fig. 7. Temperature dependence of $(\delta_B - \delta_A)$ for the $x = 0.2$ sample.