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Electrical Properties of Cadmium Substitution in Nickel Ferrites

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ABSTRACT

Electrical transport properties such as conductivity (σ) and thermo electric power (S) of Cadmium substituted Nickel Ferrites, forming chemical formula $Ni_{1-x}Cd_xFe_2O_4$, where x = 0.0, 0.2, 0.4 have been investigated from room temperature to well beyond the Curie temperature. Plots of log (σT) versus 10^3/T are linear and show a transition near the Curie temperature. The transition temperature is found to decrease with increase of Cd content. On the basis of Seebeck coefficient (S), the ferrites under investigation have been classified as n-type and p-type semiconductors. The values of charge carrier concentration and mobility have been computed from experimental values of Seebeck coefficient and electrical conductivity. The activation energy in the ferrimagnetic region is in general less than that in the paramagnetic region. An attempt is made to explain the conduction mechanism in these ferrites.

Keywords: Ni-Cd Ferrite; Thermo Electric Power; Seebeck Coefficient; Charge Carrier Concentration; Electrical Conductivity

1. Introduction

The conditions of the preparation play an important role in site preference of the cations and all other properties of the spinal ferrites. The characteristic physical properties from the ability of the cation were distributed among the available tetrahedral A-site and octahedral B-site. The $NiFe_2O_4$ is completely inverse spine, because Ni^{2+} has a strong preference for the electrical conductivity octahedral site (B-site) [1]. Cadmium is the non magnetic divalent ions which occupy essentially tetrahedral A-site [2] when substituted in ferrites.

As far as the authors are aware of the study, the ac electrical conductivity and thermo electric power of the mixed Ni-Cd ferrites play as a function of composition and temperature. Therefore a systematic study of the electrical conductivity and thermo electric power of the mixed Ni-Cd ferrite system from room temperature to well beyond Curie temperature was undertaken. The results of such a study presented in this communication are explained on the basis of the hopping model.

2. Experimental

2.1. Materials Preparation

Specimens of the Ni-Cd ferrites having the compositional

formula $Ni_{1-x}Cd_x Fe_2O_4$ where x = 0.0, 0.2, 0.4 were prepared by solgel method. The samples were presintered for 24 hr in air at 600°C.

2.2. Methods

Electrical conductivity measurements were made by the two probe method [3] from room temperature to well beyond the Curie temperature using a Keithley electrometer model 6517A. The electrical conductivity (σ) of the Ni-Cd ferrites under investigation has been computed using the formula,

$$\sigma = It/VA$$

where I is the current passing through the specimen in amperes, V is the voltage applied to the specimen in volts, t is the thickness of the sample in cm and A denotes the area of the sample in cm^2.

Thermo electric power studies were carried out as a function of composition and temperature by the differential method [4]. The sample holder for measuring the thermo emf consists of 2 pairs of non magnetic copper electrodes between which the sample is firmly fixed to the upper electrode for additional heating to maintain a temperature difference about 10 K between the 2 faces of the sample. A temperature of both surfaces of the sample

was measured by 2 Chromel-Alumel thermo couples.

Thermo electric power (S) was calculated using the relation

$$S = \Delta E / \Delta T$$

where ΔE is the thermo emf produced across the sample due to the temperature difference ΔT.

3. Results and Discussions

3.1. Composition Dependence of Lattice Parameter (a)

X-Ray Diffraction of all the ferrites under investigation has been obtained using Ni K_α radiation. The XRD for Ni-Cd ferrites are given in **Figures 1-3**. The lattice parameters of the mixed ferrites were calculated from d-spacings and are given in **Table 1**. It can be seen from the table that the value of lattice parameter increases with increase of cadmium content. The variation in the lattice parameter with Cd content is presented in **Figure 4** (*i.e.*, lattice parameter versus Cd content). It can be seen from

the figure that the lattice parameter increases with increase in a Cd content.

It may be observed from the figure that the lattice parameter varies linearly with the Cd ion content. A similar linear dependence has also been observed in Ni-Zn [5], Mn-Zn [6], Li-Cd [7], Cd-Co [8] ferrites.

3.2. Composition Dependence of Seebeck Coefficient (S)

The values of the Seebeck coefficient of all mixed Ni-Cd ferrites were calculated from the observed values of the thermo emf and are given in **Table 2**. It can be seen that the sign of the Seebeck coefficient is negative for $x = 0$ and 0.2 compositions of the ferrites under investigation, indicating that the predominant conduction mechanism in these ferrites is of n-type semiconductors. From the observation, it follows that the predominant conduction mechanism in all the Ni-Cd ferrites is hopping of electrons [9] from Fe^{2+} to Fe^{3+} ions.
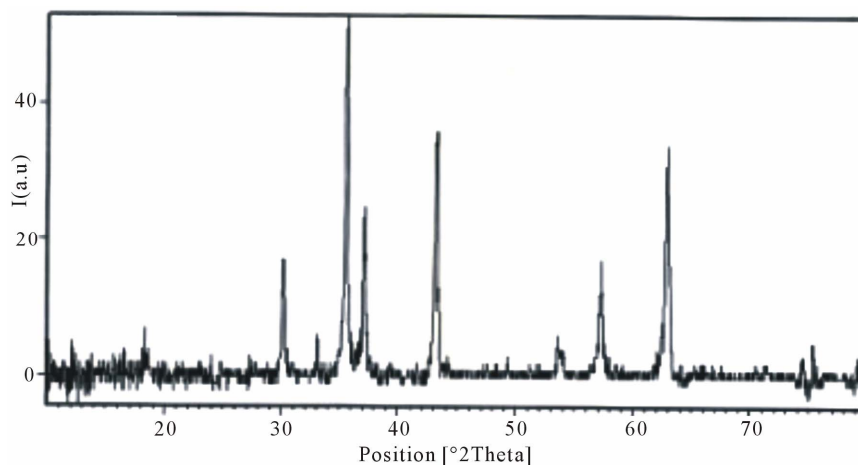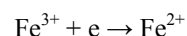
$$Fe^{3+} + e \rightarrow Fe^{2+}$$

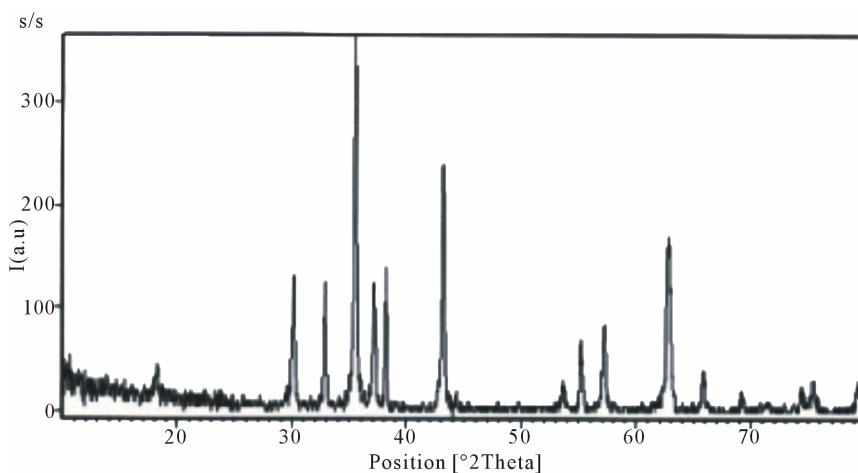**Figure 1. X-ray diffraction pattern for $NiFe_2O_4$ ferrite.**

Figure 2. X-ray diffraction pattern for $Ni_{0.8}Cd_{0.2}Fe_2O_4$ ferrite.

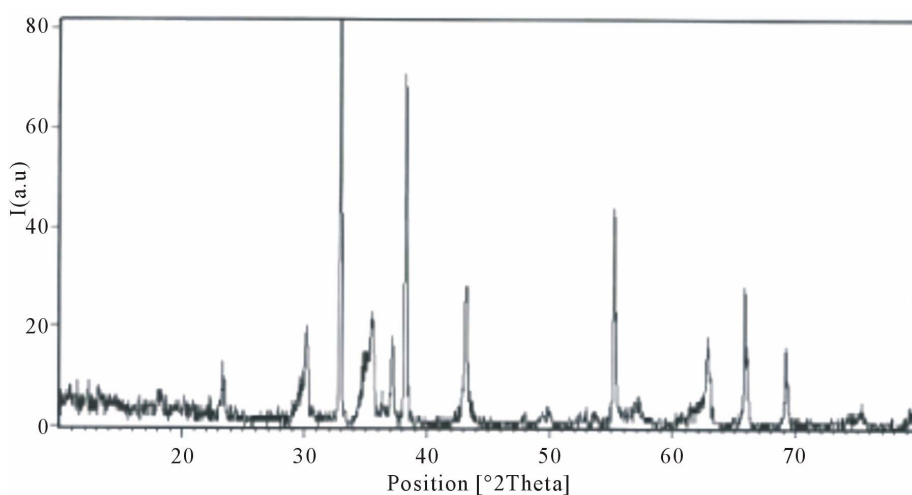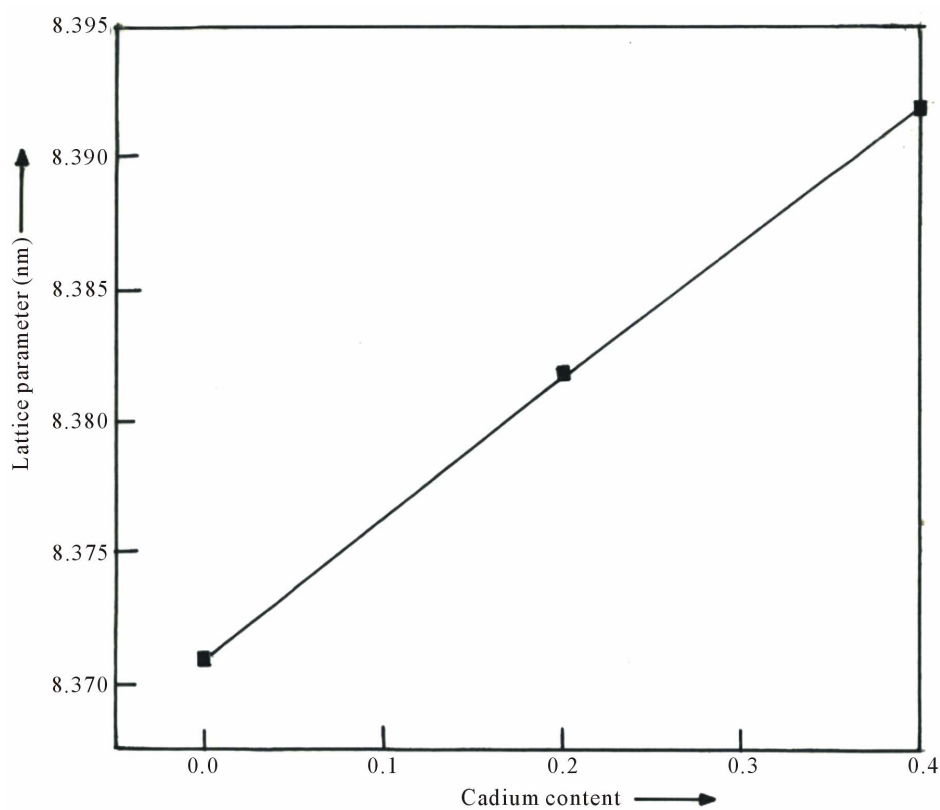**Figure 3. X-ray diffraction pattern for Ni$_{0.6}$Cd$_{0.4}$Fe$_2$O$_4$ ferrite.**

Figure 4. Variation of lattice parameter with cadmium content.

Table 1. Lattice parameter, density, crystalline size and volume data for Ni-Cd ferrites.

s. No	X	a (Å)	Density (gm/cm^3)	Crystalline size (Å)	Volume (V)
1	0.0	8.3709	5.30	5.05	586.5654
2	0.2	8.3837	5.52	4.98	589.2603
3	0.4	9.0185	5.57	4.58	733.5047

And the composition 0.4 for the Seebeck coefficient is positive and its conduction mechanism in these ferrites is of p-type semiconductors and it follows the hopping of holes.

The values of S are found to increase continuously from 0.0 to 0.2 μV/K, with addition of cadmium from 0.0 to 0.4 mol.

The variation of the Seebeck coefficient (S) with temperature is shown in **Figure 5**. It can be seen that the value of Seebeck coefficient increases with increase in temperature up to a certain temperature, which is designnated as the Seebeck coefficient transition temperature $T_s(K)$. However, beyond this temperature, the value of the Seebeck coefficient was found to decrease with increasing temperature. The negative value of the Seebeck coefficient was found over the entire temperature range studied and shows the majority charge carriers are electrons. In the case of positive value of the Seebeck coefficient were explained the majority charge carriers are holes and these results designated in **Figure 6**.

Table 2. Thermoelectric power data for mixed Ni-Cd ferrites.

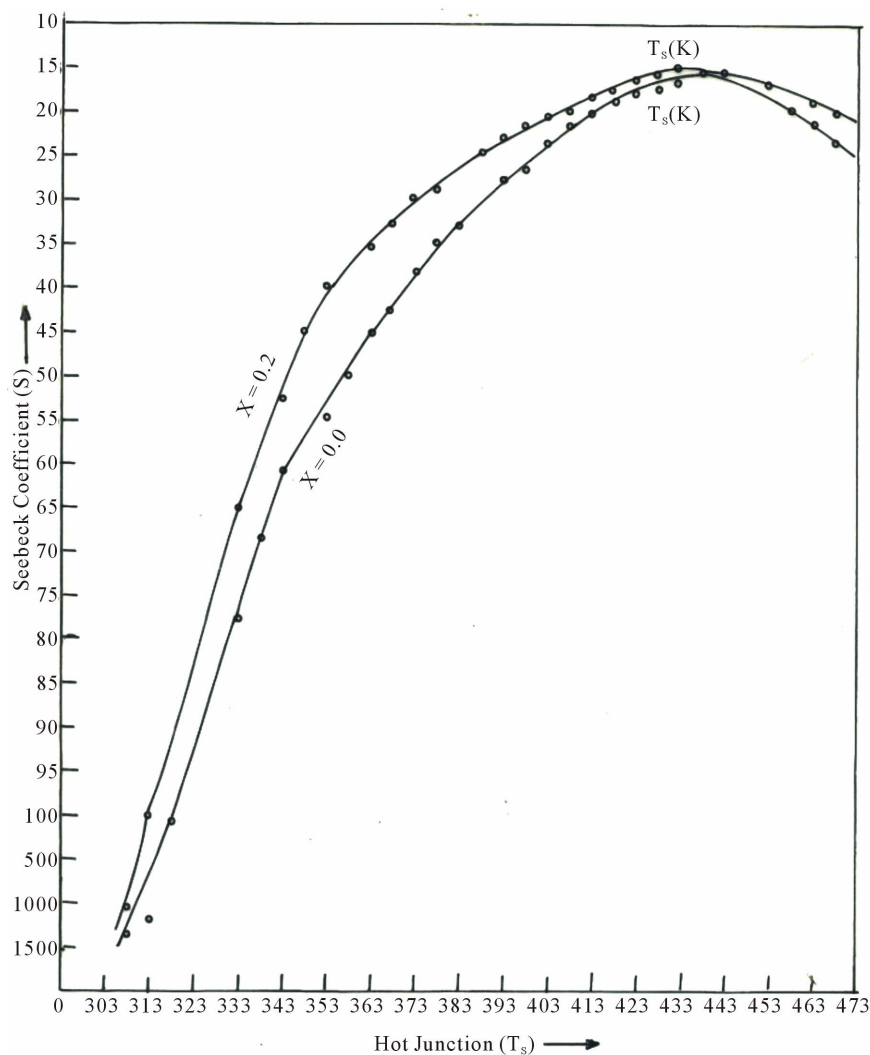| S.no.	Ferrite	Seebeck coefficient S (μV/K)	Type of semi conductor	Seebeck coefficient transition temperature	Curie temperture	$T_n(K)$
1	$NiFe_2O_4$	−1419	n-type	458	438	438
2	$Ni_{0.8}Cd_{0.2}Fe_2O_4$	−850	n-type	453	433	432
3	$Ni_{0.6}Cd_{0.4}Fe_2O_4$	10	p-type	368	373	370

Figure 5. Plot of Seebeck coefficient (S) verses temperature for $Ni_{1−x}Cd_xFe_2O_4$ Ferrites (Where x = 0.0 and 0.2).
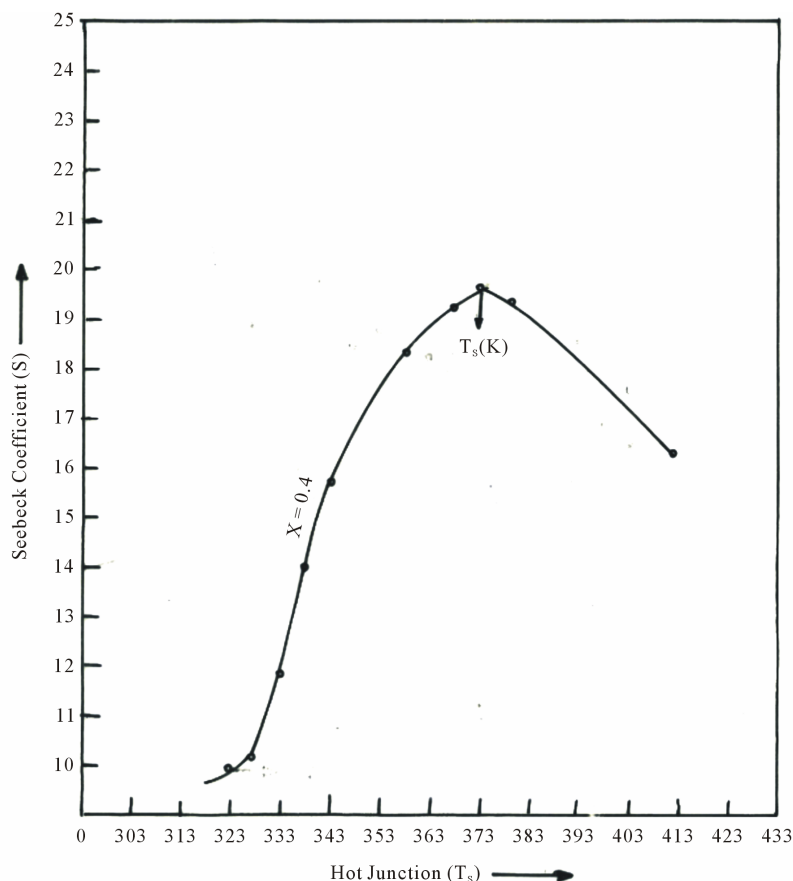
Figure 6. Plot of Seebeck coefficient (S) verses temperature for $Ni_{0.6}Cd_{0.2}Fe_2O_4$.

The values of $T_s(K)$ for each composition are given in **Table 2**. The curie is for the purpose of comparison. It can be seen that the value of $T_s(K)$ and $T_c(K)$ are in good agreement. The transition temperatures obtained in the present investigation in all the mixed Ni-Cd ferrites may be attributed to ferrimagnetic to paramagnetic transitions. A similar result has been reported by Whall *et al*. [10,11] in the case of Manganese and Lithium ferrites.

3.3. Electrical Conductivity (σ)

Table 3 gives the experimental values of electrical conductivity and Seebeck coefficient values at room temperature. The carrier concentration for these ferrites was calculated using the formula given by morin and gebella [12].

$$n = N \exp(-Se/k)$$

where S is seebeck coefficient; e is charge of electron; k is Boltzmann constant; N is density of states or concentration of electronic levels involved in the conduction process.

An examination of **Table 3** reveals that the electrical conductivity of the mixed Ni-Cd ferrites is found to decrease with an increase in cadmium content to 0.4 mol.

This shows that $Ni_{0.6}Cd_{0.4}Fe_2O_4$ poses the highest resistivity among all the compositions investigated from the **Table 3** that the $Ni_{0.6}Cd_{0.4}Fe_2O_4$ composition has the high electrical conductivity correspondingly, the high electrical conductivity for this specimen has a value of 2.6469×10^{-5} $ohm^{-1}cm^{-1}$. This high value can be explained on the basis of the fact that it has a maximal no. of ferrous ions whose exchange $Fe^{2+} \Leftrightarrow Fe^{3+}$ gives rise to a maximal electrical conductivity. **Table 3** reveals that the variation of the electrical conductivity of Cu-Cd ferrites runs parallel to the variation of available ferrous ions on octahedral sites. It is significant to note that $Ni_{1-x}Cd_xFe_2O_4$, has the lowest ferrous ion concentration and possesses the lowest electrical conductivity. It is also pertinent to mention that the variation of electrical conductivity with the composition **Table 3** runs parallel to the variation of the ferrous ions concentration [13]. Thus it is the number of ferrous ions on octahedral sites that place a dominant role in the process of conduction. This result is in agreement with the assumption of Rabankin and Novikova [13]. The temperature dependence of electrical conductivity of mixed Ni-Cd ferrites of different compositions has been investigated from room temperature to well beyond the Curie temperature. **Figures 7-9** gives

Table 3. Electrical conductivity for Ni-Cd ferrites at room temperature.

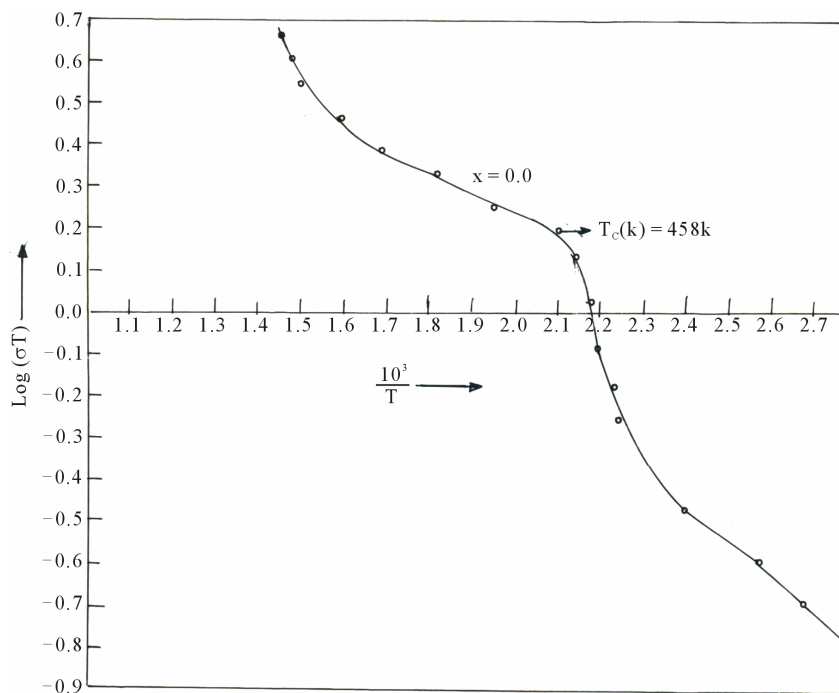| S. No	Ferrite	T_s(K)	Electrical conductivity σ (Ω^{-1} cm^{-1})	Electrical resistivity ρ (Ω cm)
1	$NiFe_2O_4$	458	9.3489×10^{-3}	1.07×10^4
2	$Ni_{0.8}Cd_{0.2}Fe_2O_4$	453	3.7623×10^{-4}	2.66×10^5
3	$Ni_{0.6}Cd_{0.4}Fe_2O_4$	368	2.6469×10^{-4}	3.78×10^5

Figure 7. Plot of Log(σT) versus 10^3/T for $NiFe_2O_4$.
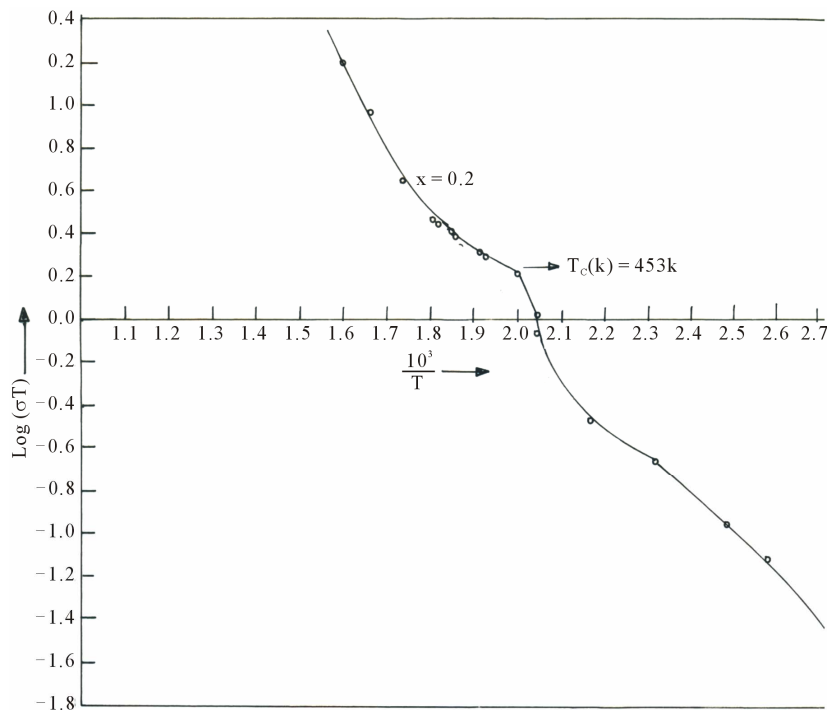
Figure 8. Plot of Log(σT) versus 10^3/T for $Ni_{0.8}Cd_{0.2}Fe_2O_4$.
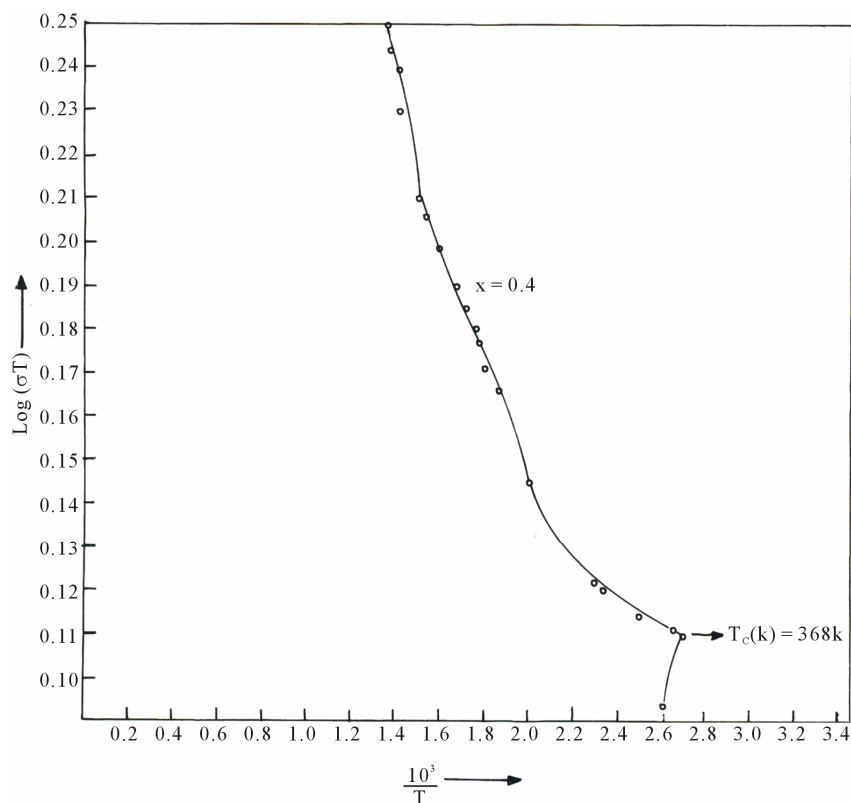
Figure 9. Plot of Log(σT) versus 10^3/T for $Ni_{0.6}Cd_{0.4}Fe_2O_4$.

gives a plot of log(σT) versus 10^3/T. It can be seen that the value of log(σT) increases linearly with increaseing temperature up to a certain temperature T_s(K) at which a change of slope has occurred.

The activation energies in the ferromagnetic and paramagnetic regions are calculated from the slopes of plots of log(σT) versus 10^3/T and presented in **Table 4**. The activation energy in the paramagnetic region is higher than that in the ferromagnetic region.

A high activation energy goes hand in hand with a low conductivity of the ferrites. Similar result was observed by samokhralov and rustmov [14]. The activation energy decreases with increase in cadmium content. The magnitude of the kink as determined by the difference between the activation energies in the paramagnetic and ferromagnetic regions (ΔE) which is given in column (5) of **Table 4**. Column 5 of the **Table 3** gives the values of resistivity for the specimens under investigation. An inspection of these results reveals that (ΔE) decreases as resistivity decreases.

Generally, the change of slope is attributed to change in conductivity mechanism. The conduction at a lower temperature (below curie temperature) is due to hopping of electrons [15] between Fe^{2+} and Fe^{3+} ions, where as at a higher temperature (above curie temperature) due to hopping of polarons [16-18]. The calculated values of activation energy in a paramagnetic region (E_2) are greater than 0.40 eV which clearly suggest that the conduction is due to hopping of polarons.

3.4. charge Carrier Mobility (μ)

The charge carrier mobility (μ) of mixed Ni-Cd ferrites was calculated from the experimental values of electrical conductivity (σ) and charge carrier concentration (n) using the relation.

$$\sigma = ne\mu$$

where e is the exchange of electron.

The calculated values of the mobility are given in **Table 4**. It can be seen that the value of the mobility varies from 4.95×10^{-6} to 1.65×10^{-9} cm^2/VS. Such low values of mobility have been reported by several researches [19-22]. The variation of charge carrier mobility values increases continuously with increasing temperature. The increase in mobility with an increase in temperature suggests that the conduction in these ferrites is due to a hopping mechanism of electrons from Fe^{2+} to Fe^{3+}.

3.5. Temperature Variation of Charge Carrier Concentration (n)

The temperature variation of charge carrier concentration is shown in **Figures 10-12**. It can be seen from the figures that the charge carrier concentration increases

Table 4. Activation energies, Charge carrier concentration and mobility for Ni-Cd ferrites.

S. No	x	Activation énergies (eV)			Carrer concentration (cm)	Mobility cm^2/VS
		FM E_1(eV)	PM E_2(eV)	E(ev)		
1	0.0	0.89	0.91	0.90	11.788×10^{22}	4.9568×10^{-6}
2	0.2	0.63	0.75	0.69	10.997×10^{22}	2.1383×10^{-8}
3	0.4	0.41	0.52	0.46	9.9676×10^{22}	1.6597×10^{-9}
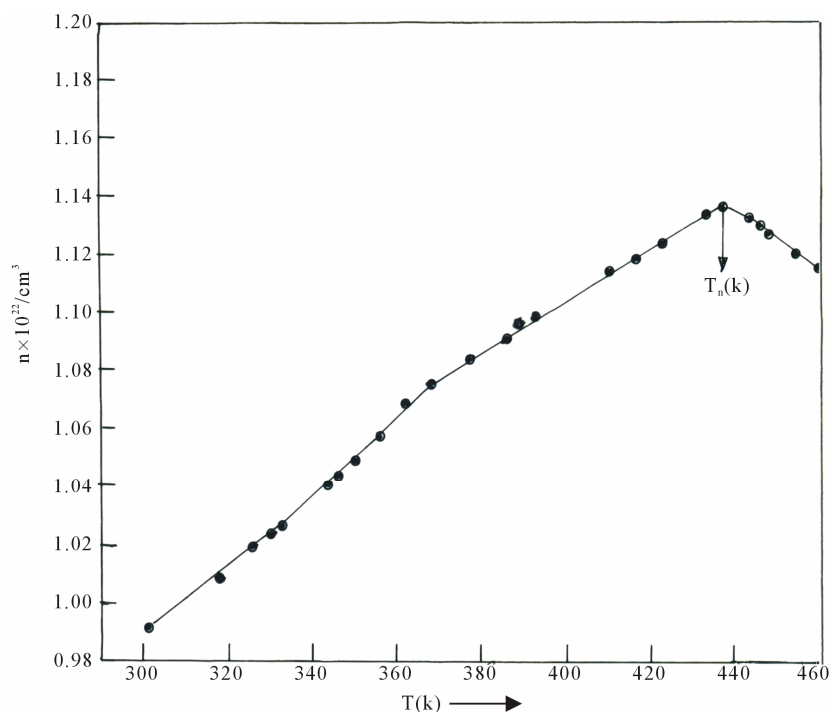
Figure 10. Variation of charge carrier concentration with temperature for Ni$_{0.8}$Cd$_{0.2}$Fe$_2$O$_4$.
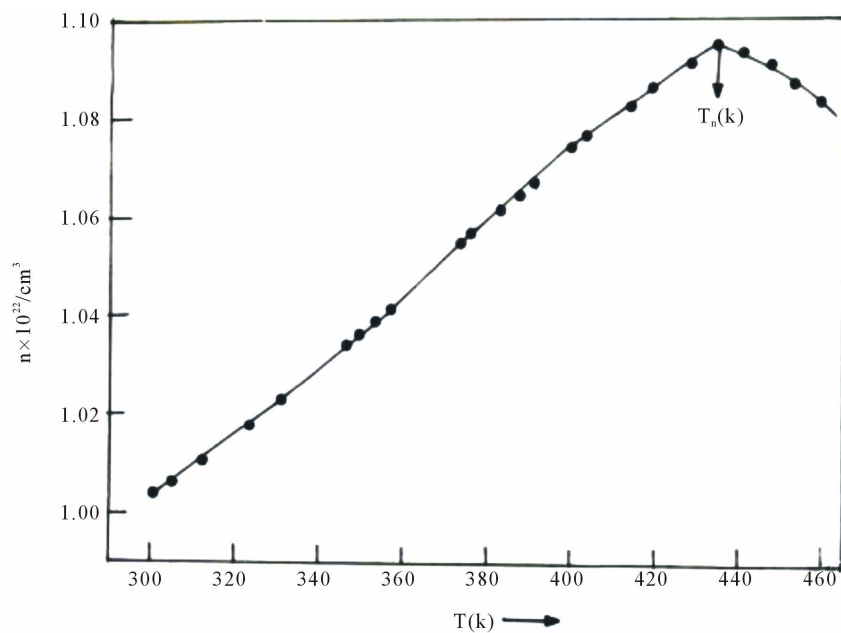

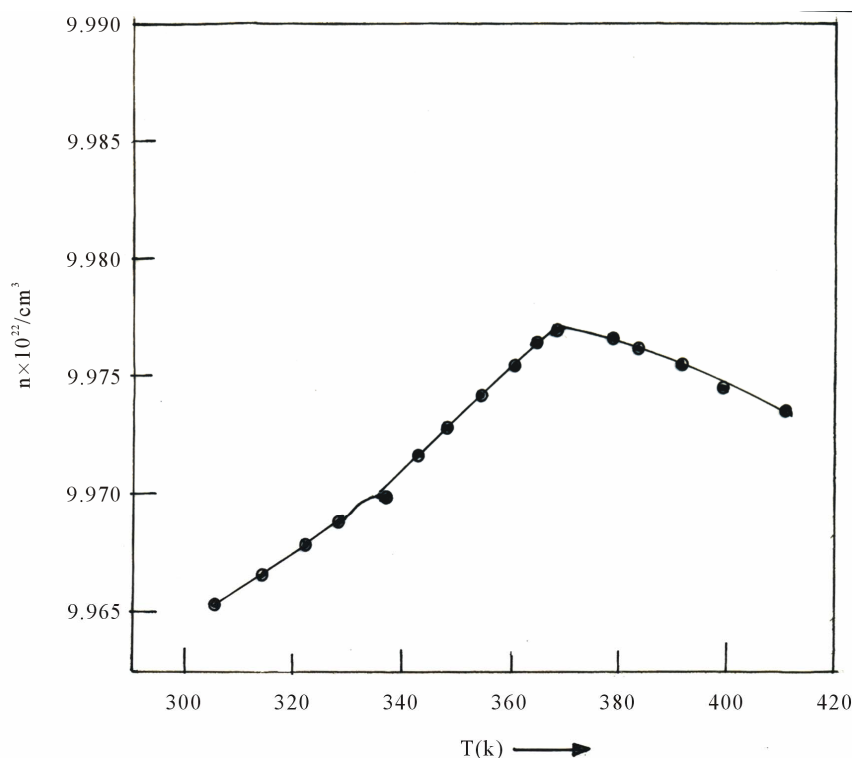Figure 11. Variation of charge carrier concentration with temperature for NiFe$_2$O$_4$.

Figure 12. Variation of charge carrier concentration with temperature for $Ni_{0.6}Cd_{0.4}Fe_2O_4$.

with increase in temperature continuously up to $T_n(K)$. However above this temperature the carrier concentration decreases continuously for all the ferrites. The values of $T_n(K)$ for all the ferrites under investigation are listed and compared with their respective curie temperatures in **Table 2**. It can be seen that values of $T_n(K)$ and $T_c(K)$ are in good agreement. Similar variations of n and T were also observed by Reddy and Mulay *et al*. in the case of Li-Ti [23] and Mg-Al [24] ferrites.

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