

## A study of $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ ( $0 \leq x \leq 1$ ) system

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**Abstract.** A series of solid solutions of composition  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  has been studied. For  $0 < x < 1.1$ , the members crystallize in the cubic spinel structure. Measurements of dc electrical conductivity and Seebeck coefficient show that there is a transition from semiconducting state to semi-metallic state around  $x=0.5-0.6$ . All compositions with  $x > 0.5$  are semimetallic and ferrimagnetic. The results have been rationalised on the basis of the cation distribution  $(\text{Co}^{2+})_t [\text{Ni}_x^{\text{III}}\text{Co}_{2-x}^{\text{III}}]_0 \text{O}_4$  for the solid solutions which permits formation of  $\sigma^*(e_g)$  band through strong covalent interaction between octahedral-site low spin  $\text{Co}^{\text{III}}/\text{Ni}^{\text{III}}$  and oxide ion in the spinel structure.

**Keywords.** Oxide spinels;  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  system; structure and electrical properties.

### 1. Introduction

Recently many cobaltites  $\text{ACo}_2\text{O}_4$  ( $A = \text{Zn}, \text{Ni}, \text{Fe}, \text{Mn}$  and  $\text{Cu}$ ) have been investigated (Miyatani *et al* 1966; Holgerson and Karlson 1929; Kawano and Achieva 1966; Boucher *et al* 1970; Shimada *et al* 1975). Of these  $\text{NiCo}_2\text{O}_4$  is an interesting case showing ferrimagnetism ( $\mu_B = 1.25$ ). To account for the magnetic behaviour, Blasse (1963) suggested that the valence and site distribution of cations in this compound is  $(\text{Co}^{2+})_t [\text{Ni}^{\text{III}}\text{Co}^{\text{III}}]_0 \text{O}_4$  (where the roman superscripts indicate low spin oxidation state and the arabic superscripts high spin state) while Knop *et al* (1968) suggested a distribution  $(\text{Co}^{3+})_t [\text{Ni}^{2+}\text{Co}^{\text{III}}]_0 \text{O}_4$  that accounts equally well for the observed ferrimagnetic moment. The results of neutron diffraction study are not inconsistent with either model. A survey of the literature reveals that no systematic study of electrical transport properties of cobaltite-spinel oxides seem to have been made excepting for reports that  $\text{Co}_3\text{O}_4$  is a *p*-type semiconductor (Rao and Subbarao 1974). It was thought that a study of the electrical behaviour of  $\text{NiCo}_2\text{O}_4$  and  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  ( $0 \leq x \leq 1$ ) system would shed light on the oxidation state and cation-distribution in this system. The present paper reports the results of preparation and studies of crystallographic and electrical behaviour of solid solutions of the system  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  ( $0 \leq x \leq 1$ ).

### 2. Experimental

AnalaR grade hydrated cobalt and nickel nitrates were made use of in the preparation of  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  solid solutions. Compositions corresponding to different values of

$x$  were made by mixing requisite volumes of aqueous solutions (1M) of the nitrates, evaporating them to almost dryness on a water bath and decomposing the dried mass in air at higher temperatures.  $\text{Co}_3\text{O}_4$  was obtained by firing at  $600^\circ\text{C}$  whereas for members containing nickel, a lower temperature ( $300\text{--}350^\circ\text{C}$ ) was employed. Determination of the oxidising power and hence the average oxidation state of the transition metal ion in the samples were carried out by oxidimetric analysis. About 100 mg of the sample is treated with excess  $\text{Fe}^{2+}$  solution in  $4\text{N H}_2\text{SO}_4$ . After dissolution of the sample, the excess  $\text{Fe}^{2+}$  is determined by titration with standard  $\text{K}_2\text{Cr}_2\text{O}_7$ . From the volume of  $\text{Fe}^{2+}$  consumed, the oxidising power and the average oxidation state of the transition metal ions are calculated. The results are given in table 1.

The analytical results (table 1) indicate that in the  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  solid solutions for  $0 \leq x \leq 1$ , two of the three transition metal ions exist in the trivalent state as in  $\text{Co}_3\text{O}_4$ .

The samples were further characterised by x-ray powder diffraction using  $\text{CoK}\alpha$  radiation. Electrical conductivity and Seebeck coefficient measurements on sintered cylindrical pellets were made by the methods described elsewhere (Palanisamy 1974).

### 3. Results and discussion

X-ray diffraction data of the  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  solid solutions (table 1) clearly indicate that monophasic spinel type products are formed up to  $x=1.0$ . For values of  $x \geq 1.1$ , apart from the diffraction lines characteristic of the spinel structure, additional lines,

Table 1. Crystallographic and analytical data of  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  samples.

$x$	$a_0, \text{\AA}$	Average oxidation state of T.M. ion
0.00	8.080	2.66
0.10	8.083	2.70
0.25	8.087	2.69
0.40	8.093	2.68
0.50	8.099	2.67
0.60	8.106	2.70
0.75	8.114	2.66
0.90	8.116	2.68
1.00	8.119	2.70

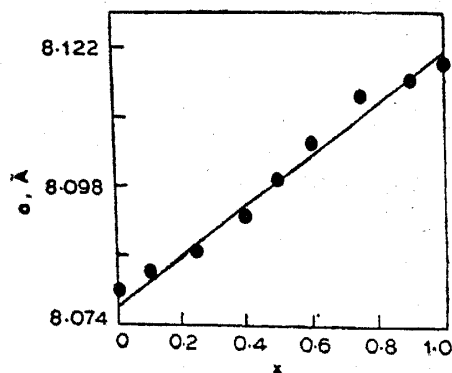


Figure 1. Variation of lattice parameter in  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  system.

mostly of NiO, appear in the x-ray pattern, indicating that monophasic spinel solid solutions can be obtained for the system  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  only in the composition range  $0 \leq x \leq 1.0$ . The variation of unit cell parameters refined by Nelson-Riely plots, as a function of composition  $x$ , is given in figure 1. The unit cell parameters of  $\text{Co}_3\text{O}_4$  (8.08 Å) and  $\text{NiCo}_2\text{O}_4$  (8.119 Å) obtained in this work compare well with those reported in the literature (Knop *et al* 1968). The variation of unit cell parameters across the series  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  is almost linear following Vegard's law in the region  $0 \leq x \leq 1$  (figure 1).  $\text{Co}_3\text{O}_4$ , a normal spinel has the cation distribution  $(\text{Co}^{2+})_t [\text{Co}^{\text{III}}\text{Co}^{\text{III}}]_0 \text{O}_4$ . Assuming that the substitution of nickel takes place in the octahedral site as low spin  $\text{Ni}^{\text{III}}$ , one can write the cation-distribution for  $\text{NiCo}_2\text{O}_4$  as  $(\text{Co}^{2+})_t [\text{Ni}^{\text{III}}\text{Co}^{\text{III}}] \text{O}_4$  as suggested by Blasse (1963). The fact that  $\text{NiCo}_2\text{O}_4$  crystallizes in a slightly larger unit cell than  $\text{Co}_3\text{O}_4$  is understandable in terms of the larger ionic radius of low spin  $\text{Ni}^{\text{III}}$  (0.56 Å) as compared to low spin  $\text{Co}^{\text{III}}$  (0.525 Å) in the octahedral oxygen coordination. The general cation distribution for the solid solution series may then be written as  $(\text{Co}^{2+})_t [\text{Ni}_x^{\text{III}}\text{Co}_{2-x}^{\text{III}}]_0 \text{O}_4$ . The alternative distribution suggested by Knop *et al* (1968),  $(\text{Co}^{3+})_t [\text{Ni}^{2+}\text{Co}^{\text{III}}]_0 \text{O}_4$  is not consistent with the electrical properties as seen below.

### 3.1. Electrical behaviour of $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ system

The variations of room temperature electrical resistivity and Seebeck coefficient with composition  $x$  in  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  are given in figures 2 and 3.  $\text{Co}_3\text{O}_4$  is a *p*-type semiconductor ( $\rho \sim 10^4$  ohm cm) with a large positive Seebeck coefficient (+600  $\mu\text{V}/^\circ\text{K}$ ). Substitution of nickel up to  $x \sim 0.5$  brings about a drastic decrease of both the resistivity and Seebeck coefficient. In the composition range  $0.5 < x < 1.0$ , there is no significant variation, the values remaining almost constant around  $\rho \sim 10$  ohm cm and  $\alpha \sim 30 \mu\text{V}/^\circ\text{K}$ . These values of resistivity were obtained by two-probe measurements. For compositions with  $x > 0.5$  showing low resistivity,

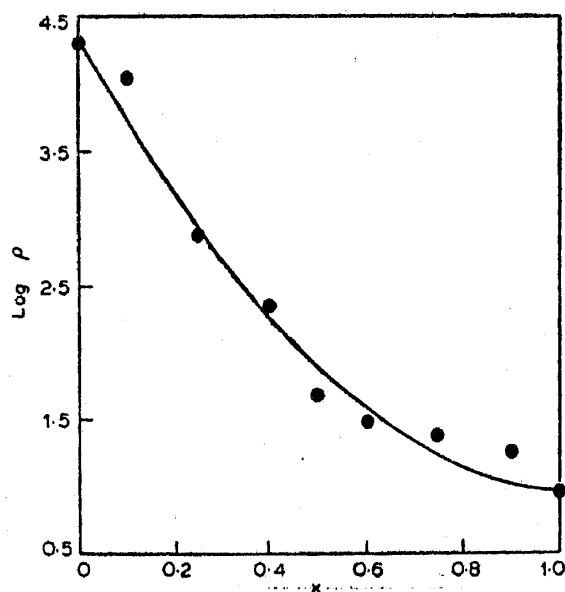


Figure 2. Room temperature resistivity in  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  system.

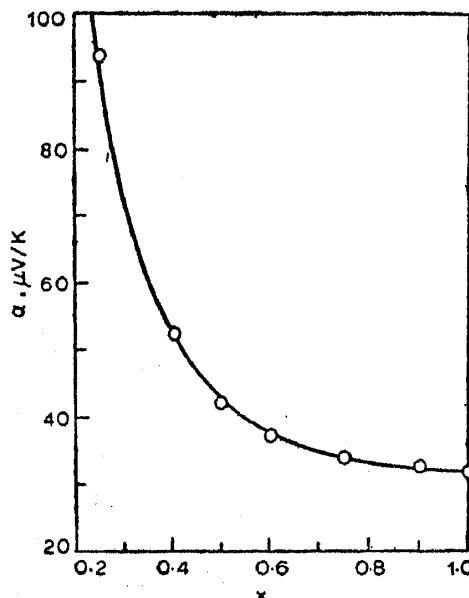


Figure 3. Variation of Seebeck coefficient at room temperature.

measurements by four-probe technique have been carried out. The results show that for these samples the resistivity is much lower ( $\sim 0.2$  ohm cm) and its variation with temperature from 30–100°C is almost constant indicating semi-metallic nature.

For samples with  $x \leq 0.5$ , the variation of electrical resistivity with temperature in the range 30–400°C is shown in figure 4. Activation energies for conduction obtained from these plots of  $\log \rho$  vs  $1/T$  are given in figure 5. The data show that the activation energy steadily decreases with  $x$  and disappears almost completely between  $x=0.5$  and 0.6.

The electrical transport behaviour of  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  is very similar to that of  $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$  (Rao *et al* 1975; Gopalakrishnan *et al* 1976) wherein a semiconductor-to-metal transition is observed. Recently a large number of such extrinsic semiconductor systems showing a transition to metallic or semimetallic-state has been discussed (Mott 1972; Rao *et al* 1975; Rao and Om Prakash 1977). The transition to semi-metallic nature in  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  system for  $x > 0.5$  is understandable in terms of the cation distribution suggested by Blasse (1963) for  $\text{NiCo}_2\text{O}_4$ ;  $(\text{Co}^{2+})_t[\text{Ni}^{\text{III}}\text{Co}^{\text{III}}]_0\text{O}_4$ . The solid solutions would then have the distribution  $(\text{Co}^{2+})_t[\text{Ni}_x^{\text{III}}\text{Co}_{2-x}^{\text{III}}]_0\text{O}_4$ . Goodenough (1965, 1969) has discussed the electrical transport properties of spinels in terms of qualitative one-electron energy band schemes. It has been suggested that the electrical behaviour in oxide spinels result mainly from the octahedral *B*-site cations and interactions thereof. In the spinel structure the *B*-site octahedra share their edges so that both direct *B-B* interaction as well as  $90^\circ\text{B-O-B}$  interaction are important in deciding the electronic behaviour. For  $\text{Co}_3\text{O}_4$ , Goodenough (1965) has suggested that a  $\sigma^*(e_g)$  band is formed by strong covalent *B-O-B* type interaction between the octahedral site low-spin  $\text{Co}^{\text{III}}$  ions to account for its anti-ferromagnetic

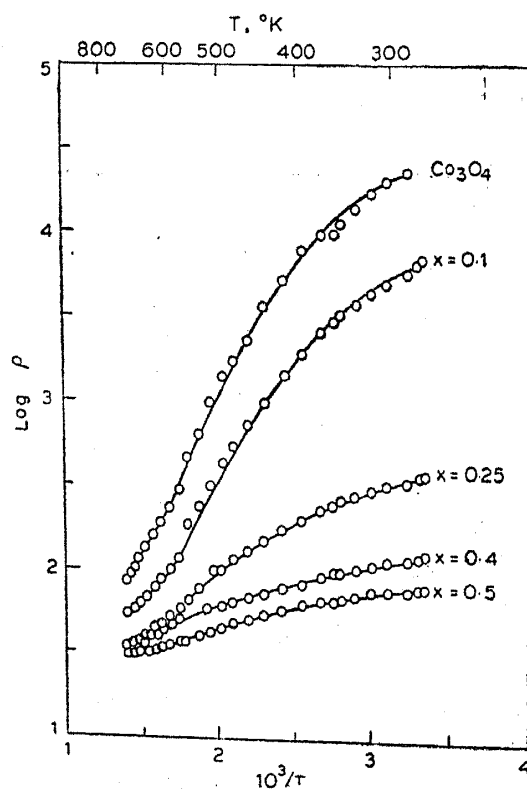


Figure 4. Electrical resistivity in  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  system.

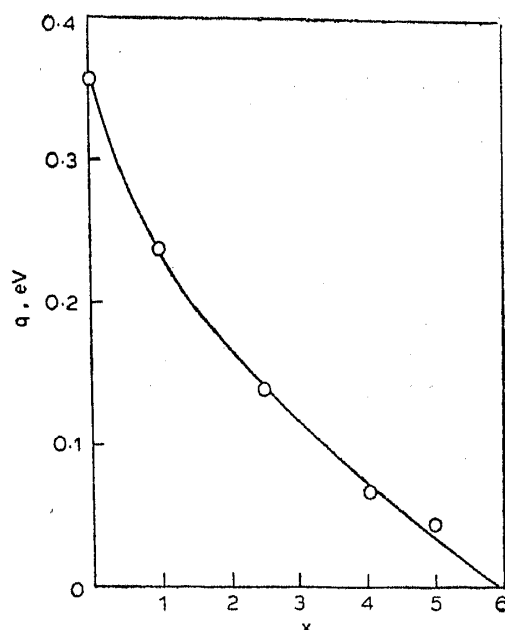


Figure 5. Activation energy for resistivity in  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  system.

nature ( $T_N=40^\circ\text{K}$ ). However  $\text{Co}_3\text{O}_4$  is only a semiconductor because the  $\sigma^*$  ( $e_g$ ) band is empty ( $\text{Co}^{\text{III}}$  has the electronic configuration  $t_{2g}^6 e_g^0$ ). In  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  system, if the nickel ions substitute for  $\text{Co}^{\text{III}}$  in the octahedral site as low spin  $\text{Ni}^{\text{III}}$  ( $t_{2g}^6 e_g^1$ ) then it would result in placing charge carriers in the  $\sigma^*(e_g)$  band. However, for small values of  $x$ , and at low temperatures (below about  $450^\circ\text{K}$ ) the samples of  $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$  system show still only semiconducting behaviour, perhaps because the charge carriers are 'Anderson-localised' (Mott 1972), since the donor centres ( $\text{Ni}^{\text{III}}$ ) would be randomly distributed. Plots of  $\ln \rho$  vs  $T^{-1/4}$  for samples with  $x < 0.5$  show approximately linear behaviour below  $\sim 450^\circ\text{K}$ .

Qualitative magnetic measurements have shown that the samples become ferrimagnetic for values  $x > 0.5$ .  $\text{NiCo}_2\text{O}_4$  has already been reported to be ferrimagnetic with magnetization  $1.25 \mu_B$ . Further work on the magnetic behaviour of this system is in progress.

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### References

- Blasse G 1963 *Philips Res. Rep.* **18** 383
- Boucher B, Bull R, di Bella R and Perrin M 1970 *J. Phys.* **31** 113
- Goodenough J B 1965 Colloques Internationaux du CNRS No. 157, *Propriétés Thermodynamiques Physiques et structurales des Dérivés, Semi-métalliques*, Orsay (Paris: CNRS ed 1967) p. 263

- Goodenough J B 1969 *J. Phys. Chem. Solids* **30** 261  
Gopalakrishnan J, Colsmann G and Reuter B 1976 *Z. anorg. allg. Chem.* **424** 155  
Holgerson S and Karlson A 1929 *Z. anorg. allg. Chem.* **183** 384  
Kawano S and Achieva N 1976 *Mat. Res. Bull.* **11** 911  
Knop O, Reid K I G, Sutarno and Nakagawa Y 1968 *Can. J. Chem.* **46** 3463  
Miyatani K, Kohn K, Kamimura H and Iida S 1966 *J. Phys. Soc. Jpn.* **21** 464  
Mott N F 1972 *Adv. Phys.* **21** 785  
Palanisamy T 1974 *Solid State aspects of some ternary oxides of vanadium* Ph. D. thesis Indian Institute of Technology, Madras.  
Rao C N R, Bhide V G and Mott N F 1975 *Phil. Mag.* **32** 1277  
Rao C N R and Om Parkash 1977 *Phil. Mag.* **35** 1111  
Rao C N R, Om Prakash and Ganguly P 1975 *J. Solid State Chem.* **15** 186  
Rao C N R and Subbarao G V 1974 *Transition metal oxides* (Washington: NBS US Dept. of Commerce).  
Shimada M, Kanamaru F and Kolzumi M 1975 *Mat. Res. Bull.* **10** 733