

## Structural, magnetic and electrical study of $\text{CoMnAlO}_4$

S G JOSHI, D K KULKARNI and P V KHANDEKAR

Department of Physics, Institute of Science, Nagpur 440 001, India

MS received 2 July 1981 ; revised 22 September 1981

**Abstract.** A spinel  $\text{CoMnAlO}_4$  has been synthesised by the oxide method. It has a tetragonal structure with  $A=8.10$  Å and  $C=8.22$  Å. A break is found in the plot of  $\log \rho$  against  $1/T$  at  $573^\circ\text{K}$  when activation energy changes from  $0.62$  eV to  $0.52$  eV. The electrical properties show that it can be regarded as a properly substituted  $\text{CoMn}_2\text{O}_4$  by  $\text{Al}^{+3}$  ions. It is paramagnetic with  $C_M = 4.72$  and  $\theta_a = -298^\circ\text{K}$ . These results show the ionic configuration of the compound as  $\text{Co}^{+2}[\text{Mn}^{+3}\text{Al}^{+3}]\text{O}_4$ .

**Keywords.** Spinel; magnetic susceptibility ; electrical resistivity ; ionic configuration.

### 1. Introduction

A survey of literature on the spinels shows that in cobalt-manganites with chemical formula  $\text{CoMnMeO}_4$  where Me represents divalent ions  $\text{Cu}^{+2}$  (Kulkarni and Mande 1970),  $\text{Ni}^{+2}$  (Devale 1980), and  $\text{Zn}^{+2}$  (Kulkarni 1970), the combination  $(\text{Co}^{+2} + \text{Mn}^{+4})$  is more stable than the  $(\text{Co}^{+3} + \text{Mn}^{+3})$  combination. On the other hand in  $\text{CoMnMeO}_4$ , for trivalent Me ions  $\text{Cr}^{+3}$  (Kulkarni 1970),  $\text{Fe}^{+3}$  (Kulkarni 1970),  $\text{Ga}^{+3}$  (Bhalerao *et al* 1974) and  $\text{Mn}^{+3}$  (Boucher *et al* 1968), the combination  $(\text{Co}^{+3} + \text{Mn}^{+2})$  is favoured in the first three compounds giving rise to cubic symmetry. However, in a tetragonal  $\text{CoMn}_2\text{O}_4$ , the combination  $(\text{Co}^{+2} + \text{Mn}^{+3})$  is found to be more stable. In all the cases of ternary cobalt manganites with cations of transition metal (Fe, Cr, etc.), several valence structures are possible due to their variable oxidation states. Therefore, to check the configurational stability of  $(\text{Co}^{+2} + \text{Mn}^{+3})$  or  $(\text{Co}^{+3} + \text{Mn}^{+2})$ , we have prepared  $\text{CoMnAlO}_4$  as aluminium exists only in trivalent state. Balakirev *et al* (1978) studied spinel type solid solutions in systems like Mg-Mn-Al-O, Co-Mn-Al-O, etc. However, the present compound has not been studied in detail so far.

### 2. Experimental

#### 2.1 Preparation and identification

The compound was prepared by the oxide method (Economos 1955) by intimately mixing under acetone, the AR grade oxides  $\text{Al}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{CoO}$  in the molar ratio

1:1:2. The oxide  $Mn_2O_3$  was not easily available and was prepared by the method described by Durrant and Durrant (1964). The heat treatment of the compound was the same as described by Deshpande *et al* (1974). The x-ray diffractometer patterns were taken on a Phillips diffractometer at a speed of  $2^\circ/\text{min}$  using filtered  $MoK\alpha$  radiation. The diffractograms of the compound did not show the peaks due to reacting oxides and all the peaks indicated a single phase of spinel structure.

## 2.2 Magnetic susceptibility

Magnetic susceptibility was measured by Faraday's method in the temperature range  $80^\circ\text{K}$  (liquid  $N_2$ ) to room temperature using a cryostat similar to that of Figgis and Nyholm (1959) with a few modifications.  $HgCo(CNS)_4$  was used as a calibrant. The diamagnetic corrections for the tube and wire assembly were also taken into account, as only a few milligrams of the sample were used.

## 2.3 Electrical resistivity

To measure electrical resistivity, a thin layer of colloidal graphite was applied on the pellets so as to have a good electrical contact. Measurements were made in the temperature range  $373^\circ\text{K}$  to  $873^\circ\text{K}$  in steps of  $20^\circ\text{K}$  by applying a constant potential difference of 2 V across the pellet. The potential difference was measured by a VTVM having 11 meg-ohm input resistance and a microammeter was used to measure the current.

## 3. Results

The crystallographic results are given in table 1. The relative intensities of the various planes measured from the areas under each peak in the diffractogram are also included in table 1. In cases where the reflection peaks overlapped due to limited resolving power of diffractometer, the components were resolved and evaluated in the manner described by Paulik *et al* (1969). The compound is found to be tetragonal spinel with  $a = 8.10 \text{ \AA}$  and  $c = 8.22 \text{ \AA}$ . A break is found in the plot of  $\log \rho$  vs  $1/T$  at  $573^\circ\text{K}$  (figure 1) when activation energy changes from  $0.62 \text{ eV}$  to  $0.52 \text{ eV}$ . The room temperature resistivity is found to be  $2.2 \times 10^6 \text{ ohm-cm}$ . From the plot of  $1/\chi_M$  against  $T$  (figure 2) the compound is found to obey Curie-Weiss law and is paramagnetic in the temperature range covered. The Curie molar constant  $C_M$  and the asymptotic Curie temperature  $\theta_a$  are determined from the graph and have the values  $4.72$  and  $-298^\circ\text{K}$  respectively.

## 4. Discussion

The possible valence structures for the compound are (i)  $Co^{+2}Mn^{+3}Al^{+3}O_4$  or (ii)  $Al^{+3}Co^{+3}Mn^{+2}O_4$ . It is well-known that  $Mn^{+3}$  ( $d^4$ ) ions at the  $B$  sites give rise to distortion of the lattice with  $c > a$ . Our crystallographic results show that

the compound has a tetragonal structure with  $c > a$ . This can only be explained to be due to the presence of distortive ions  $\text{Mn}^{+3}$  at the  $B$  sites. The valence structure (ii) is therefore ruled out. From the site preference energies calculated by Miller (1959) for  $\text{Al}^{+3}$  (2.5 k cal/g. at. wt. -  $A$  sites), ( $\text{Co}^{+2}$  10.5 k cal/g. at. wt. -  $A$  sites) and  $\text{Mn}^{+3}$  (3.1 k cal/g. at. wt. -  $B$  sites) it is evident that  $\text{Co}^{+2}$  will occupy  $A$  sites and  $\text{Al}^{+3}$ ,  $\text{Mn}^{+3}$  will share  $B$  sites. The ionic structure for the compound can, therefore, be written as  $\text{Co}^{+2} [\text{Mn}^{+3} \text{Al}^{+3}] \text{O}_4$ .

Table 1. Results of x-ray diffraction study of  $\text{CoMnAlO}_4$ .

$d$ in Å (Obs.)	$d$ in Å (Cal.)	$I/I_0$ (Obs)	Plane ( $h k l$ )
2.857	2.864	37	2 2 0
2.451	2.446	100	3 1 1
2.055	2.055	6	0 0 4
2.020	2.025	11	4 0 0
1.659	1.657	15	4 2 2
1.563	1.560	32	5 1 1
	1.566		3 3 3
1.436	1.432	29	4 4 0

Tetragonal :  $a = 8.10 \text{ \AA}$        $c = 8.22 \text{ \AA}$

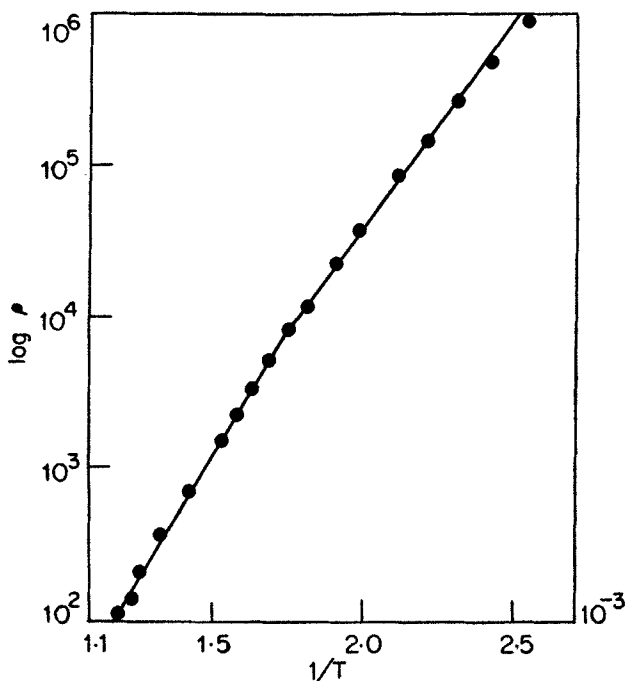


Figure 1. Plot of  $\log \rho$  vs  $1/T$  for  $\text{CoMnAlO}_4$ .

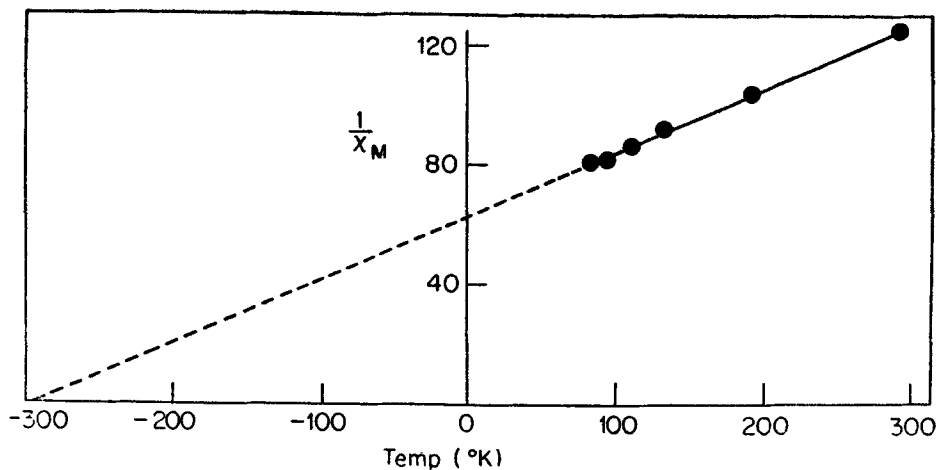


Figure 2. Plot of  $1/X_M$  vs  $T$  for  $\text{CoMnAlO}_4$ .

The observed magnetic susceptibility also confirms the above valence structure. The theoretical values of  $C_M$  (spin only) for the above valence structures are 4.88 and 7.38 respectively. The observed  $C_M$  value (4.72) is close to the theoretical value for the first valence structure than for the second valence structure. Thus the combination ( $\text{Co}^{+2} + \text{Mn}^{+3}$ ) is found to be more stable than ( $\text{Mn}^{+2} + \text{Co}^{+3}$ ) combination.

A comparison of the lattice parameters of  $\text{CoMnAlO}_4$ ,  $\text{CoMn}_2\text{O}_4$  (Boucher *et al* 1968) and  $\text{CoAl}_2\text{O}_4$  (Tretjakov *et al* 1965) shows that lattice parameter  $a$  in all the three compounds is nearly equal ( $\approx 8.10 \text{ \AA}$ ). However, the  $c/a$  ratio for the present compound (1.013) is smaller than that of  $\text{CoMn}_2\text{O}_4$  ( $\approx 1.13$ ). Thus the observed ionic configuration and the comparison of lattice parameter, indicate that the present compound may be viewed as a solid solution of  $\text{CoMn}_2\text{O}_4$  and  $\text{CoAl}_2\text{O}_4$ . The smaller  $c/a$  in  $\text{CoMnAlO}_4$  as compared to  $\text{CoMn}_2\text{O}_4$  can be attributed to the replacement of octahedral  $\text{Mn}^{+3}$  (J-T) ions by the non-distortive  $\text{Al}^{+3}$  ions.

It can be seen that the present compound with 50% concentration of  $\text{Mn}^{+3}$  ion on  $B$  sites is tetragonal. Bhaduri *et al* (1974) have pointed out that the strong  $B$ - $B$  interactions, which tend to align the distorted octahedra surrounding  $\text{Mn}^{+3}$  ions in parallel directions, are the primary driving force for the bulk distortion of lattice. In the present case the value of  $\theta_a$  ( $-298^\circ\text{K}$ ) indicates that the  $B$ - $B$  interactions are sufficiently strong. Thus it appears that the presence of  $\text{Al}^{+3}$  ions has not sufficiently weakened the  $B$ - $B$  interactions so as to remove the long range order (bulk distortion) completely.

It has been observed that aluminates in general have high values of resistivities and activation energies (Bradburn and Rigby 1953) because  $\text{Al}^{+3}$  ions have inert gas configuration and hence are not likely to participate in the hopping process at the  $B$  sites. The electrical behaviour of the compound can be explained by regarding it

as a properly substituted  $\text{CoMn}_2\text{O}_4$  in which half of the  $\text{Mn}^{+3}$  ions on the  $B$  sites are replaced by  $\text{Al}^{+3}$  ions. The activation energy of  $\text{CoMnAlO}_4$  is close to that of  $\text{CoMn}_2\text{O}_4$  (0.39 eV) (Kshirsagar and Sabane 1971) but much lower than that for  $\text{CoAl}_2\text{O}_4$  (1.55 eV) (Bradburn and Rigby 1953). Similarly its room temperature resistivity is also close to that of  $\text{CoMn}_2\text{O}_4$  (Kshirsagar *et al* 1971). It is well-known that in spinels, electrical conduction takes place through hopping of charge carriers between ions at  $B$  sites as  $B$ - $B$  distance is smaller than  $A$ - $B$  and  $A$ - $A$  distances. Thus in  $\text{CoMn}_2\text{O}_4$ ,  $\text{Mn}_B^{+3}$  -  $\text{Mn}_B^{+3}$  ions are responsible for conduction, while in  $\text{CoMnAlO}_4$ ,  $\text{Mn}_B^{+3}$  and  $\text{Al}^{+3}$  ions will determine the conductivity and the activation energy. The slightly higher resistivity and activation energy of  $\text{CoMnAlO}_4$  in comparison to  $\text{CoMn}_2\text{O}_4$  may, therefore, be attributed to the presence of inert ions  $\text{Al}^{+3}$  at the  $B$  sites in the former. Rogers *et al* (1963) have similarly observed an increase in activation energy and resistivity in a series  $\text{CoAl}_x\text{V}_{2-x}\text{O}_4$  as percentage of  $\text{Al}^{+3}$  on the  $B$  sites increases. Thus the structural, magnetic and electrical results lead to the ionic structure of the compound as  $\text{Co}^{+2} [\text{Mn}^{+3} \text{Al}^{+3}] \text{O}_4$ .

### Acknowledgements

The authors thank the authorities of Tata Institute of Fundamental Research, Bombay for permission to carry out some of the investigations. One of the authors (SGJ) thanks the University Grants Commission, for a research fellowship.

### References

- Balakirev V F, Barkhatov V P, Golikov Yu V, Zhuravleva M G, Zalazinskii A G and Chufarov G T 1978 *Strukt. Faz Protsessy Vosstanov. Elem. Tverd. Zhidk Sist. (Mater.Vses. Nauchn. Semin.)* 27-39
- Bhaduri A, Keer H V and Biswas A B 1974 *Indian J. Pure Appl. Phys.* 12 745
- Bhalerao P D, Kulkarni D K and Kher V G 1974 *Curr. Sci.* 43 113
- Boucher B, Buhl R and Perrin M 1968 *J. Appl. Phys.* 39 632
- Bradburn T E and Rigby G R 1953 *Trans. Br. Ceram. Soc.* 52 417
- Deshpande P D, Kulkarni D K and Khandekar P V 1974 *Curr. Sci.* 43 474
- Devale A B 1980 *Structural, electrical and x-ray spectroscopic study of substituted nickel manganites* Ph. D. Thesis, Nagpur University, Nagpur
- Durrant P J and Durrant B 1964 *Introduction to advanced inorganic chemistry* (London: Longmans)
- Economos G 1955 *J. Am. Ceram. Soc.* 38 241
- Figgis B N and Nayholm R S 1959 *J. Chem. Soc.* 331
- Kshirsagar S T and Sabane C D 1971 *Jpn. J. Appl. Phys.* 10 794
- Kulkarni D K 1970 *x-ray spectroscopic study of some spinels* Ph. D. Thesis, Nagpur University, Nagpur
- Kulkarni D K and Mande C 1970 *J. Phys.* D3 434
- Miller A 1959 *J. Appl. Phys.* 30 Suppl. 24 S
- Paulik F, Paulik J and Erdey L 1969 *Derivatograph operating instruction manual Hungarian optical works, Budapest*
- Rogers D B, Arnott R J, World A and Goodenough J B 1963 *J. Phys. Chem. Solids* 24 347
- Tretjakov J D and Schmalzried H 1965 *Ber. Bunsenges. Phys. Chem.* 69 396