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Influence of the presence of Fe^{2+} ion in nickel-zinc ferrite

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Abstract. The presence of small amounts of Fe^{2+} ion in nickel zinc ferrite significantly influences some of its magnetic properties. The lattice parameter increases slightly and the increase Δa is independent of x. The variation of magnetization with zinc concentration is explained on the basis of the Yafet–Kittel model. Increase in the Néel temperature on Fe^{2+} substitution in $Zn_xNi_{1-x}Fe_2O_4$ is remarkable. This has been explained on the basis of a four sublattice model. Our analysis shows that J_{AB} (d^5-d^5) interaction is most affected. The influence of Fe^{2+} ions on the relaxation processes in the Mössbauer line shapes of Ni–Zn ferrite is also investigated and is compared with Cu^{2+} doped Ni–Zn ferrite.

Keywords. Electron exchange; exchange constants; Jahn–Teller ion spinels; sublattices; nickel–zinc ferrite.

1. Introduction

Introduction of small amounts ($\sim 10\%$) of Jahn–Teller ion like Cu^{2+} in Ni–Zn and Fe–Zn ferrites produces local distortion which significantly affects their various magnetic properties (Srivastava *et al* 1981a) and influences their Mössbauer spectra (Srivastava *et al* 1981b). To further investigate the effect of such a crystal distortion on the properties of exchange coupled magnetic ions in magnetically ordered systems we have introduced small quantity of Fe^{2+} ions in Ni–Zn ferrites. In the present investigation we have studied the compositions $Ni_{1-x-y}Zn_xFe_y^{2+}$ $(0 < x < 0{\cdot}7;\ y = 0$ and $0{\cdot}1)$ $Fe_2^{3+}O_4$. The results obtained from Néel temperature, magnetization and Mössbauer measurements are discussed here.

2. Experimental

Samples with compositions $Ni_{1-x-y}Zn_xFe_yFe_2O_4$ $(0 < x < 0{\cdot}7;\ y = 0$ and $0{\cdot}1)$ were prepared using the ceramic technique. In order to maintain the ferrous content, the samples were sintered in purified nitrogen atmosphere. The presintered samples were sintered between 1250 and 1350°C. Nitrogen atmosphere was also maintained during the cooling cycle.

The x-ray analysis carried on the above samples identified them as single phase spinels. The lattice parameter a is plotted in figure 1. The lattice constant increases slightly for all values of x and this increase, Δa, is independent of x. The ferrous content of the samples was determined using the standard chemical analysis (Srivastava *et al* 1976).

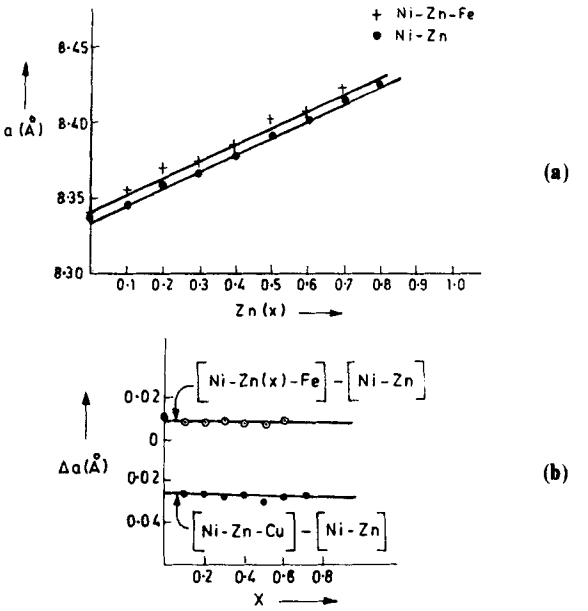

Figure 1. **a.** Variation of lattice parameter with Zn concentration in Ni–Zn and Ni–Zn–Fe systems. **b.** Change in lattice parameter as a function of Zn concentration for Ni–Zn–Cu and Ni–Zn–Fe systems.

3. Results and discussion

3.1 *The Néel temperature measurements*

The Néel temperature (T_N) for $Ni_{0\cdot9-x}Zn_xFe^{2+}_{0.1}Fe_2O_4$ series is found by the initial susceptibility (χ_i) method. A typical χ_i *vs* T curve is shown in figure 2. The sharp fall in the χ_i curve as seen in figure 2 is characteristic of a single phase spinel ferrite. Variation of T_N with Zn concentration is given in figure 3. The T_N is found to increase on Fe^{2+} ($\sim 10\%$) substitution in Ni–Zn ferrites. The change in T_N for 10% Fe^{2+} substitution in $Zn_xNi_{1-x}Fe_2O_4$ is about 100°C for values of x from 0 to 0·7. So far such a large increase in T_N has not been reported. The observed variation of T_N can be explained on the basis of the four sublattice model. The tetrahedral (A) site in the spinnel ferrite is occupied by Fe^{3+} ions while the octahedral (B) site is split into three sublattices, corresponding to Fe^{3+}, Fe^{2+} and Ni^{2+} ions. On fitting the experimental data on the above model one observes that the exchange constants show a very minor dependence on Zn concentration. The $J_{AB}(d^5-d^5)$ interaction is most affected, and seems to have largest influence on T_N. In Ni–Zn ferrite this is 30°K while in the Ni–ZnFe^{2+} ferrite it is 35°K. The increase in $J_{AB}(Fe^{3+}$–$Fe^{3+})$ interaction on Fe^{2+} introduction may be attributed to the propagating local distortion resulting from electron hopping $Fe^{3+} \rightleftharpoons Fe^{2+}$ on the B-sublattice. The experimental and theoretically obtained T_N is plotted in figure 3.

3.2 *Magnetization measurements*

The observed variation of the magnetization at room temperature for Ni–Zn and Ni–Zn–Fe^{2+} systems is shown in figure 4. It is observed that the magnetization

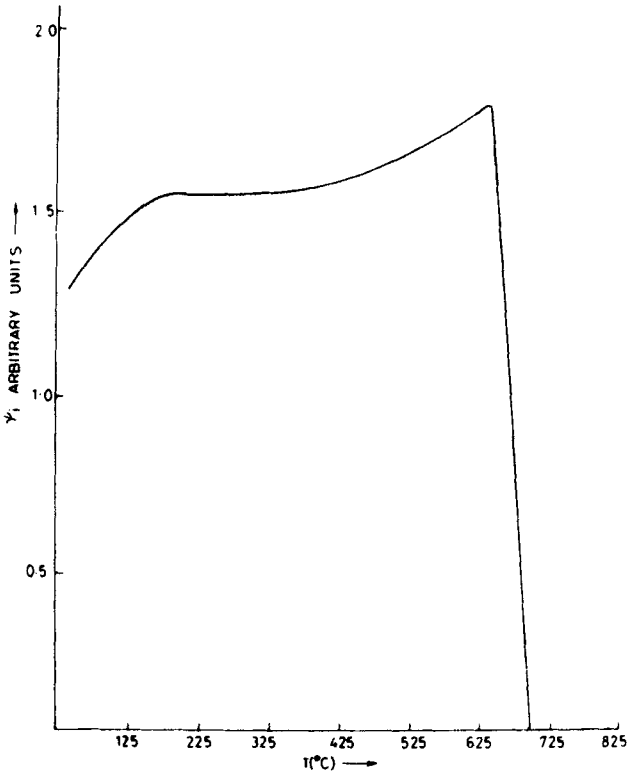

Figure 2. Initial susceptibility *vs* temperature.

increases with Zn-concentration upto $x = 0{\cdot}3$ and then falls off with further increase in Zn-concentration. This variation of magnetization with Zn concentration can be explained on the basis of the Yafet–Kittel model of spin-canting on the *B*-sublattice (Satya Murthy *et al* 1969).

3.3 *Mössbauer effect measurements*

Introduction of 10% of Cu^{2+} in Ni–Zn ferrite creates local distortion inhibiting the localised domain wall oscillations responsible for the occurrence of central doublet superimposed on the magnetic spectra (Srivastava *et al* 1981b). However, when Fe^{2+} ion which is also a Jahn–Teller ion is introduced in Ni–Zn system, it is observed that the central doublet continues to be present in the system and does not disappear as in the case of Cu substitution.

A possible explanation for this observation is as follows.

From previous studies (Srivastava *et al* 1976) it was shown that the atoms which lie within the range of domain wall displacements, give rise to the doublet. A local distortion produced due to Cu^{2+} seems to inhibit the localised domain wall oscillations. However, if the distortion propagates at the rate higher than the rate of the domain wall oscillations then it is possible to see again the effect of localised domain wall oscillation in the Mössbauer spectrum. Introduction of Fe^{2+} leads to a propagating local distortion due to electron hopping $Fe^{2+} \rightleftharpoons Fe^{3+}$ on the B-sublattice.

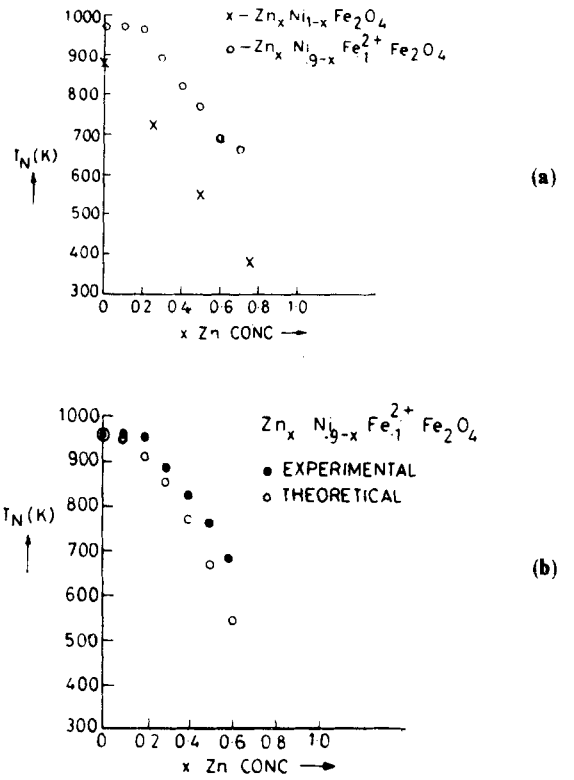

Figure 3. **a.** Dependence of the Néel temperature T_N on Zn concentration **b.** Dependence of the Néel temperature T_N on Zn concentration.

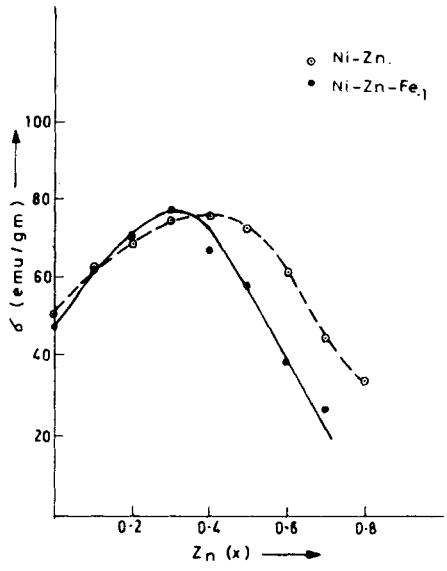

Figure 4. Variation of magnetization with Zn concentration (x), in Ni–Zn and Ni–Zn–Fe systems at 300 K.

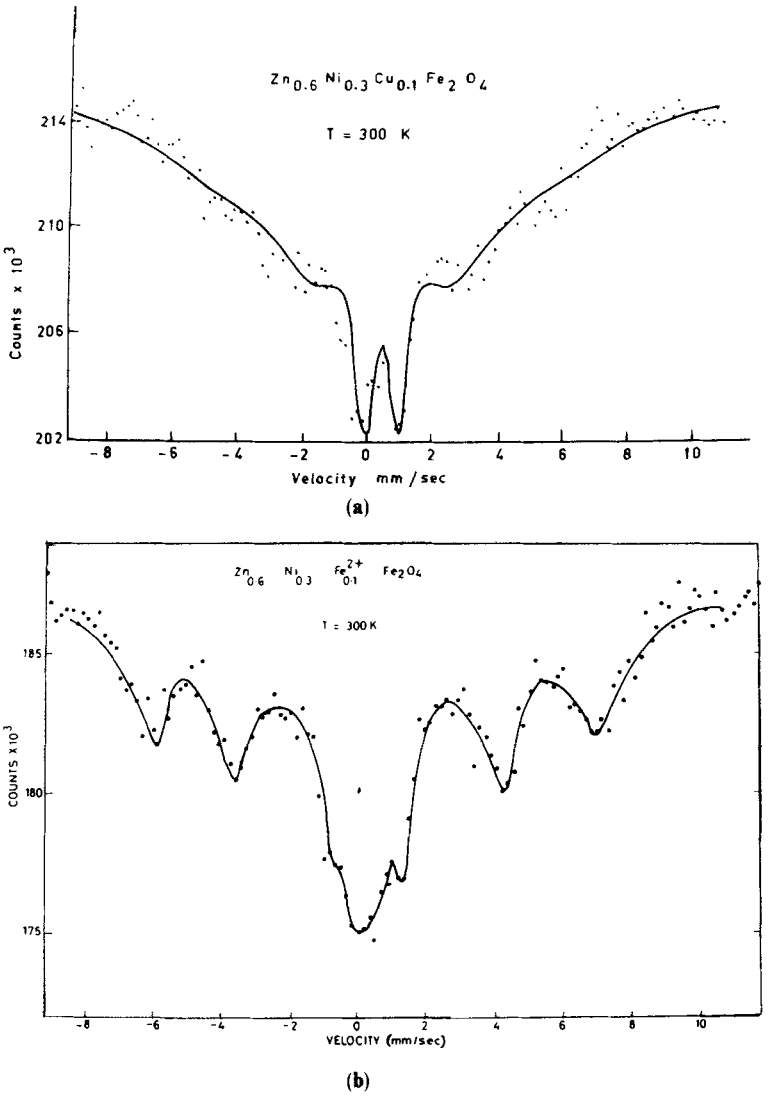

Figure 5. Mössbauer spectra of **a.** $Zn_{0\cdot6}Ni_{0\cdot3}Cu_{0\cdot1}Fe_2O_4$ and **b.** $Zn_{0\cdot6}Ni_{0\cdot3}Fe_{0\cdot1}Fe_2O_4$ at 300 K.

This electron exchange frequency is higher than the frequency of domain wall oscillations. As a result the Mössbauer spectrum remains unaffected after Fe^{2+} substitution. For comparison we give 300 K Mössbauer spectra of Ni–Zn–$Cu^{2+}_{0\cdot1}$ and Ni–Zn–$Fe^{2+}_{0\cdot1}$ for $x = 0\cdot6$ in figure 5.

4. Conclusions

The effect of crystal distortion due to Jahn–Teller effect on thermally-excited localised domain wall oscillations in Ni–Zn spinel ferrites has been studied by substituting small amounts of ferrous ions in these ferrites. The changes in lattice constant, magnetization,

Néel temperature and Mössbauer line shapes is different from the changes observed when Cu^{2+} is substituted in Ni–Zn ferrites. The observed effects are explained on the basis of propagating local distortion resulting from the electron exchange $Fe^{2+} \rightleftharpoons Fe^{3+}$ on the *B*-sublattice.

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