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Electrical conductivity studies of copper-substituted and non-substituted Ni–Zn mixed ferrites

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The electrical conductivity of Ni–Zn and copper-substituted Ni–Zn ferrites is investigated in the range 300 to 1000 K. It is seen that the plots of log ϱ against $10^3/T$ exhibit a linear relationship. There are four distinct regions exhibited by the Ni–Zn ferrite. However, with the substitution of copper there appears to be gradual disappearance of the fourth region. Also for the samples of Ni–Zn ferrite with more than 80% Zn, there are only three regions in the variation of log ϱ with $10^3/T$. The breaks and discontinuities are attributed to several sources. The electrical conduction in these ferrites is explained on the basis of a hopping mechanism. The activation energy in the paramagnetic region is found to be more than that for the ferrimagnetic region. This is attributed to the effect of the magnetic ordering in the conduction process.

1. Introduction

Studies on the electrical conductivity of Ni–Zn ferrites with composition and temperature variation have been carried out [1]. The electrical conductivity of iron-rich and iron-deficient Ni–Zn ferrites was measured from room temperature to 300° C [2]. The same system has been studied through magnetization studies by many workers [3–7]. However, no data are available on the electrical conductivity studies of copper-substituted Ni–Zn ferrites. The present paper reports comparative studies of electrical conductivity of copper-substituted and non-substituted Ni–Zn mixed ferrite systems. These studies are carried out to gain information regarding the role of copper ions in influencing the lattice parameter, Curie temperature, electrical conductivity and saturation magnetization. An interesting behaviour is exhibited by Ni–Zn ferrite with addition of copper and is explained on the basis of the Jahn–Tellor ion.

2. Experimental procedure

The ferrite samples were prepared by standard ceramic methods using AR grade CuO, ZnO, NiO and Fe_2O_3. The powders of these oxides were mixed in proportion and sintered for 48 h at 1100° C in a globar furnace. The product was cooled at the rate of 80° C h^{-1} in the furnace. The completion of the solid-state reaction was checked from X-ray diffractometer studies carried out using a Siemens computerized X-ray diffractometer.

The Curie temperatures of the samples were determined by using the method suggested by Loria and Sinha [8].

A high-field loop tracer HS869 supplied by the Electronics Corporation of India was used for the measurements on hysteresis.

3. Results and discussion

The variation of log ϱ against $10^3/T$ (where T = absolute temperature) has been studied for the ferrites

$$Ni_{1-x}Zn_xFe_2O_4$$

where x = 0, 0.2, 0.4, 0.6, 0.8, 1.0 (Series A)

and

$$Ni_{0.8-x}Zn_xCu_{0.2}Fe_2O_4$$

where x = 0, 0.2, 0.4, 0.6, 0.8 (Series B)

in the temperature range from 300 to 1000 K. Figs 1, 2 and 3 show these plots. The variation of resistivity exhibits two trends. In Fig. 1 four regions are seen with three breaks and in Figs 2 and 3 three or two regions with two or one break.

All the plots exhibit a linear relationship suggesting that the resistivity obeys a relation of the type

$$\varrho = \varrho_0 \exp(\Delta E/kT) \quad (1)$$

where ΔE is the activation energy, T is the absolute temperature and k is Boltzmann's constant, and ϱ_0 is resistivity of 0° C.

The breaks and discontinuities can be attributed to several sources. Komer and Klivshin [9] have observed changes in activation energies for conduction which occur at high temperature in several ferrites and are correlated with the ferromagnetic Curie temperature of the ferrites. This offers solid evidence for the influence of magnetic ordering upon conductivty in ferrites [10]. The breaks may also be due to change in conduction mechanism [11]. Recently Ghani *et al.* [12] have shown more than one break in the temperature variation of resistivity in the case of Cu–Ni ferrites. They have attributed the conduction mechanism in the first region to the presence of impurities, in the

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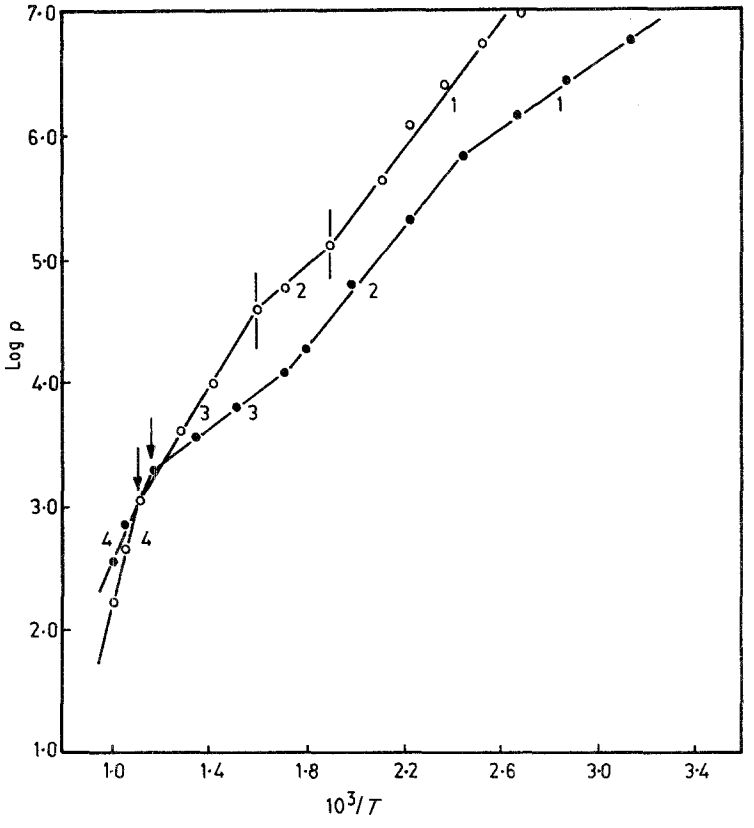

Figure 1 Log ϱ against $10^3/T$ for (○) $NiFe_2O_4$ (T_c = 893 K) and (●) $Ni_{0.8}Zn_{0.2}Fe_2O_4$ (T_c = 844 K).

second region to the phase transition from tetragonal to cubic and in the third region to a magnetic ordering change.

A detectable change in the slope of log ϱ against $10^3/T$ plots for various compositions has been observed. This change in the slope indicates the change in activation energy. Table I shows these changes in the activation energy in the four different regions. It is clearly seen that the activation energy goes on changing, becoming a maximum in the region at highest temperature and a minimum in the region of low temperatures. The low values of ΔE in Region 1 (at low temperatures) mean less activation energy for the conduction electron. This may well be attributed to the impurity conduction which is generally observed in ferrites at low temperatures. In Region 2, characterized by slightly higher values of ΔE, the conductivity may be influenced either by a phase transition as suggested by Ghani *et al.* [12] or may be due to some impurity phase present in the ferrites and the formation of some undetected phases at that temperature.

The electrical resistivity, the change in activation

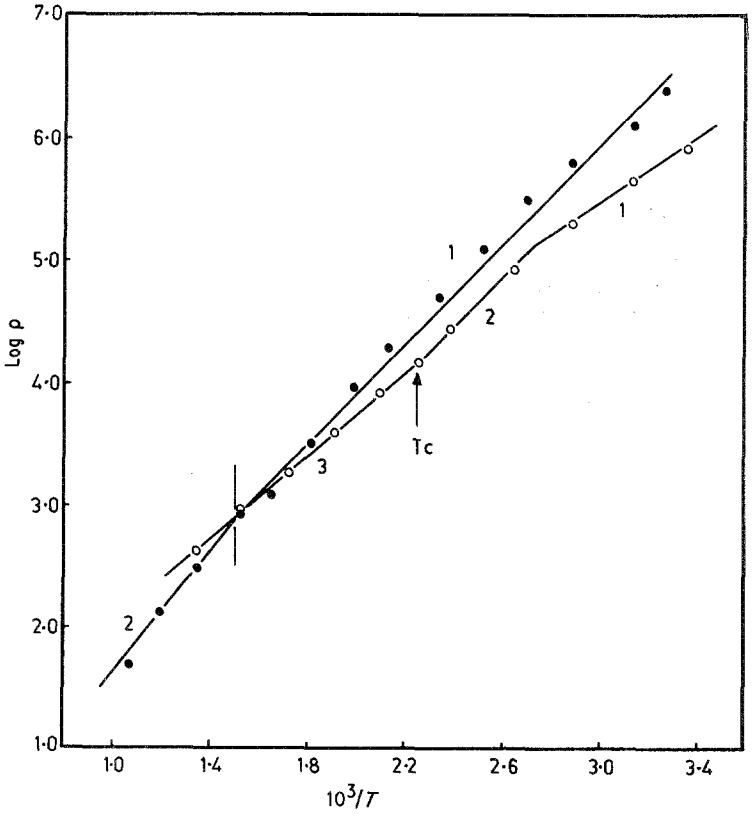

Figure 2 Log ϱ against $10^3/T$ for (●) $ZnFe_2O_4$ and (○) $Ni_{0.2}Zn_{0.8}Fe_2O_4$ (T_c = 444.4 K).

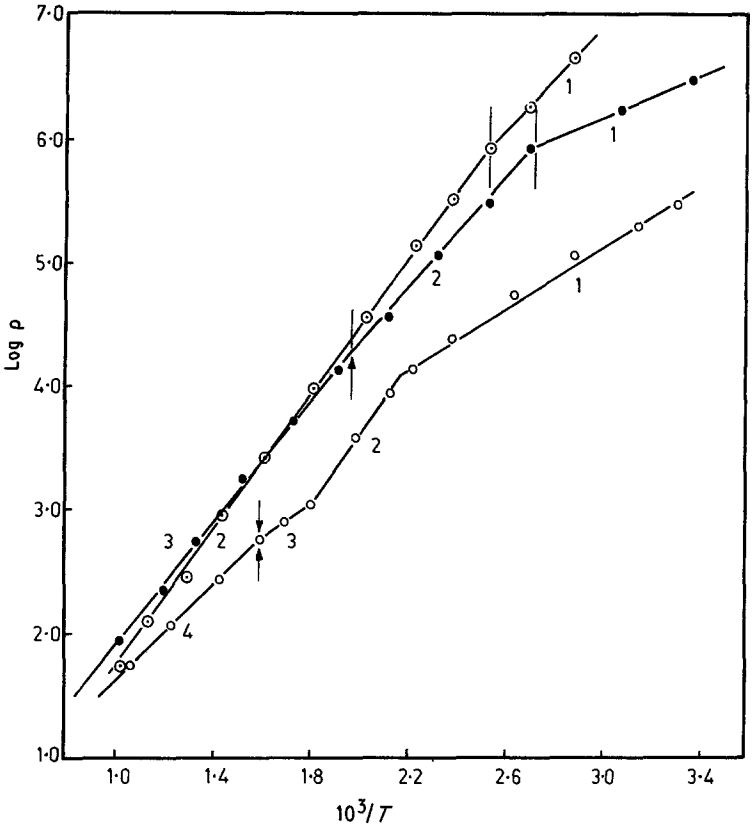

Figure 3 Log ϱ against $10^3/T$ for (⊙) $Zn_{0.8}Cu_{0.2}Fe_2O_4$, (●) $Ni_{0.2}Zn_{0.6}Cu_{0.2}Fe_2O_4$ (T_c = 505 K) and (○) $Ni_{0.4}Zn_{0.4}Cu_{0.2}Fe_2O_4$ (T_c = 625 K).

energy at the Curie point and the relationship of the activation energy with the composition can be explained and discussed only in the light of the mechanism of the hopping polarons, which has been successfully employed to explain the conduction mechanism in ferrites [13]. Therefore, the polaron hopping, although thermally activated in both the temperature regions appears to have a lower activation energy in the magnetic region below the Curie temperature. This is bound to be the case as the polaron in the case of ferrite does not significantly involve a strain in the ionic lattice as in the case of other ionic solids, due to the fact that the "d" electrons contribute the polaron. The cooperative behaviour would be characteristic of such a polaron, giving rise to a lower activation energy.

The conductivity in ferrites has been associated in general with the presence of ions of a given element in more than one valance state [14]. These ions get distributed over the crystallographically equivalent sites. The high conductivity of Fe_3O_4, for example, has been explained as

$$Fe^{2+} \rightleftharpoons Fe^{3+}$$

The values of ΔE to cause normal electron hopping are of the order of 0.2 eV and less [15].

The values of ΔE (Table I) suggest that the hopping process due to polarons is favoured. The theory of conductivity has been explained on the hopping of polarons due to thermal activation [16].

In solids with a large coupling constant and a narrow conduction band, small polaron formation is more probable. In oxides of the iron group of metals the overlap of 3d wave functions between neighbouring metal ions is relatively small. There is strong experimental proof for the existence of small polarons and the hopping process [17, 18]. The energy levels and bands for ferrites have been calculated only after making simplifying assumptions and using suitable approximations [17]. Of late, Klinger [18] has explained the conduction mechanism in magnetite-like solids using a two-phase

TABLE I Variation of activation energy with composition

Sample No.	Composition	Activation energy, ΔE (eV)			
		Region 1	Region 2	Region 3	Region 4
1	$NiFe_2O_4$	0.4899	0.3386	0.6455	1.3510
2	$Ni_{0.8}Zn_{0.2}Fe_2O_4$	0.2648	0.4766	0.2979	0.8341
3	$Ni_{0.6}Zn_{0.4}Fe_2O_4$	0.3664	0.4668	0.2327	0.4519
4	$Ni_{0.4}Zn_{0.6}Fe_2O_4$	0.2880	0.5030	0.1906	0.4807
5	$Ni_{0.2}Zn_{0.8}Fe_2O_4$	0.2648	0.3904	0.3297	–
6	$ZnFe_2O_4$	0.3976	0.4866	–	–
7	$Ni_{0.8}Cu_{0.2}Fe_2O_4$	0.1887	0.4866	0.3526	0.5363
8	$Ni_{0.6}Zn_{0.2}Cu_{0.2}Fe_2O_4$	0.2402	0.4766	0.3078	0.5114
9	$Ni_{0.4}Zn_{0.4}Cu_{0.2}Fe_2O_4$	0.2391	0.4567	0.2532	0.2863
10	$Ni_{0.2}Zn_{0.6}Cu_{0.2}Fe_2O_4$	0.1588	0.4567	0.4967	–
11	$Zn_{0.8}Cu_{0.2}Fe_2O_4$	0.3313	0.5363	–	–

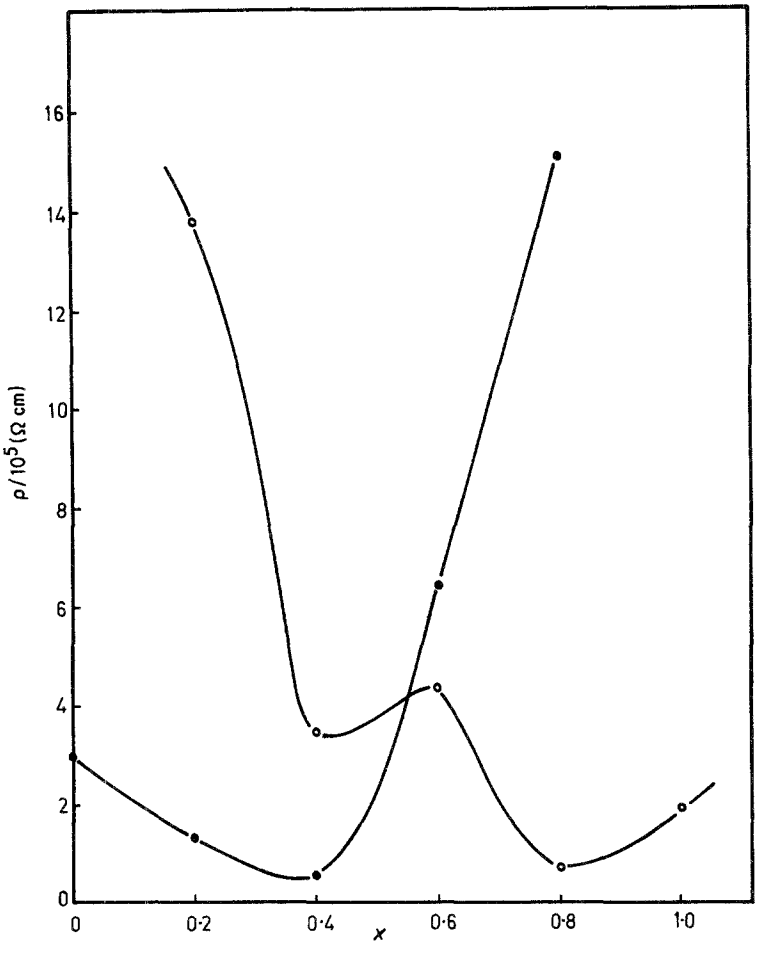

Figure 4 Resistivity (ϱ) against content of zinc (x) for (○) $Ni_{1-x}Zn_xFe_2O_4$ and (●) $Ni_{0.8-x}Zn_xCu_{0.2}Fe_2O_4$ at 373 K.

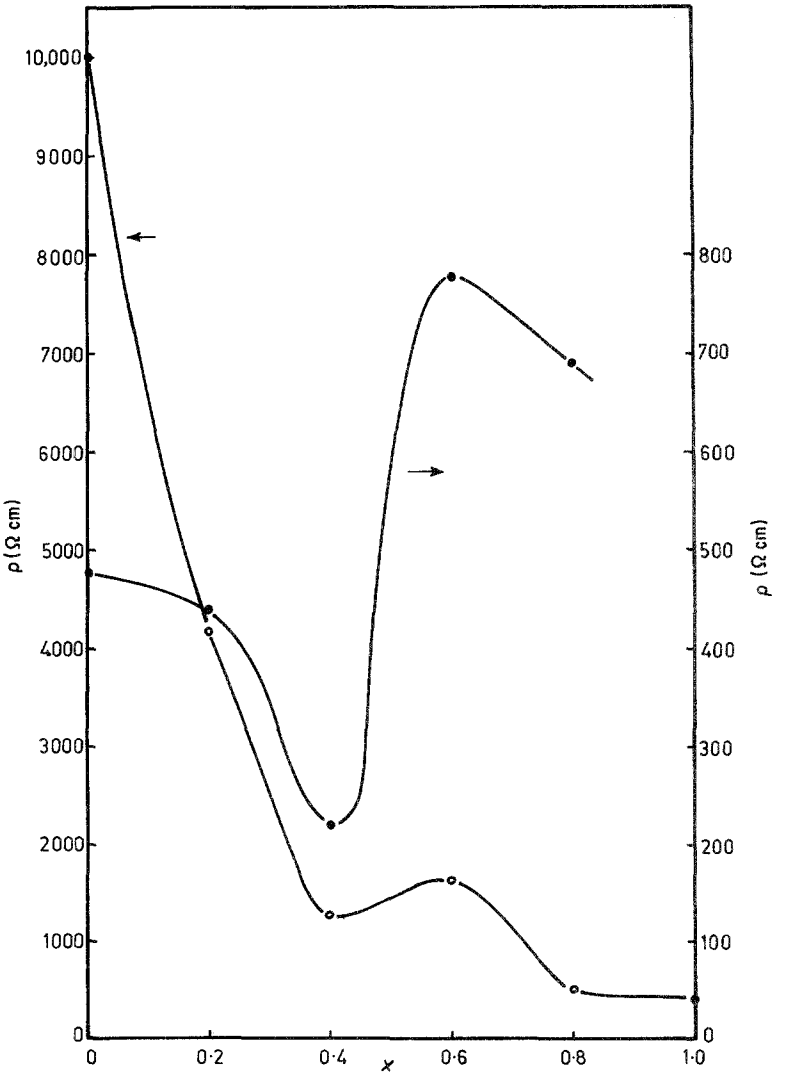

Figure 5 Resistivity (ϱ) against content of zinc (x) for (○) $Ni_{1-x}Zn_xFe_2O_4$ and (●) $Ni_{0.8-x}Zn_xCu_{0.2}Fe_2O_4$ at 714 K.

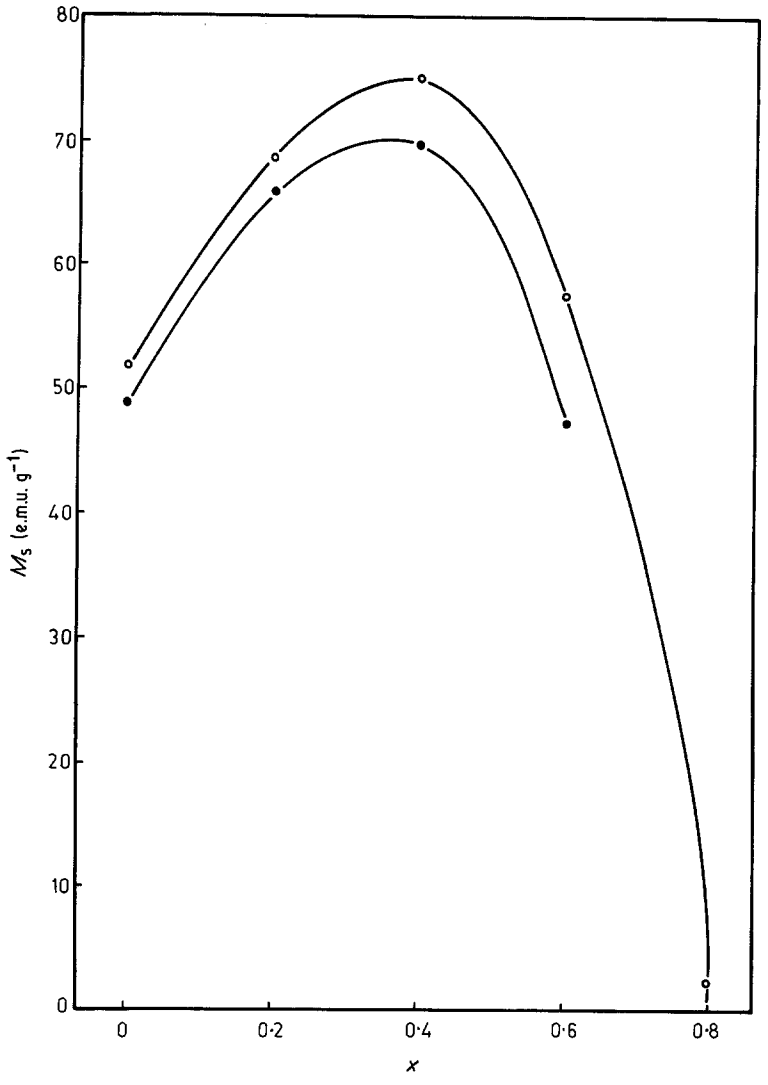

Figure 6 Saturation magnetization (M_s) against content of zinc (x) for (○) $Ni_{1-x}Zn_xFe_2O_4$ and (●) $Ni_{0.8-x}Zn_xCu_{0.2}Fe_2O_4$.

polaron model. He has concluded that at low temperatures the conduction is via thermally activated motion of strongly correlated polarons and at high temperatures via weakly activated hopping motion or a non-activated Brownian-like tunnelling motion of polarons.

The activation energy in the paramagnetic region is found to be more than that for the ferrimagnetic region (Fig. 1). This can be attributed to the effect of magnetic ordering in the conduction process [19]. According to strict theoretical considerations the anomalous changes in the activation energy occur at the disordered temperature.

The compositional variation of resistivity are shown in Figs 4 and 5 for the temperatures 373 and 714 K, respectively. A similar variation is exhibited by these samples at the two temperatures indicated for Ni–Zn ferrites; at first the resistivity decreases with increase in the zinc content. For the sample $Ni_{0.4}Zn_{0.6}Fe_2O_4$ the resistivity shows a slight increase, while it shows a decrease in value for the sample $Ni_{0.2}Zn_{0.8}Fe_2O_4$. For $ZnFe_2O_4$ the value of ϱ shows again an increasing trend. ϱ is found to be a maximum for nickel ferrite and a minimum for $Ni_{0.2}Zn_{0.8}Fe_2O_4$. This trend is repeated at 714 K. For the copper-substituted Ni–Zn ferrite system an almost similar trend can be seen in the compositional variation of resistivity at 373 and 714 K. The resistivity shows two regions. In the first region a decreasing trend with increase in the zinc content up to 40% Zn is revealed, while the resistivity is on the increase beyond 40% content of zinc in the samples.

The compositional variation of resistivity and the compositional variation of M_s (Fig. 6) bear a one-to-one correspondence, indicating the role of magnetic ordering in influencing the resistivity of the ferrite samples. This statement is corroborated by the fact that there is a decrease in T_c with increase in zinc content (Fig. 7). Guillaud [20] and Gorter [21] have given compositional variations of M_s for a series of ferrites. The magnetization behaviour of zinc-containing ferrites has been explained on the basis of a three sub-lattice model by Yafet and Kittel [22]. Recently Srivastava [23] has used a three sub-lattice model to determine exchange constants in spinel ferrites.

The variation of lattice parameter with the content of zinc (Fig. 8) shows that the unit cell dimension goes on increasing with the addition of zinc. The decrease in ϱ can be attributed to the more room available for polaron hopping on the B sites up to 40% content of zinc. Beyond 40% Zn there is a weakening of the A–B interaction leading to the dominant non-magnetic behaviour of the sample. As a result of the phase transition the conduction is also modulated, and this shows an interesting trend with increase of zinc content.

An interesting behaviour is exhibited by Ni–Zn

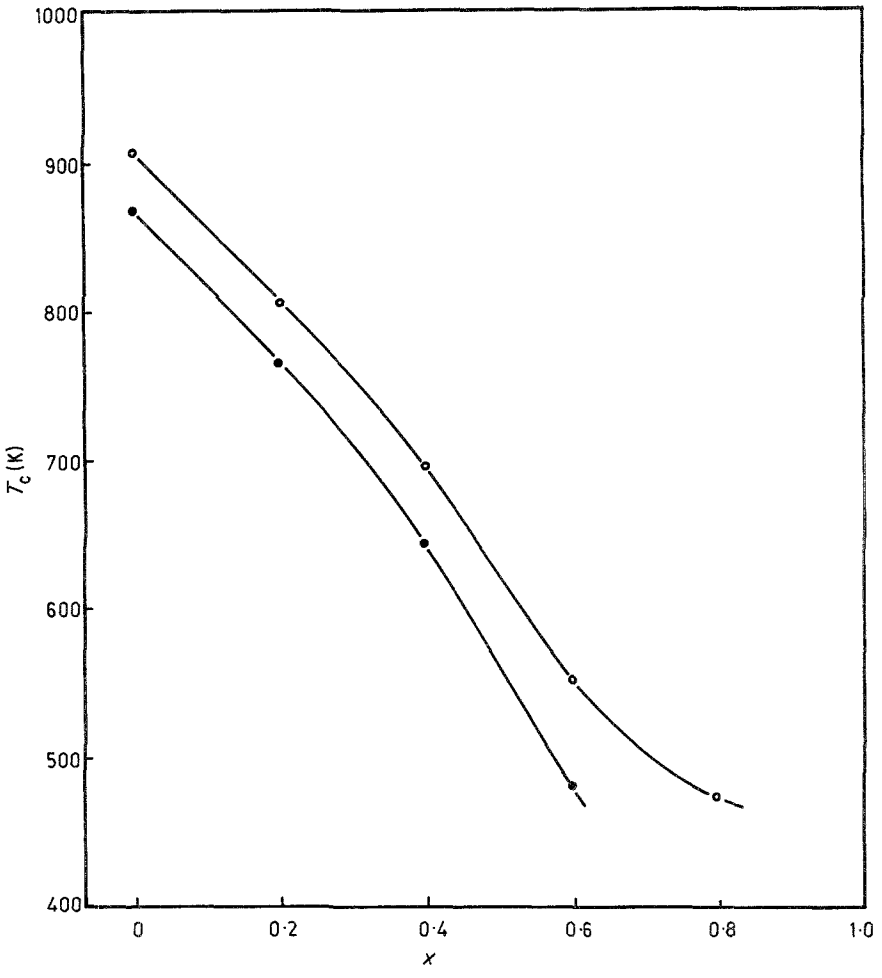

Figure 7 Curie temperature (T_c) against content of zinc (x) for (○) $Ni_{1-x}Zn_xFe_2O_4$ and (●) $Ni_{0.8-x}Zn_xCu_{0.2}Fe_2O_4$.

ferrites with the addition of copper. The peak in the variation of ϱ that is observed for 60% Zn in Ni–Zn ferrite disappears with the addition of copper. Copper is a Jahn–Teller ion. This deviation may be attributed to the effect of the Jahn–Teller ion on the ground states of Fe^{2+} and Ni^{2+} ions in spinel ferrites [24].

The variation of log ϱ with $10^3/T$ has shown more than one break for 40% Zn; however, the samples of Ni–Zn ferrite and Ni–Zn ferrite containing copper with more than 60% Zn show only one break. This can be explained on the magnetic ordering change taking place in the samples due to excessive addition of zinc.

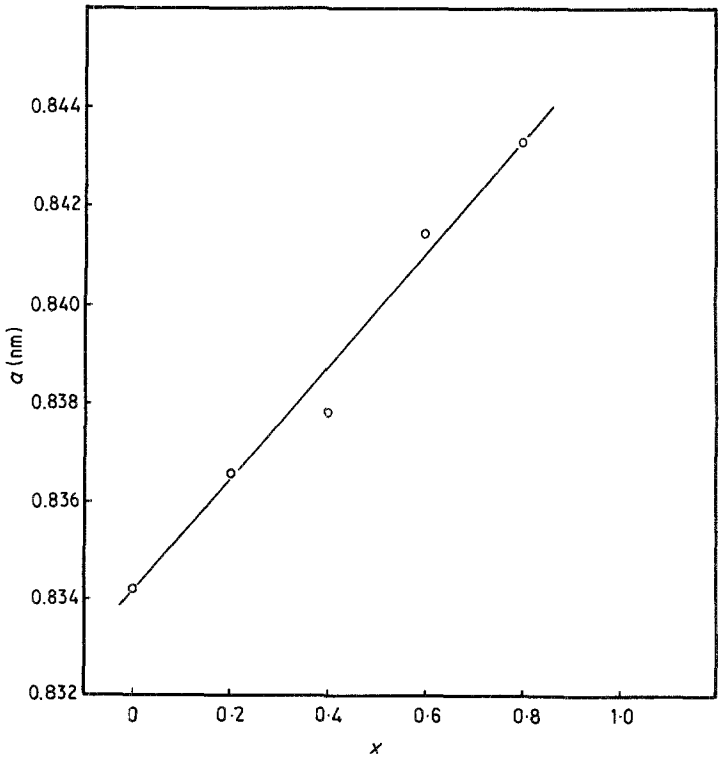

Figure 8 Lattice parameter (a) against content of zinc (x) for $Ni_{0.8-x}Zn_xCu_{0.2}Fe_2O_4$.

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