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## Physical studies on mixed crystals of $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3\cdot\text{XH}_2\text{O}$

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### ABSTRACT

The temperature dependence of the dc-and ac-electrical conductivity  $\sigma$  dielectric constant  $\epsilon'$ , dielectric loss  $\epsilon''$ , and molar magnetic susceptibility  $\chi_M$  for  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3\cdot\text{XH}_2\text{O}$  ( $x=0.0, 0.57, 1.15, 1.83, 2.40$  and  $3.0$ ) was studied over a temperature range of 78-400K. The electrical conductivity ( $\sigma$ ) was found to increase with increasing the nickel content in the sample. An anomalous behavior in  $\sigma\text{-T}^{-1}$  relation is observed for all samples. At lower temperatures, the conductivity showed semimetallic behavior and the conduction is explained on the basis of an electron hopping near the Fermi level. At low temperatures, the ac-conductivity increases with frequency according to  $\sigma_{ac}=A\omega^s$ , where  $s$  has a value that lies in the range 0.30-0.63, depending on the temperature and the composition of the sample. The temperature dependence of both dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$  showed a maximum at the dissociation temperature of the sample. Magnetic susceptibility  $\chi$  showed antiferromagnetic character for all samples. The results have been correlated and discussed.

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### KEYWORDS

Mixed complex;  
Electrical conductivity;  
Dielectric constant;  
Dielectric loss;  
Magnetic susceptibility

### INTRODUCTION

Organic materials have attracted the attention of many researchers due to their wide applications in physics, biology and medicine<sup>[1,2]</sup>. In the present time many publications have been related the chemical structures of organic compounds to their physical properties<sup>[3-7]</sup>. The importance of these organic materials comes mainly from the point that their preparation in pure form is much easier and cheaper than that of inorganic ones. Moreover, the chemical structure can be easily changed in organic compounds for preparing materials with different chemical composition to be used in different elec-

tronic applications.

Many crystallographic studies were performed on some mixed organic salts<sup>[3,6]</sup>. From these studies it is well known that the metal oxalates  $\text{MC}_2\text{O}_4\cdot\text{XH}_2\text{O}$  ( $\text{M}=\text{Co}, \text{Mn}$  and  $\text{Ni}$ ) are found in isostructural monoclinic system with the space group  $\text{C}_{2c}$ . So due to the deficiency present in the electrical and magnetic data of these mixed metal oxalates, which occur in monoclinic crystal structure, the present work was designed to study the electrical and magnetic properties of  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3\cdot\text{XH}_2\text{O}$  in a temperature range from 78K to temperatures near the decomposition temperatures of the individual compounds.

## EXPERIMENTAL

All chemicals used in this work were of analytical grade. Oxalate samples with a composition of  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3 \cdot \text{XH}_2\text{O}$  ( $x=0.0, 0.57, 1.15, 1.83, 2.40$  and  $3.0$ ) were prepared by the method reported elsewhere<sup>[4]</sup>. The contents of cobalt and nickel in the samples were determined by atomic absorption.

X-ray diffraction patterns of the investigated samples were carried out using X-ray diffractometer, Philips unit type PW 2103 100, with copper target and Ni-filter. All samples  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3 \cdot \text{XH}_2\text{O}$  were found to be crystallized in the monoclinic system, in agreement with the literature<sup>[4]</sup>. An increase in the lattice parameters ( $a_0=1199$ ,  $b_0=540$ ,  $c_0=994$  ppm,  $\beta=127.8^\circ$  for  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and  $a_0=1183$ ,  $b_0=524$ ,  $c_0=973$  ppm,  $\beta=126.9^\circ$  for  $\text{NiC}_2\text{O}_4 \cdot 2.4\text{H}_2\text{O}$ ) with increasing composition parameter  $x$  were observed. This is explained on the basis of increasing the ionic radius of  $\text{Co}^{2+}$  ion in comparison with that of  $\text{Ni}^{2+}$  ion<sup>[8]</sup>.

The electrical measurements ( $\sigma_{dc}$  - and  $\sigma_{ac}$  - conductivity, real part of dielectric constant  $\epsilon'$  and dielectric loss  $\epsilon''$ ) were measured as a function of temperature on pellets (of diameter 7mm and thickness  $\sim 1$ mm) prepared under a pressure of  $\sim 1800$  Kg/cm<sup>2</sup>. The two surfaces of each pellet were coated with silver paint and checked for good conduction. The ac-measurements were carried out using an LCR bridge, model SRS 720 (USA). The frequencies used were in the range of  $10^2$ - $10^6$ Hz. The dc-conductivity was measured using the two probe method by applying 1 volt using stabilized power supply and measuring the current and the voltage applied on the sample by means of an electrometer, Keithley model 610 C and a voltmeter Keithley model 175 A respectively. Seebeck coefficient, ( $\theta_v$ ), measurements were done at temperature intervals of  $\Delta T \sim 40$ K (against platinum).

The I-V characteristics for the investigated samples were measured at room temperature, in the range of  $10^3$ - $10^5$  V/cm. The plot of the data fit the  $\ln I$ - $\ln V$  dependence with slope  $\sim 1$ , i.e. obeying Ohm's law.

The room temperature resistance was measured as a function of time by applying a constant electric field of about  $2 \times 10^5$  V/cm for 3 hours. The resistance was found to be constant with time indicating that the oxalate samples behave essentially as electronic conductors. This is supported by Seebeck voltage measurements, which showed negative values for all inves-

TABLE 1 : Electrical conductivity data for  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3 \cdot \text{XH}_2\text{O}$  samples

Composition	$\sigma_{333}$ $\text{ohm}^{-1}\text{cm}^{-1}$	$T_b$ (K)	$\theta_v$ u V/K	DTA (K)	$\perp$ S
$\text{Ni}(\text{C}_2\text{O}_4)_3 \cdot 2.4\text{H}_2\text{O}$	$6.8 \times 10^{-7}$	250,356	-207	356,endo 603,endo	$0.48 \pm 0.15$
$\text{Co}_{0.57}\text{Ni}_{2.43}(\text{C}_2\text{O}_4)_3 \cdot 2.2\text{H}_2\text{O}$	$6.84 \times 10^{-9}$	250,365	-194	360,endo 610,endo	$0.43 \pm 0.12$
$\text{Co}_{1.15}\text{Ni}_{1.85}(\text{C}_2\text{O}_4)_3 \cdot 2.6\text{H}_2\text{O}$	$1.79 \times 10^{-9}$	250,370	-160	364,endo 600,endo	$0.40 \pm 0.10$
$\text{Co}_{1.83}\text{Ni}_{1.17}(\text{C}_2\text{O}_4)_3 \cdot 2.4\text{H}_2\text{O}$	$1.21 \times 10^{-9}$	200,375	-141	370,endo 615,endo	$0.42 \pm 0.08$
$\text{Co}_{2.40}\text{Ni}_{0.60}(\text{C}_2\text{O}_4)_3 \cdot 2.6\text{H}_2\text{O}$	$9.45 \times 10^{-10}$	200,378	-112	377,endo 590,endo	$0.50 \pm 0.05$
$\text{Co}(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$	$6.79 \times 10^{-10}$	200,385	-90	390,endo 603,endo	$0.40 \pm 0.05$

\*:  $T_b$  are the break temperatures in  $\ln \sigma$  vs.  $1/T$  plots; # :  $\theta_v$  is the Seebeck coefficient;  $\perp$ : s is the frequency exponent of  $\sigma_{ac} = A \omega^s$ .  
tigated samples, TABLE 1.

The magnetic susceptibility was carried out using the conventional Gouy's method, which was modified to measure at lower temperatures, down to liquid nitrogen temperature. Diamagnetic correction was carried out by measuring the magnetic susceptibility  $\chi$  of the isomorphous cadmium oxalate.

Differential thermal analysis (DTA) and thermal gravimetric analysis (TG) for investigated samples were conducted using thermal analyzer, Schimadzu model 30, at a heating rate of 10 K/min. in air. The DTA/TG-thermograms showed similar behavior, in which the decomposition of each sample occurs in two stages. The first one, which is accompanied by an endothermic peak, is attributed to separation of hydrated water. The dissociation temperatures and the number of hydrated molecules for each investigated sample are shown in TABLE 1. There exists higher thermal stability with increasing cobalt content in the sample, i.e. with increasing lattice constant of the sample. In order to investigate the presence of any phase transition at low temperatures the samples were investigated by means of a DSC thermal analyzer, Setaram model 131, at temperatures between 78 and 400K. The thermograms obtained did not show any peaks due to phase transitions at temperatures below the dehydration temperatures of the samples.

## RESULTS AND DISCUSSION

The dc- electrical conductivity ( $\sigma_{dc}$ ) for  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3 \cdot \text{XH}_2\text{O}$  samples was measured over a tem-

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perature range of 78-400K. The conductivity was found to increase with increasing nickel content in the sample. The plots of  $\ln \sigma_{\text{dc}}$  vs.  $T^{-1}$ , Figure 1, showed many breaks depending on the composition of the sample. Because the thermal analysis of the samples did not show any phase transition, therefore the break in  $\sigma_{\text{dc}}-T$  curves at temperatures below the dissociation temperatures should be attributed to either a change in conduction mechanism or due to going from the extrinsic to the intrinsic region. At lower temperatures and before the first break the conductivity is almost temperature independent, i.e. semimetallic behavior predominates, Figure 1. This behavior could be explained on the basis of a hopping model<sup>[9]</sup> by postulating an electron just below the Fermi level hopping to a distant state for which the required energy is as small as possible.

The Seebeck coefficient ( $\theta_v$ ) measurements showed negative values for all samples investigated (TABLE 1). This indicates that the electrons are the main charge carriers in our system. The carrier concentration was estimated using the following equation<sup>[10]</sup>:

$$n = 2(2\pi m^*kT/h^2)^{3/2} \exp(-E/kT) \quad (1)$$

where  $m^*$  is the effective mass of the charge carrier (assumed to be equal to the rest mass of an electron),  $h$  is the Planck's constant,  $k$  is Boltzman's constant and  $E$  is the activation energy of the conduction process.

The calculation showed that  $n$  increases with increasing nickel content in the sample and has a value in the range of  $10^{18}$ - $10^{21}$  at room temperature. The mobility  $\mu$  of charge carriers was also estimated using the equation<sup>[10]</sup>.

$$\sigma = n e \mu \quad (2)$$

where  $e$  is the electronic charge,  $\mu$  showed values on the order of  $10^{-9}$ - $10^{-11} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  at room temperature.

These values are much smaller than  $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  which can be used here as a criterion for applying the hopping model.

Chelation bonds between metal ions and ligand molecules (oxalate and water) allows delocalized electrons to stretch from the ligand molecules to another across d-shell electrons of  $\text{Co}^{2+}$  and/or  $\text{Ni}^{2+}$  ions. The increase in conductivity with increasing the nickel content in the sample (TABLE 1) can be understood on the basis of the decrease occurring in the lattice constant with increasing nickel concentration (as mentioned above). This causes an enhancement in the hopping rate and hence in the conductivity value.

The application of ac-field affects upon the charge

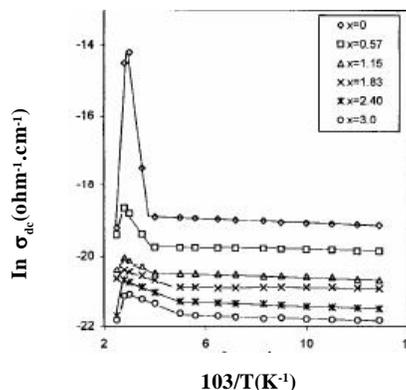


Figure 1: Effect of temperature on the dc- electrical conductivity for  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3\cdot x\text{H}_2\text{O}$ .

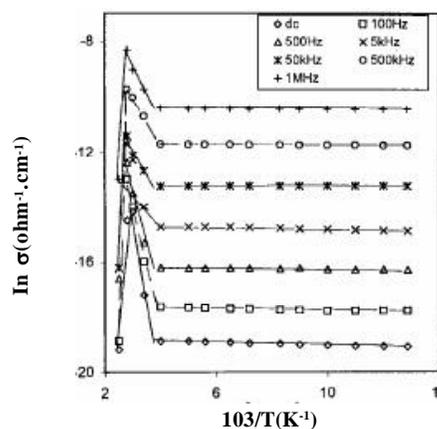


Figure 2: Plots of temperature dependence of conductivity for nickel oxalate at different frequencies

transfer and electric dipoles and hence a change in conductivity may be occurred with the variation of the frequency of applied field. Therefore, the ac-conductivity  $\sigma_{\text{ac}}$ , relative permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$ , for the investigated samples have been studied at temperatures between 78 and 400K and at frequency range of  $10^2$ - $10^6\text{Hz}$ . The ac-conductivity  $\sigma_{\text{ac}}(\omega)$  was calculated by subtracting the measured dc-conductivity  $\sigma_{\text{dc}}$  from the measured total frequency-dependent conductivity  $\sigma_t(\omega)$  such that<sup>[11]</sup>.

$$\sigma_{\text{ac}}(\omega) = \sigma_t(\omega) - \sigma_{\text{dc}}(\omega) \quad (3)$$

The plots of  $\ln \sigma_{\text{ac}}$  vs.  $T^{-1}$  showed similar behavior to the dc-plots; a typical plot is shown in figure 2. At lower temperatures,  $\sigma_{\text{ac}}(\omega)$  was found to be always higher than  $\sigma_{\text{dc}}$ , indicating the presence of barrier effects due to some types of electrical polarization occurring in the sample, such as ionic polarization between the oxygen and metal ion as well as an interfa-

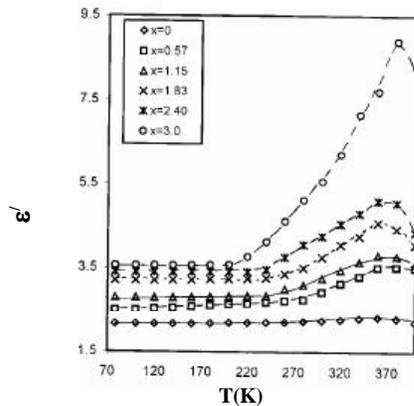


Figure 3: Effect of temperature on the dielectric constant  $\epsilon'$  at 50kHz for  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}$

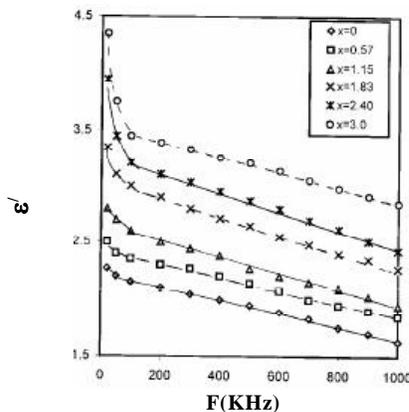


Figure 4: Effect of frequency on the dielectric constant  $\epsilon'$  at 150K for  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}$

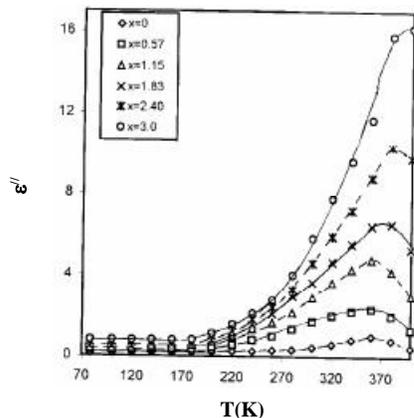


Figure 5: Effect of temperature on the dielectric loss  $\epsilon''$  at 1kHz for  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3 \cdot x\text{H}_2\text{O}$

cial polarization produced at the grain boundaries of the polycrystalline sample. The frequency dependence  $\sigma_{ac}(\omega)$  was found to obey the relation<sup>[12]</sup>.

$$\sigma_{ac}(\omega) = A \omega^s \quad (4)$$

where A is a frequency independent parameter and the exponent s depends on composition and temperature and has a value that lies in the range 0.30-0.63, TABLE1. This behavior of ac-conductivity supports the suggested hopping conduction mechanism in our system<sup>[9]</sup>.

In order to study the polarization in our samples, the temperature and frequency dependence of relative permittivity  $\epsilon'$  are investigated. All samples showed similar behavior; typical plots are shown in Figure (3).  $\epsilon'$  increases with increasing cobalt content in the sample. At  $T < 220\text{K}$ ,  $\epsilon'$  changes slightly with T indicating that the dipoles found in the crystals are frozen and the field applied is not sufficient to align them at such low temperatures. Whereas, at higher temperatures  $\epsilon'$  increases rapidly with T due to that the dipoles increase the rotational degree of freedom and align easily with the field direction. The  $\epsilon'$  values show maxima at temperature which agree well with the decomposition temperature for each one of the investigated samples. This is because when the compound starts to decompose the electric dipoles are going to distribute more randomly in the hydrated and dehydrated crystals causes a decrease in dielectric constant and then the appearance of  $\epsilon'$ -maximum in the vicinity of decomposition temperature.

The isothermal measurements  $\epsilon'$  (at  $T=150\text{K}$ ) as a function of frequency for all investigated samples are shown in figure 4. From the figure it is shown that the dielectric constant values and their dispersion increase with increasing cobalt content in the sample. This could be explained on the basis of the ability of  $\text{Co}^{2+}$  to be more polarized than  $\text{Ni}^{2+}$  in the crystal structure investigated (due to the larger ionic radius of  $\text{Co}^{2+}$  in comparison with  $\text{Ni}^{2+}$ )<sup>[8]</sup>. The decrease of  $\epsilon'$  with frequency, Figure 4, can be explained as due to that by increasing the frequencies, the oriental dipoles will no longer be able to rotate enough rapidly and hence

their cooperation to the polarization as well as the relative permittivity  $\epsilon'$  decrease.

The temperature dependence of dielectric loss  $\epsilon''$  for all investigated samples showed an increase in  $\epsilon''$  (slightly at lower temperatures and highly at higher ones) to reach a maximum value before starting to decrease again; typical plots are given in figure 5. The temperature at which the maximum in  $\epsilon''$  was observed is not changed with the applied frequency and agrees well with the dissociation temperature of the sample. The growth in  $\epsilon''$  with rising the temperature is brought about by an increase in both the conduction of residual and

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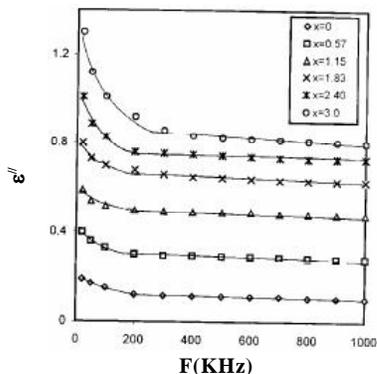


Figure 6: Effect of frequency on the dielectric loss  $\epsilon''$  at 50K or  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3\cdot\text{XH}_2\text{O}$

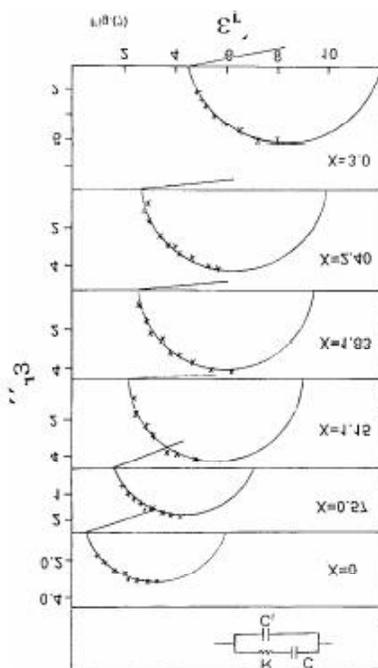


Figure 7: Cole-Cole diagram for the real permittivity  $\epsilon'$  versus imaginary permittivity  $\epsilon''$  of  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3\cdot\text{XH}_2\text{O}$  at 300 K and the equivalent circuit

conduction of the absorption currents. In fact, the rise in temperature causes an increase in the lattice constant and hence produces a decrease in the internal friction of the molecules in the sample. This will cause in turn an increase in the degree of the dipole orientations through unit angle, i.e. an increase in the polarization and the loss factor.

The frequency dependence of  $\epsilon''$ , Figure 6, shows a slight decrease in  $\epsilon''$  value i.e. a decrease in the relaxation time with increasing the frequency. This relaxation may result either from the rotation of the metal oxalate molecules or from the diffusion of metal ions in the crystal

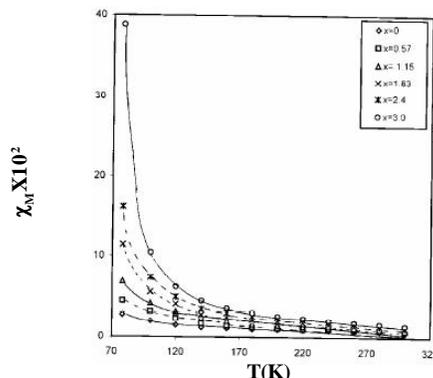


Figure 8: Effect of temperature on the molar magnetic susceptibility  $\chi_M$  for  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3\cdot\text{XH}_2\text{O}$

lattice. The change in  $\epsilon''$ - values with frequency was found to decrease with increasing  $\text{Co}^{2+}$  content in the sample indicating that the diffusion or the rotation of  $\text{Co}^{2+}$  or cobalt oxalate in the crystal is higher than that of  $\text{Ni}^{2+}$  or nickel oxalate molecule. This is expected on the basis of the ionic radius of both ions ( $R_{\text{Ni}}=0.68$  and  $R_{\text{Co}}=0.73 \text{ \AA}$ )<sup>[8]</sup>.

Figure 7 illustrates complex permittivity diagrams as plots of the imaginary part  $\epsilon''$  against the real part  $\epsilon'$  at 300 K for  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3\cdot\text{XH}_2\text{O}$ . The plots show semicircular behavior which becomes progressively more circular in the compounds containing both the nickel and cobalt ions. This implies that the interactions between the dipoles produced from the different elements are not greatly different.

The complex permittivity diagram suggests that the electrode/sample/electrode cells for the system investigated are equivalent to the electronic circuit shown in Figure(7), where the resistance R and capacitance C describe the bulk properties of the sample and  $C_i$  is the capacitance of domain interfaces.

The magnetic susceptibility  $\chi$  for the  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3\cdot\text{XH}_2\text{O}$  samples was measured at a magnetic field strength of 4000 Oe and at temperature ranging from 78K to a temperature just below the decomposition temperature of the investigated sample. This is so because the evolution of water at the dissociation temperature might affect the weight of the sample and hence the magnetic results. The temperature dependence of the corrected molar magnetic susceptibility  $\chi_M$ , Figure 8, shows that in all samples  $\chi_M$  decreases in an exponential manner with increasing the temperature. Replacing the  $\text{Ni}^{2+}$  by  $\text{Co}^{2+}$  causes a change in the magnetic interaction in the investigated system and hence in  $\chi_M$

**TABLE 2 : Magnetic constants of  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3\cdot\text{XH}_2\text{O}$  samples**

Composition	Curie-weiss constant $\theta$ (K)	Curie constant(C)	Eff. mag. moment $\mu_B$
Ni	- 14	1.82	3.82
$(\text{C}_2\text{O}_4)_3\cdot 2.4\text{H}_2\text{O}$			
$\text{Co}_{0.57}\text{Ni}_{2.43}$	- 29	2.11	4.11
$(\text{C}_2\text{O}_4)_3\cdot 2.2\text{H}_2\text{O}$			
$\text{Co}_{1.15}\text{Ni}_{1.85}$	- 44	2.34	4.32
$(\text{C}_2\text{O}_4)_3\cdot 2.6\text{H}_2\text{O}$			
$\text{Co}_{1.83}\text{Ni}_{1.17}$	- 54	2.77	4.71
$(\text{C}_2\text{O}_4)_3\cdot 2.4\text{H}_2\text{O}$			
$\text{Co}_{2.40}\text{Ni}_{0.60}$	- 61	2.91	4.82
$(\text{C}_2\text{O}_4)_3\cdot 2.6\text{H}_2\text{O}$			
$\text{Co}(\text{C}_2\text{O}_4)_3\cdot 2\text{H}_2\text{O}$	- 70	3.14	5.02

values where  $\chi_M$  decreases with increasing  $\text{Co}^{2+}$  contents in the sample. All samples were found to obey the Curie-Weiss law. The magnetic constants were calculated from the plots of  $1/\chi_M$  versus T and are given in TABLE(2). Generally, the negative  $\theta$  values obtained for all samples indicate that the compounds investigated can be considered as antiferromagnetic materials. The effective magnetic moments of  $3.82 \mu_B$  for  $\text{Ni}(\text{C}_2\text{O}_4)_3\cdot 2.4\text{H}_2\text{O}$  and  $5.02 \mu_B$  for  $\text{Co}(\text{C}_2\text{O}_4)_3\cdot 2\text{H}_2\text{O}$  agree well with the reported values for  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions in different symmetries<sup>[13]</sup>.

The X-ray results showed that the cobalt and nickel ions have the same symmetry and environment in the  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3\cdot\text{XH}_2\text{O}$  system (monoclinic structure). Moreover, the lattice constants were found to be decreasing with increasing cobalt content. But the magnetic susceptibility results, TABLE 2, showed an increase in  $\chi_M$  with increasing cobalt concentration. This refers to that the higher magnetic moment of  $\text{Co}^{2+}$  caused an increase in the magnetic interactions between the magnetic ions ( $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ ) more than the decrease in the magnetic interaction produced as a result from increasing lattice constants.

## CONCLUSIONS

1. All samples of the investigated system  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3\cdot\text{XH}_2\text{O}$  possess monoclinic structure. Their lattice constants and thermal stability increase with increasing Co content in the sample.
2. Increasing the nickel content in  $\text{Co}_x\text{Ni}_{3-x}(\text{C}_2\text{O}_4)_3\cdot\text{XH}_2\text{O}$  causes an increase in the electrical conductivity and a decrease in magnetic susceptibility.
3. Electrical conduction occurs by hopping electrons

via metal ions.

4. The conductivity increases with increasing the applied frequency due to the presence of a barrier effect produced from the polarization of the ionic molecules in the sample.
5. The interactions between the electric dipoles produced from both cobalt and nickel ions are not greatly different.
6. A break in each of conductivity, dielectric constant and dielectric loss values was observed at the decomposition temperature of the sample.
7. All samples of the investigated system behave as Antiferromagnetic material at temperatures below the dissociation temperatures and the magnetic susceptibility increases with increasing cobalt content in the sample.

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