

Magnetic properties of $\text{Ni}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4$ ($0 \leq x \leq 1$) compounds

B L DUBEY, N NATH, B N TIWARI and A TRIPATHI

Department of Chemistry, Gorakhpur University, Gorakhpur 273 001, India

MS received 27 July 1982

Abstract. The compounds $\text{Ni}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4$ ($0 \leq x \leq 1$) have been synthesised by solid-state reaction between basic nickel(II) carbonate, basic copper(II) carbonate and chromium (III) carbonate in required molar ratios at $800 \pm 10^\circ\text{C}$ for 20 hr. The reaction products have been characterized by chemical analyses and powder x-ray diffraction patterns. Magnetic susceptibility has been measured in the temperature range of 300–900 K at 10 kOe. All the products show ferrimagnetic behaviour with the ferrimagnetic Curie temperature (T_c) in the range of 50–150 K. The curie temperature increases when copper(II) ion is substituted for nickel(II) ion in NiCr_2O_4 . The experimental values of the average effective magneton number (\bar{g}) agree with theoretical values.

Keywords. Nickel(II) chromite; copper(II) doped nickel(II) chromite; solid state reaction; powder x-ray diffraction; magnetic susceptibility; magneton number.

1. Introduction

Ferroelectric, semiconducting and magnetic properties of mixed oxides of transition metals are interesting and these oxides have considerable technological applications in ceramic technology, porcelain and earthenwares, ceramic colours, special electrical engineering and other materials. The mixed-metal oxides are also interesting for the electronic industries with respect to electrical and magnetic properties of these compounds (Taylor 1971; Katz 1959; Methfessel and Mattis 1968; Rastogi *et al* 1978a; Budnikov and Ginstling 1968; Alper 1971; Rastogi *et al* 1979; Dubey *et al* 1978a, b; Tiwari 1979). The chromites of copper(II) and nickel(II) have been reported to be efficient catalysts in many reactions of technological importance (Rastogi *et al* 1980; Dubey *et al* 1982; Pechance 1977; Stiles 1976; Rastogi *et al* 1978b; Jacobs and Whitehead 1969; Inami *et al* 1968; Pearson 1970). As regards their magnetic behaviours, there exist different opinions (Walter *et al* 1967; Banerjee *et al* 1975; Fricon and Perrin 1973; Tachiro Tsushima 1963; Prince 1961). The present authors have earlier reported that $\text{Ni}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4$ ($0 \leq x \leq 1$) compounds act as potential burning rate catalyst for ammonium perchlorate (AP) + PS (polystyrene) composite solid propellant (Dubey *et al* (in press)). Since there is a correlation between catalytic activity and magnetic nature of the catalysts, the magnetic properties of $\text{Ni}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4$ ($0 \leq x \leq 1$) compounds are studied in this paper.

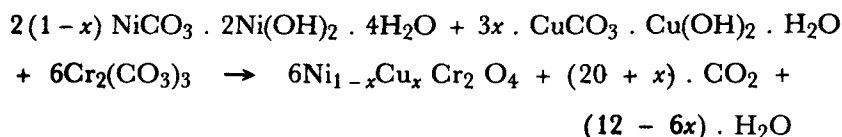
2. Materials

Basic nickel(II) carbonate, $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (LR, BDH, England); Basic copper(II) carbonate, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ (LR, BDH, England); chromium (III) carbonate, $\text{Cr}_2(\text{CO}_3)_3$, USSR.

3. Experimental Techniques

3.1 Method of preparation

$\text{Ni}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4$ ($x = 0, 0.2, 0.5, 0.8$ and 1) was prepared by the solid-state reaction between basic nickel(II) carbonate, copper(II) carbonate and chromium(III) carbonate.



The homogeneous reaction was prepared by mixing carbonates of basic nickel(II), basic copper(II) and chromium(III) in 4:0:12 ($x = 0$), 3.2:1.2:12 ($x = 0.2$), 2.3:12 ($x = 0.5$), 0.8:4.8:12 ($x = 0.8$) and 0.6:12 ($x = 1$) molar ratios respectively and mixing thoroughly with acetone (AR) in an agate mortar. The dried reaction mixtures were taken in platinum crucibles and heated in a furnace maintained at $800 \pm 10^\circ\text{C}$ for 1 hr. The calcined products were cooled, crushed with acetone two to three times and reheated at $800 \pm 10^\circ\text{C}$ for 19 hr.

3.2 Chemical analysis

The metals nickel, copper and chromium present in the sample, $\text{Ni}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4$, were estimated quantitatively by the standard method (Vogel 1964).

The sample was fused with sodium peroxide two to three times on strong flame and extracted with distilled water and filtered. The residue contained Ni(II) and Cu(II) as their oxides. The aqueous extract contained Cr(VI) as Na_2CrO_4 . The residue was leached with dilute hydrochloric acid from which Ni(II) was estimated as nickel dimethylglyoximate. Cu(II) was converted into Cu(I) by reducing with a saturated solution of sulphurous acid and precipitated as CuCNS by adding NH_4CNS solution to the acidic medium.

Cr(VI) was estimated volumetrically by titrating against standard ferrous ammonium sulphate using potassium ferricyanide as external indicator. The sodium chromate present in the extract was therefore converted to sodium dichromate by acidification with dilute sulphuric acid. The results tabulated in table 1 show the overall error in quantitative chemical analyses to be 0.5 to 1.5%.

Table 1. Chemical analysis data for $\text{Ni}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4$ ($0 \leq x \leq 1$) system.

Sample	Percent metals					
	Nickel		Copper		Chromium	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
NiCr_2O_4	25.9	25.7	-	-	45.9	45.6
$\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Cr}_2\text{O}_4$	20.6	20.5	5.6	5.5	45.7	45.2
$\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{O}_4$	12.8	12.6	13.9	13.7	45.4	44.7
$\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Cr}_2\text{O}_4$	5.1	5.0	22.1	21.7	45.1	44.4
CuCr_2O_4	-	-	27.4	26.9	44.9	44.3

3.3 Powder patterns

The powder x-ray diffraction patterns of $Ni_{1-x}Cu_xCr_2O_4$ were taken with a vertical Guinier Camera using $CuK\alpha$ radiation at IIT, Kanpur and results given in tables 2 and 3.

3.4 Magnetic susceptibility measurements

The magnetic susceptibility of the powdered samples was measured employing Faraday's method (Rastogi *et al* 1979). Ferrous ammonium sulphate has been used as a standard salt. The glass correction for the sample container has also been taken into account. Overall error was 2% around 300 K and 5% above 600 K. The results are given in table 4.

4. Results and discussion

The compounds have been analysed quantitatively and stoichiometry established to be $Ni_{1-x}Cu_xCr_2O_4$ ($x = 0, 0.2, 0.5, 0.8, 1$). The x-ray data indicated the formation of a single phase $Ni_{1-x}Cu_xCr_2O_4$, since the diffraction lines corresponding to basic nickel carbonate, basic copper carbonate, chromium carbonate, nickel oxide, copper oxide and chromium oxide are absent. The patterns have been indexed by Hesse-Lipson's method and accuracy checked by de Wolff criteria. Agreement between observed and calculated $\text{Sin}^2 \theta_{hkl}$ values (table 2) is satisfactory. Figure of merit for $Ni_{1-x}Cu_xCr_2O_4$ showed that indexing is correct. The lattice parameters (table 3) of the system have been refined by the least square method. All the systems are tetragonal.

The molar magnetic susceptibility (χ_m) of $Ni_{1-x}Cu_xCr_2O_4$ powdered samples was measured at 300–900 K at 10 kOe using Faraday's method (Rastogi *et al* 1979). χ_m values were practically the same in heating and cooling cycles. The plot of χ_m^{-1}

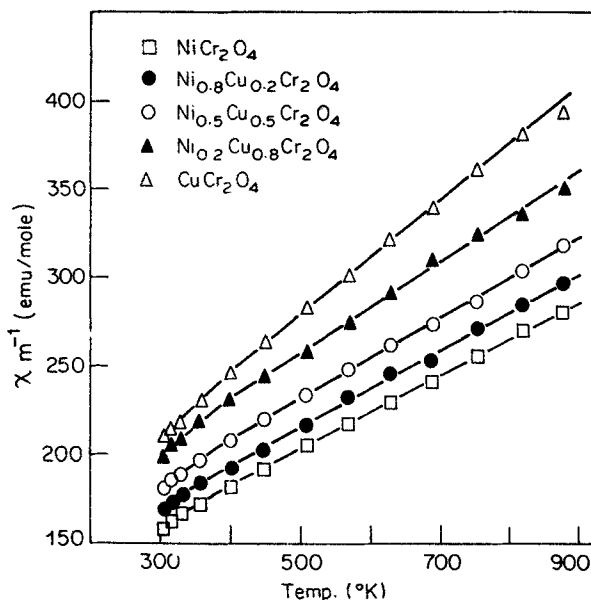


Figure 1. Variation of inverse molar magnetic susceptibility with temperature.

vs T (K) (figure 1) is linear above 400 K but show a downward trend at lower temperatures and are similar to the standard curves for ferrimagnetic materials. The deviation from linearity at lower temperatures indicate the onset of short range ordering just above the ferrimagnetic Curie temperature (T_c).

Table 2. Powder x-ray diffraction data for $\text{Ni}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4$ ($0 \leq x \leq 1$) system.

Sin ² θ				Sin ² θ			
Obs.	Cal	<i>hkl</i>	<i>I/I</i> ₀	Obs.	Cal	<i>hkl</i>	<i>I/I</i> ₀
<i>x</i> = 0*				<i>x</i> = 0			
0.0256	0.0250	110	20	0.0250	0.0250	110	18
0.0692	0.0723	211	30	0.0696	0.0723	211	36
0.0904	0.0892	202	100	0.0865	0.0882	003	10
0.1385	0.1382	203	35	0.0904	0.0892	202	100
0.2047	0.2017	322	15	0.1017	0.1017	212	10
0.2248	0.2500	420	60	0.1355	0.1348	311	20
0.2730	0.2713	511	80	0.2019	0.2017	322	10
0.3455	0.3450	225	10	0.2298	0.2500	420	26
0.3723	0.3723	521	25	0.2715	0.2713	511	40
0.4115	0.4098	441	10	0.3723	0.3723	521	8
0.5087	0.5075	515	25	-	-	-	-
<i>x</i> = 0.2				<i>x</i> = 0.5			
0.0256	0.0220	110	18	0.0256	0.0263	101	16
0.0447	0.0440	200	12	0.0657	0.0660	200	24
0.0691	0.0648	211	45	0.0705	0.722	112	40
0.0831	0.0832	202	21	0.0914	0.0923	211	100
0.0934	0.0942	212	100	0.1007	0.0992	222	51
0.0970	0.0978	221	62	0.1320	0.1320	220	22
0.1022	0.1002	103	18	0.1489	0.1485	300	8
0.1343	0.1322	203	21	0.2033	0.2042	312	13
0.2033	0.2008	204	12	0.2233	0.2228	204	30
0.2118	0.2118	214	19	0.2523	0.2532	313	11
0.2269	0.2298	421	27	0.2637	0.2640	400	19
0.2313	0.2312	323	15	0.2808	0.2805	410	35
0.2684	0.2670	115	16	0.3689	0.3692	422	13
0.2777	0.2752	413	36	-	-	-	-

Table 2. (Continued)

Obs.	Sin ² θ			Obs.	Sin ² θ		
	Cal	hkl	I/I ₀		Cal	hkl	I/I ₀
$x = 0.8$				$x = 1.0^*$			
0.0261	0.0260	101	9	0.0256	0.0261	101	15
0.0661	0.0656	200	20	0.0653	0.0652	200	25
0.0719	0.0720	102	34	0.0723	0.0718	112	35
0.0919	0.0918	211	100	0.0914	0.0913	211	100
0.1044	0.1046	103	54	0.1039	0.1044	202	60
0.1320	0.1312	220	22	0.1308	0.1304	220	25
0.1565	0.1568	004	8	0.1565	0.1565	301	10
0.2026	0.2032	312	11	0.2019	0.2022	312	15
0.2233	0.2230	204	36	0.2233	0.2219	320	40
0.2350	0.2358	303	10	0.2861	0.2869	411	40
0.2622	0.2624	400	25	0.3757	0.3754	225	15
0.2887	0.2886	411	37	-	-	-	-
0.3672	0.3672	422	15	-	-	-	-
$x = 1.0$				$x = 1.0$			
0.0261	0.0261	101	12	0.2024	0.2022	312	15
0.0655	0.0653	200	22	0.2118	0.2119	320	35
0.0727	0.0718	112	35	0.2871	0.2869	411	38
0.0914	0.0913	211	100	0.3757	0.3754	225	15
0.1049	0.1044	202	56	-	-	-	-
0.1320	0.1304	220	20	-	-	-	-
-	-	-	-	-	-	-	-

* Taken from ASTM data.

Table 3. Lattice parameter for $Ni_{1-x}Cu_xCr_2O_4$ ($0 \leq x \leq 1$) system

	a (Å°)	C (Å°)	C/a
$x = 0$	7.61	7.78	1.02
$x = 0.2$	7.35	7.78	1.058
$x = 0.5$	6.001	7.78	1.296
$x = 0.8$	6.019	7.78	1.292
$x = 1$	6.04	7.78	1.289

Table 4. Magnetic parameters of $\text{Ni}_{1-x}\text{Cu}_x\text{Cr}_2\text{O}_4$ ($0 \leq x \leq 1$) system.

Parameters	Compounds				
	NiCr_2O_4	$\text{Ni}_{0.8}\text{Cu}_{0.2}\text{Cr}_2\text{O}_4$	$\text{Ni}_{0.5}\text{Cu}_{0.5}\text{Cr}_2\text{O}_4$	$\text{Ni}_{0.2}\text{Cu}_{0.8}\text{Cr}_2\text{O}_4$	CuCr_2O_4
Magnetic ions	$\text{Ni}^{2+}, \text{Cr}^{3+}$	$\text{Ni}^{2+}, \text{Cu}^{2+}, \text{Cr}^{3+}$	$\text{Ni}^{2+}, \text{Cu}^{2+}, \text{Cr}^{3+}$	$\text{Ni}^{2+}, \text{Cu}^{2+}, \text{Cr}^{3+}$	$\text{Cu}^{2+}, \text{Cr}^{3+}$
T_c (K)	50	75	100	125	150
θ (K)	45	70	95	120	145
θ_p (K)	-471	-464	-481	-467	-331
θ_b (K)	51	52	54	54	49
C (m^3/mole)	4.77	4.44	4.23	3.75	2.93
$\bar{\rho}_{\text{obs}}$ (μB)	3.57	3.44	3.36	3.16	2.80
$\bar{\rho}_{\text{cal}}$ (μB)	3.56	3.51	3.44	3.36	3.31
χ_{m}^{-1} (obs)	181.7	192.30	208.2	230.8	247.6
χ_{m}^{-1} (cal)	181.06	192.75	206.02	228.38	246.27

$$\rho \text{Ni}^{2+} = 2.83 \mu\text{B}, \quad \rho \text{Cu}^{2+} = 1.73 \mu\text{B}, \quad \rho \text{Cr}^{3+} = 3.87 \mu\text{B}$$

For a wide range of temperatures the data for χ_m for the systems can be expressed by the following standard equation (Goodenough 1966).

$$\frac{1}{\chi_m} = \frac{T - \theta_p}{C} - \frac{\theta_b^2}{C(T - \theta)} \quad (1)$$

where C is the Curie constant of the material, θ_p is the paramagnetic (asymptotic) Curie temperature and θ and θ_b are the parametric temperatures calculated from the curves (figure 1) given in table 4. The ordering temperature T_c , has been obtained at $T = T_c$, $\chi_m^{-1} = 0$. It is evident from table 4 that T_c values increase when copper(II) ions are substituted for nickel(II) ions in $NiCr_2O_4$. These materials have three magnetic ions namely Ni(II), Cu(II) and Cr(III) and therefore at least six types of magnetic interactions (Cu-Cu, Cu-Ni, Cu-Cr, Ni-Ni, Ni-Cr and Cr-Cr) are possible. Their relative magnitude is not clear at this stage. However, chromium(III) ions probably go into ordered state at T_c . Since T_c in all cases is well below room temperature, magnetic exchange interaction energy is smaller than the thermal energy at room temperature. At temperature, $T \gg T_c$, the magnetic susceptibility of each ion will follow the Curie Weiss law and the molar magnetic susceptibility of these compounds can be approximated by the relation,

$$\chi_m = \frac{N \mu_B^2}{3K} \left[\frac{(1-x)p_1^2}{T - \theta_{p_1}} + \frac{x p_2^2}{T - \theta_{p_2}} + \frac{2 p_3^2}{T - \theta_{p_3}} \right] \quad (2)$$

where N is the Avogadro number, p_1 , p_2 and p_3 are the magneton numbers for Ni(II), Cu(II) and Cr(III) ions respectively. θ_{p_1} , θ_{p_2} and θ_{p_3} are paramagnetic Curie temperatures which take into account the various interactions involving Ni(II), Cu(II) and Cr(III) ions respectively. At higher temperatures cooperative magnetism gives a single θ_p , therefore, (2) can be written as,

$$\chi_m = \frac{N \mu_B^2}{3K(T - \theta_p)} \left[(1-x)p_1^2 + x p_2^2 + 2p_3^2 \right] \quad (3)$$

$$\text{or } \chi_m^{-1} = \frac{3K(T - \theta_p)}{3N \mu_B^2 \bar{p}^2} \quad (4)$$

$$\text{where } \bar{p}^2 = \frac{(1-x)p_1^2 + x p_2^2 + 2p_3^2}{3} \quad (5)$$

Equation (4) shows that at $T > T_c$, the variation of χ_m^{-1} vs T will be a straight line. Thus, equation (1) at $T \gg T_c$ can be approximated to,

$$\chi_m^{-1} \approx \frac{T - \theta_p}{C} \quad (6)$$

Experimentally, it is observed that the variation of χ_m^{-1} with T is linear and expressed by (6) whereas theoretically it should be given by (4). Comparing these two equations we get,

$$\bar{p}^2 = \frac{K_c}{N \mu_B^2} \quad (7)$$

The \bar{p} values for different materials using experimental values of C have been calculated using (7). Since p_1 , p_2 , p_3 and x are known for the materials under investigation the theoretical p values have been obtained using (5) (table 4). It is seen that there is good agreement between theoretical and experimental \bar{p} values for nickel(II) chromite. However, the experimentally derived p values are less than the theoretical values for copper(II) doped nickel(II) chromites. The reason for this discrepancy may be that when copper(II) is substituted for Ni(II) in NiCr_2O_4 , the covalency between Cr-O linkage increases as has been observed by previous workers (Tripathi and Lal 1982; Koehler and Wollan 1957), that p_{eff} for Cr(III) decreases in the case of some rare-earth orthochromites (RCrO_3). Tripathi and Lal (1982) have reported that out of three electrons only two, on an average, are localized at Cr(III) ions in LaCrO_3 . The remaining electron takes part in the covalent bonding of Cr-O linkage.

From the magnetic data of Curie-Weiss law at low temperatures the compounds are ferrimagnetic below 400 K and become Curie-Weiss paramagnetic above this temperature. It is not possible to calculate the precise value of T_c because an adequate number of data points close to the Curie temperature is not given. However, under some approximation the values of T_c have been obtained by curve fitting. Here, it is worthwhile to point out that there are different opinions about the magnetic nature of chromites. The copper (II) chromite, prepared under different conditions, has been reported to be ferromagnetic (Walter *et al* 1967), ferrimagnetic (Banerjee *et al* 1975; Fricon and Perrin 1973) as well as paramagnetic (Banerjee *et al* 1975). Similarly nickel (II) chromite prepared at 1100–1300°C has been reported (Tachiro Tsushima 1963; Prince 1961) to be weakly ferromagnetic below a Curie temperature of 60–65 K and paramagnetic susceptibility above this temperature is said to be due to Cr(III) ions in high spin state.

Acknowledgements

The authors are grateful to Prof. R P Rastogi, for facilities. Thanks are due to Prof. C Chakravarty, and to Dr H B Lal for technical assistance.

References

- Alper A M 1971 *High temperature oxides Part IV* (New York: Academic Press) p. 11
- Banerjee A K, Dutta D, Naidu S R, Ganguli N C and Sen S P 1975 *Fertil. Technol.* **12** 299
- Budnikov P P and Ginstling A M 1968 *Principles of solid state chemistry, Reactions in solids* (London: Maclaren) p. 391
- Dubey B L, Lakshmi Das I and Tiwari B N 1978a *Indian J. Pure. Appl. Phys.* **16** 590
- Dubey B L, Lakshmi Das I and Tiwari B N 1978b *Indian J. Pure. Appl. Phys.* **16** 1066
- Dubey B L, Singh Gurdip and Sinukla C S 1982 *Fuel* **61** 129

- Dubey B L, Nath N, Shukla C S and Tripathi A 1983 *Indian J. Technol.* (in press)
- Fricon B and Perrin M 1973 (CEN Saclay, Gif-Sur-Yvette, Fr) *Tr. Mezhdunar Konf. Magn.* (Pub 1974) 5 241
- Goodenough J B 1966 *Magnetism and chemical bonds* (New York: John Wiley) p. 75
- Inami S H, Rosser Jr W A and Wise H 1968 *Combust. Flame.* 12 41
- Jacobs P W M and Whitehead H M 1969 *Chem. Rev.* 69 551
- Katz H W 1959 *Solid state magnetic and dielectric devices* (New York: Wiley)
- Koehler W C and Wollan E O 1957 *J. Phys. Chem. Solids* 2 100
- Methfessel S and Mattis D S 1968 *Encyclopedia of Physics* Vol 18/1 (ed) S Flugge (Berlin: Springer Verlag)
- Pearson G S 1970 *Combust. Flame.* 14 73
- Pechance V 1977 *Chem. Abstr.* 86 108796
- Prince E 1961 *J. Appl. Phys. Suppl.* 32 68
- Rastogi R P, Dubey B L and Das I 1978a *J. Sci. Indian Res.* 37 122
- Rastogi R P, Singh G and Singh R R 1978b *Combust. Flame* 33 305
- Rastogi R P, Dubey B L, Lakshmi Das I, Singh U and Tiwari B N 1979 *J. Am. Ceram. Soc.* 62
- Rastogi R P, Singh G, Dubey B L and Shukla C S 1980 *J. Catal.* 65 25
- Stiles A B 1976 *Chem. Abstr.* 84 112319
- Tachiro T 1963 *J. Phys. Soc. Jpn.* 18 1162
- Taylor K N R 1971 *Adv. Phys.* 20 551
- Tiwari B N 1979 *Studies on solid state chemistry of mixed metal oxides containing transition elements* Ph.D Thesis, Gorakhpur University, Gorakhpur
- Tripathi A K and Lal H B 1982 *Indian J. Pure. Appl. Phys.* 20 271
- Vogel A I 1964 *Quantitative Inorganic Analysis* 9 (ELBS)
- Walter H P, Schulz I and Scheve J 1967 (Devt. Akad. Wiss Berlin) *Z. Anorg. Allg. Chem.* 352 241-245