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The influence of Cu^{2+} substitution on the magnetic properties of Fe-Zn and Ni-Zn ferrites

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Abstract. The influence of a Jahn-Teller ion on magnetization, g-values and linewidth in $Zn_x\ Fe_{3-x}O_4$ and $Ni_{1-x}\ Zn_x\ Fe_2O_4$ spinel ferrites has been investigated by introducing small quantities of Cu^{2+} ions. The magnetization on Cu substitution in both the systems but the curie temperature is affected only in FeZn ferrites. The lattice constant in NiZn is significantly reduced while in FeZn there is only a slight increase. The change in g_{eff} on copper substitution, Δg_{eff}, is very different in the two systems. In NiZn, Δg_{eff} has a uniform value, $\sim 0{\cdot}2$, for all values of x while in FeZn it has a peak at $x = 0{\cdot}3$ and vanishes at $x = 0$ and $x \geqslant 0{\cdot}5$. The ferromagnetic linewidth ΔH does not change significantly on copper substitution in both the systems. An explanation based on the perturbation produced due to the local lattice distortion by the Jahn-Teller mechanism explains the observed results satisfactorily.

Keywords. Magnetisation; ferromagnetic resonance; linewidth; Yafet-Kittel ordering; ferrites.

1. Introduction

Recently ferromagnetic resonance studies have been used to investigate the crystal field states of the magnetic ions with strong exchange interaction (Srinivasan and Srivastava 1980). Detailed analysis (Srivastava 1966, 1971) of internal field in ferromagnetic resonance arising from various sources such as the inhomogeneous demagnetization, cavity wall effect, porosity, anisotropy and surface pores has made it possible to determine the g_{eff} with an accuracy of 1 to 2%. It is found that the g-value of ions with partial quenching of orbital angular momentum is significantly different in the case when exchange is present than when it is not present.

The magnetic ordering and ferromagnetic resonance in Fe-Zn (Srivastava *et al* 1976; Srinivasan 1979) and Ni-Zn (Satya Murthy *et al* 1969) ferrites are now well understood and have been explained on the basis of the formation of the Yafet-Kittel type of canted spin arrangement on the B-sublattice. We have introduced Cu^{2+} in these systems to study the effect of the presence of a strong Jahn-Teller ion like Cu^{2+} on the ground state of Fe^{2+} and Ni^{2+} in these systems. Zn substitution was chosen to study the variations of g_{eff} with change in the concentration of Fe^{2+} and Ni^{2+} ions.

In the present work samples with composition $Zn_xCu_{0\cdot1}Fe_{2\cdot9-x}O_4$, $Zn_x\,Ni_{0\cdot9-x}\,Cu_{0\cdot1}\,Fe_2O_4$ and $Zn_x\,Ni_{0\cdot8-x}\,Cu_{0\cdot2}Fe_2O_4$ ($0 < x \leqslant 0\cdot8$) have been studied for magnetisation, g–values and line-widths.

2. Experimental

Polycrystalline samples of $Zn_xCu_{0\cdot1}Fe_{2\cdot9-x}O_4$, $Zn_xCu_{0\cdot1}Ni_{0\cdot9-x}Fe_2O_4$ and $Zn_xCu_{0\cdot2}Ni_{0\cdot8-x}Fe_2O_4$ ($x=0$ to $0\cdot8$) were prepared by the usual ceramic techniques. The pre-sintered oxides were sintered between 1250° to 1350°C in nitrogen atmosphere in the case of Fe-Zn-Cu ferrites and in air atmosphere in the case of Ni-Zn-Cu ferrites. The samples were found to consist of single phase material by x-ray analysis and the density was found to be more than 93% of the theoretical density.

The magnetisation measurements were done from 77°K to the curie temperature using vibration sample magnetometer. The FMR measurements were done at 77°K and 300°K using an x-band microwave resonance spectrometer.

3. Results and discussion

The variation of lattice constant with Zn concentration for Fe-Zn and Fe-Zn-Cu and NiZn and Ni-Zn-Cu ferrites is shown in figures 1 and 2. As expected the lattice constant increases with increase in Zn concentration. This is due to the larger ionic radius of Zn^{2+}(0·74Å) which on substitution replaces Fe^{3+}(0·64Å) ion on the tetrahedral site. With copper substitution NiZn system shows larger change in lattice parameter compared to the FeZn system. This is shown in figure 3 where we have plotted the change in lattice parameter as a function of zinc concentration. We define, $\Delta a(x) = a(Zn_xCu_{0\cdot1}\,Fe_{2\cdot9-x}O_4) - a(Zn_x\,Fe_{3-x}O_4)$ and similarly for the NiZn system.

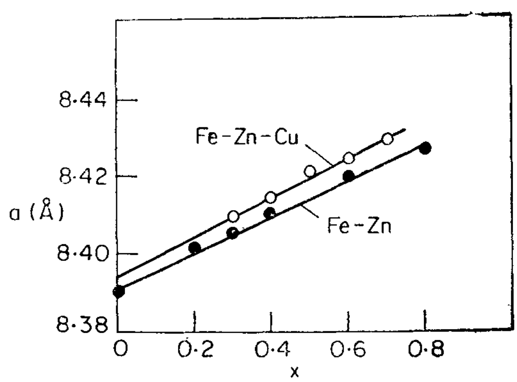

Figure 1. Variation of lattice constant with Zn concentration in Fe-Zn-Cu and Ni-Zn-Cu ferrites.

3.1 *Magnetisation*

The variation of magnetisation M_s with Zn concentration in Fe-Zn-Cu ferrites at 77°K and 300°K are shown in figure 4. For comparison we have also plotted the variation of M_s for the FeZn system.

In $Zn_xFe_{3-x}O_4$ the magnetisation increases at 77°K with Zn concentration and reaches a maxima for $x=0{\cdot}4$ and then decreases. When 0·1 of Cu is substituted in Fe-Zn it is observed that the magnetisation increases with increase in amount of Zn and shows a maxima at $x=0{\cdot}3$ (figure 4). Further the M_s value in Fe-Zn-Cu system is higher than the ferrites without Cu up to $x=0{\cdot}3$. With further increase in Zn concentration the magnetisation falls off much more rapidly in Cu-substituted system.

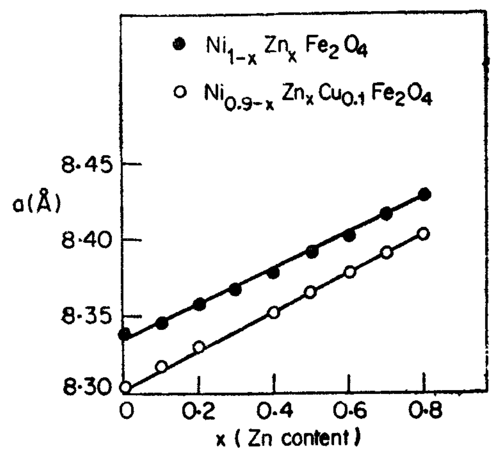

Figure 2. Variation of lattice constant with Zn concentration in Ni-Zn-Cu ferrites.

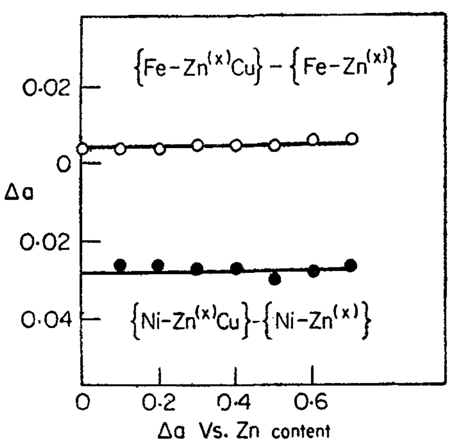

Figure 3. Change in lattice parameter as a function of zinc concentration x when Cu^{2+} is substituted in Fe-Zn and Ni-Zn ferrites.

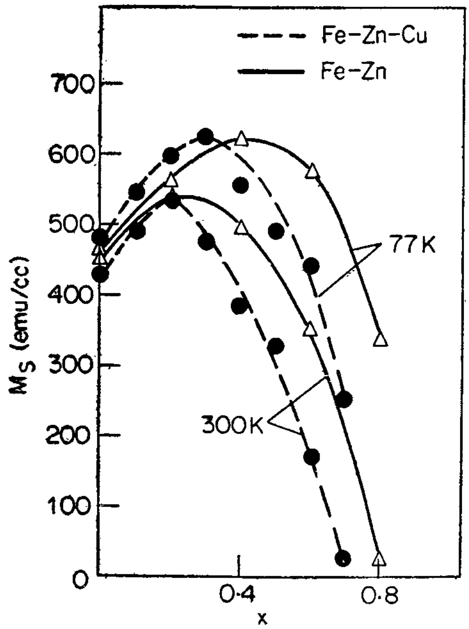

Figure 4. Variation of magnetisation M_s with zinc concentration (x) in Fe-Zn and Fe-Zn-Cu ferrites at 77°K and 300°K.

The observed variation of magnetisation with Zn concentration can be explained on the basis of the formation of the Yafet-Kittel type of spin ordering on the octahedral sublattice. The angle of canting α_{YK} in ferrous zinc copper ferrites can be computed from the magnetisation data using the relation

$$\cos \alpha_{YK} = \frac{2\, n_B(O) + (1-x)\, 5\, g^{3+}_{Fe}}{(1+x)5\, g^{3+}_{Fe} + (0{\cdot}9 - x)\, g^{3+}_{Fe} + 0.1 g^{2+}_{Cu}} \tag{1}$$

where $n_B(O)$ is the magnetic moment at 0°K expressed in Böhr magnetons. Using the g values of 2·0, 2·25 and 2·2 for Fe^{3+}, Fe^{2+} and Cu^{2+} ions respectively and the saturation magnetisation, $M_s(O)$ given in table 1 one can estimate α_{YK} from equation (1). The values of α_{YK} are given in table 1 and compared with the values in Fe-Zn ferrites (Srivastava *et al* 1976). The substitution of Cu^{2+} changes α_{YK} substantially and up to $Zn_{0{\cdot}3}$ the canting angle is lower and beyond $Zn_{0{\cdot}3}$ it is higher than the ferrites without Cu^{2+}.

The variation of magnetisation in Ni-Zn-Cu ferrites for 0·1 and 0·2 of Cu^{2+} with Zn concentration at 300°K is shown in figure 5 and is compared with pure Ni-Zn system. The magnetisation shows a maxima at Zn = 0·3 in Cu-substituted system as in the case of Ni-Zn ferrites. The magnetisation value decreases with increasing Cu substitution. The change in magnetisation with Zn substitution in Ni-Zn and Ni-Zn-Cu ferrites can be explained on the basis of Yafet-Kittel model as in Fe-Zn-Cu ferrites.

The dependence of the curie temperature on the amount of Zn in Fe-Zn-Cu and Ni-Zn-Cu ferrites is shown in figures 6 and 7 respectively. The curie temperature is not affected by Cu^{2+} substitution in Ni-Zn but is significantly decreased in the Fe-Zn-Cu system. This clearly shows that the presence of Cu in Fe-Zn ferrites influences the strength of exchange interaction whereas this is not the case in NiZnCu system.

3.2 *Ferromagnetic resonance and relaxation*

The variation of g_{eff} values with Zn concentration in Fe-Zn and Fe-Zn-Cu ferrites is shown in figure 8. The g_{eff} values were found to be the same at 77°K and 300°K. In Fe-Zn ferrites the g value decreases with increase in Zn concentration from 2·25

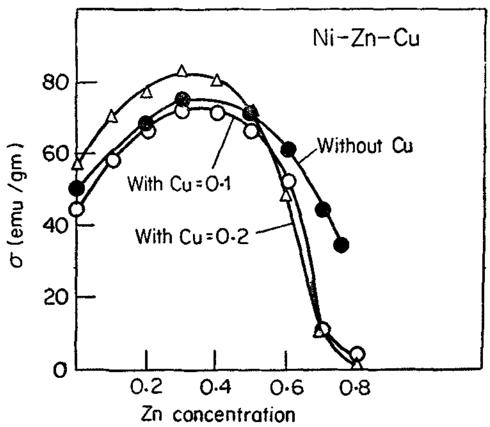

Figure 5. Variation of magnetisation σ with zinc concentration (x), in Ni-Zn-Cu for 0·1 and 0·2 of Cu^{2+} substitution and in Ni-Zn ferrites at 300 K.

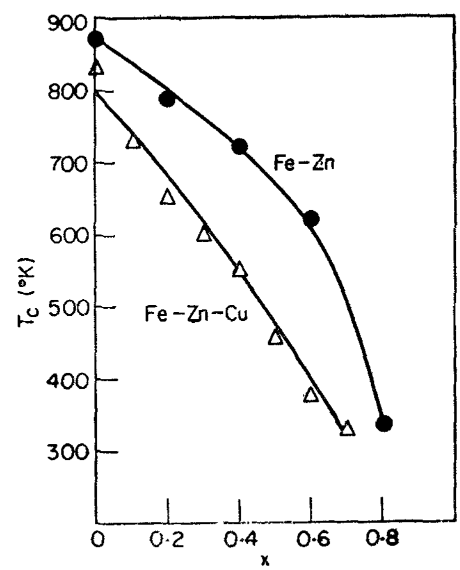

Figure 6. Dependence of the curie temperature T_c, on the amount of Zn in Fe-Zn-Cu and Fe-Zn ferrites.

for Zn = 0 to 2·08 for Zn = 0·8. In the Fe-Zn-Cu system the g_{eff} has the same value of Fe_3O_4 for $x=0$ but starts increasing for small value of x, reaches a maximum at $x=0{\cdot}3$ and then falls to the same value of Fe-Zn at $x=0{\cdot}5$. For $x > 0{\cdot}5$ the two values are the same.

The dependence of g_{eff} on the concentration of Fe^{2+} ions in Fe-Zn ferrites can be explained on the basis of Yafet-Kittel model. The observed variation of g_{eff} in ferrous zinc copper ferrites cannot be explained on the basis of canted spin structure. This is due to the fact that according to the Yafet-Kittel model the g_{eff} should decrease monotonically with increase in Zn concentration. A possible explanation could be as follows: In a magnetically ordered system the Hamiltonian can be written as

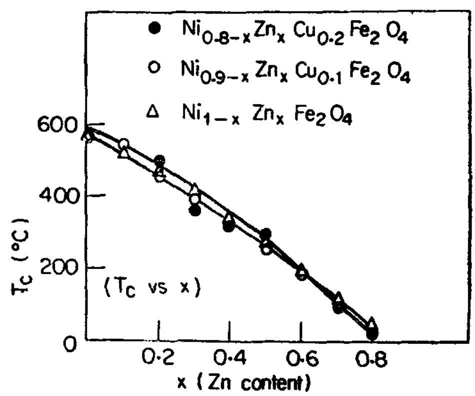

Figure 7. Dependence of the curie temperature T_c on the amount of Zn in Ni-Zn and Ni-Zn-Cu ferrites.

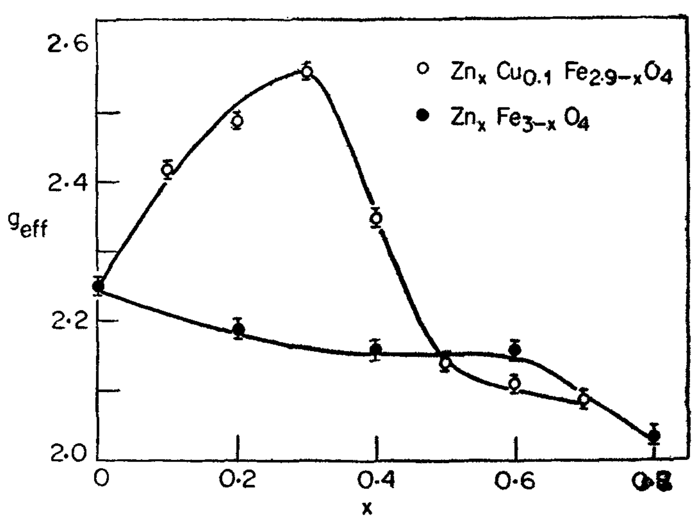

Figure 8. Variation of g_{eff} with zinc concentration (x) in Fe-Zn and Fe-Zn-Cu ferrites.

$$H = H_{\text{cubic}} + H_{\text{ex}} + H_{\text{so}} + H_{\text{trig}} . \quad (2)$$

In case of Fe_3O_4, the contribution from the cubic crystal field, H_{cubic}, is of the order of 10,000 cm^{-1}, H_{ex} is due to exchange and is of the order of 100 cm^{-1}, H_{so} is the spin orbit contribution and is of the order of 20 cm^{-1} and H_{trig} is due to trigonal field and is equal to 4 cm^{-1} (Bates and Steggles 1975). We thus find that in magnetically ordered system the effect of exchange dominates over the spin orbit and trigonal field interactions. As the spin orbit coupling is broken *g*-factor in the ground state of the ion becomes close to the value of the free spin. This explains the *g*-value of 2·25 for Fe^{2+} ion in Fe_3O_4. In Cu substituted system whenever Cu^{2+} is the nearest neighbour of Fe^{2+}, the J_{BB} super-exchange due to $b_{\sigma\sigma}$ (Srivastava *et al* 1979) transfer integral vanishes so that the exchange splitting of Fe^{2+} ion is decreased thereby increasing the effect of the spin orbit coupling on the ground state. Since in the absence of exchange with spin orbit coupling we expect a value of 3·5 the observed enhancement of g_{eff} with increase in the ratio of Fe^{2+} to Cu^{2+} is understandable.

To test the validity of the above suggestion we have considered the probability of a central Fe^{2+} ion having 4 Fe^{3+}, 1 Cu^{2+} and 1 Fe^{2+} nearest neighbours and have considered its variation with x (Srinivasan 1979). This we have done since its probability is the larger amongst other possible combinations with large number of nearest neighbour Cu^{2+} ions. The variation of probability P with Zn concentration is shown in figure 9. The dependence of P with zinc concentration closely resembles that of the g_{eff} with x. At higher Zn concentration the probability P becomes small and the Cu^{2+} will have greater probability of having only Fe^{3+} neighbours so that the g_{eff} values become closer to that of the Fe-Zn ferrites.

The plot of g_{eff} *vs* x in Ni-Zn-Cu system with 0·1 and 0·2 of Cu substitution, shown in figure 10, shows a different behaviour. The introduction of Cu in Ni-Zn system increases the g_{eff} almost uniformly for all values of x except for a small decreases in case of $Ni_{0.6}Zn_{0.2}Cu_{0.2}Fe_2O_4$. The variation of g_{eff} with Zn concentration in Ni-Zn ferrite can be explained on the basis of the Yafet-Kittel model. The presence of Cu^{2+} neighbour in Ni-Zn-Cu ferrites is not expected to affect the exchange Hamiltonian. The increase in the g_{eff} value of Ni^{2+} suggests that the splitting due to

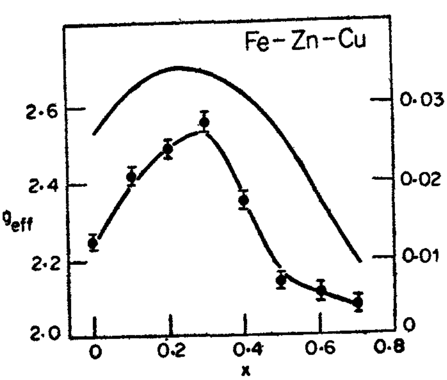

Figure 9. Variation of the g_{eff} with zinc concentration (x) in $Zn_xCu_{0.1}Fe_{2.9-x}O_4$ at 300°K. P is the probability of Fe^{2+} ion having 1 Cu^{2+}, 1 Fe^{2+} and 4 Fe^{3+} nearest neighbours.

the trigonal field is enhanced by the presence of Cu^{2+} ion leading to a greater mixing of the higher Γ_5 state on to the ground state Γ_2.

The plot of ΔH *vs* the Zn concentration, in Fe-Zn-Cu ferrites is shown in figure 11 and is compared with that of Fe-Zn system. At room temperature as well as at 77°K the linewidth in Fe-Zn-Cu ferrites is slightly smaller than the ΔH in Fe-Zn ferrites. This is due to the decrease in linewidth due to bulk conductivity in the sample as the conductivity decreases with Cu substitution in Fe-Zn ferrite. The variation of ΔH with Zn concentration shows similar behaviour in Ni-Zn-Cu ferrites as in the Ni-Zn ferrites. These are shown in figure 12.

Conclusions

The effect of Jahn-Teller ion on magnetization g_{eff} and linewidth in FeZn and NiZn spinel ferrites has been studied by substituting small amounts of copper in these

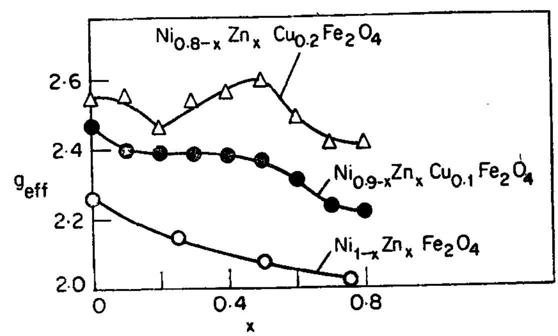

Figure 10. Dependence of g_{eff} on amount of Zn(x) in Ni-Zn-Cu and Ni-Zn ferrites.

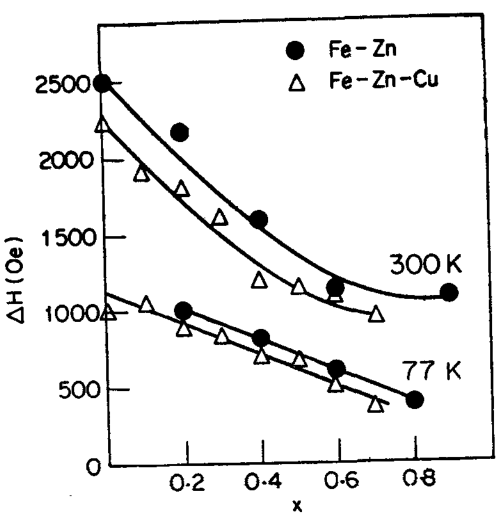

Figure 11. Variation of line width (ΔH) with zinc concentration (x) in Fe-Zn-Cu and Fe-Zn ferrites at 77°K and 300°K.

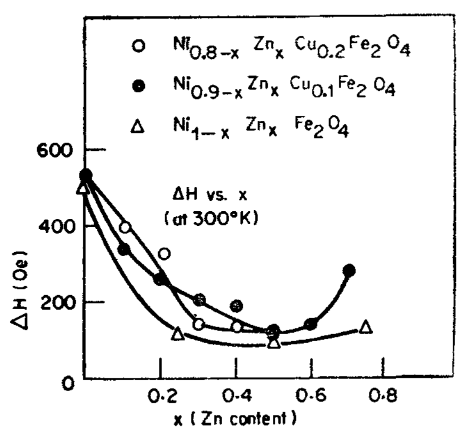

Figure 12. Variation of line width (ΔH), with the amount of Zn(x) in Ni-Zn and Ni-Zn-Cu ferrite at 300°K.

systems. The changes in lattice constant, magnetization, curie temperature, g_{eff} and ΔH on copper substitution in the two spinels show marked differences. This has been explained on the basis of the perturbation of the ground states of the Fe^{2+} and Ni^{2+} ions produced due to the local lattice distortion by the Jahn-Teller mechanism.

Table 1. The Yafet-Kittel angle α_{YK} in Fe-Zn-Cu ferrites obtained using equation (1) M_s(O) is the extrapolated value of magnetisation at 0°K. The α_{YK} values for Fe-Zn ferrites are from Srivastava *et al* (1976).

	Fe-Zn-Cu		Fe-Zn
x	$4\pi M_s(O)$ (Gauss)	α_{YK} (degrees)	α_{YK} (degrees)
0	6485	0	0
0·1	7340	0	..
0·2	8050	8	13·7
0·3	8380	18	..
0·4	7360	32	27·4
0·5	6610	42	..
0·6	6000	50	43·5
0·7	5720	63	..
0·8	..	..	63·3

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