

## A Neutron Diffraction Study of Cation Distributions in some Manganites

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The structural properties of spinel-like manganites, particularly those of copper and magnesium have been described. The distribution of the cations over the tetrahedral and octahedral sites in the lattice have been determined by neutron diffraction. The advantage of this technique and the indeterminacy of the earlier X-ray results have been pointed out.

The present study indicates that copper manganite is a cubic spinel which is about 25 percent inverted. It has been possible to assign the structural formula  $(\text{Cu}^{2+}_{.50} \text{Cu}^{1+}_{.25} \text{Mn}^{3+}_{.25}) [\text{Cu}^{2+}_{.25} \text{Mn}^{3+}_{.50} \text{Mn}^{4+}_{.25}] \text{O}_4^{2-}$ , which satisfactorily explains the observed properties of the compound.

The  $\text{Mg}^{2+}$  ions in magnesium manganite, normally present in the tetrahedral sites migrate partially to the octahedral site on thermal treatments. The activation energy for this migration has been found to be 0.29 eV. The results obtained from the x-ray and the neutron diffraction methods for  $\text{Mg}^{2+} [\text{Mn}^{3+}_2] \text{O}_4$  have also been compared.

MIXED metal oxides with spinel-like structure possess remarkable structural, electrical and magnetic properties that find numerous applications in solid state device technology. The properties of these materials depend crucially on the nature of the constituent metal ions, their valence state and distribution (cation ordering) in the crystal lattice. Although many spinel-like compounds have been investigated by several workers, much remains to be done in elucidating their properties in relation to their structures.

For convenience of discussion, a brief description of the spinel lattice is desirable. A number of double oxides, represented by the formula  $\text{A B}_2\text{O}_4$  where A and B are metal ions, crystallizes with the spinel structure. It can be described as a close-packed cubic lattice formed by the much larger oxygen anions held together by cations located in two types of interstitial sites that are called tetrahedral (A)- and octahedral (B)- sites. The unit cell of the spinel structure is shown in Fig. 1. There are eight formula units of  $\text{A B}_2\text{O}_4$  in a unit cell which contains 64 A-sites and 32 B-sites, out of which 8 A and 16 B sites are occupied by metal ions. The spinel lattice is so tolerant that myriad combinations of the metal ions,

seemingly limited by the ionic size and the charge balance, can be accommodated in it. A general representation of the cation distribution will be  $(\text{A}_m \text{B}_{1-m})_{\text{tetrahedral}} [\text{A}_{1-m} \text{B}_{1+m}]_{\text{octahedral}} \text{O}_4$ .

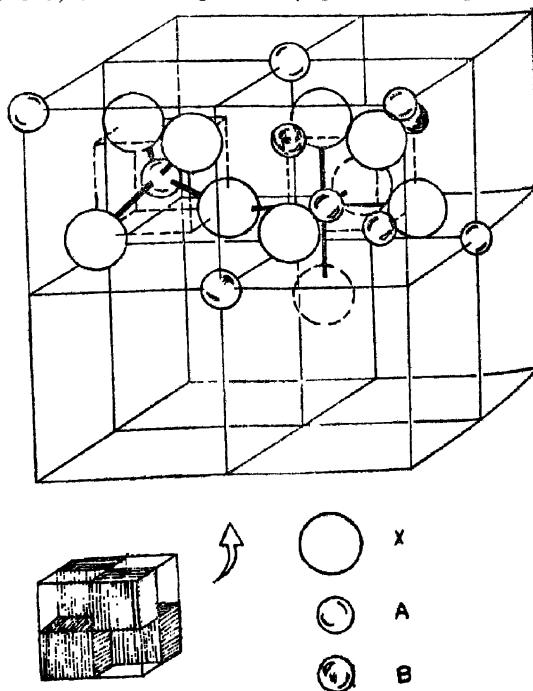


Fig. 1. The unit cell of the spinel structure

One distinguishes three particular ordering situations. When  $m=1, 0$  and  $1/3$  the spinel is said to have the normal, inverse and random distribution respectively. However, intermediate values of  $m$  have also been observed in several cases, and the term degree of inversion is used to specify the percent occupation of the A-sites by the B-sited cations.

Assuming the radius of  $1.32 \text{ \AA}$  for the oxygen anion, the maximum radius of the cation normally admissible at the tetrahedral site is  $0.30 \text{ \AA}$  (and at the octahedral site  $0.53 \text{ \AA}$ ). This is generally too small to admit the cations usually encountered in the spinel lattice ( $r_{Mg^{2+}}=0.65 \text{ \AA}$ ,  $r_{Zn^{2+}}=0.69 \text{ \AA}$ ,  $r_{Cu^{2+}}=0.92 \text{ \AA}$ ,  $r_{Mn^{2+}}=0.80 \text{ \AA}$ ,  $r_{Ni^{2+}}=0.68 \text{ \AA}$ ,  $r_{Co^{2+}}=0.70 \text{ \AA}$  and  $r_{Fe^{3+}}=0.53 \text{ \AA}$ ). Hence, an expansion of these sites takes place by displacing the nearest neighbour oxygen ions along the body diagonal of the cube as depicted in Fig. 2. The nearest neigh-

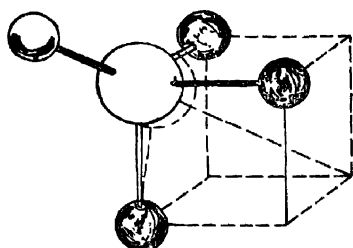


Fig. 2. The deviation of the oxygen ions from the ideal position in the spinel lattice.

bour anion configuration in the spinel structure is given in Fig. 3. Each anion is surrounded by one A- and three B-cations. The angle AOB is about  $125^\circ$  and the angle BOB is about  $90^\circ$ . The deviation from the ideal structure is given by the oxygen parameter. The distance between the octahedral site and the oxygen site, 'u' is 0.250. In practice, it is found to be always greater than 0.250.

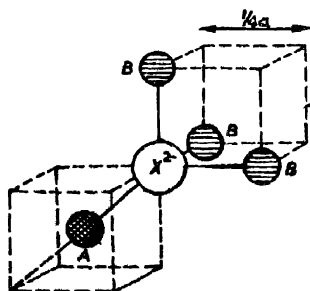


Fig. 3. Nearest neighbour anion configuration in the spinel structure.  
 $X_2$  is the oxygen anion,  $O^{2-}$   
 A and B are the metal ions.

Apart from the cubic spinel, there exist compounds which are tetragonally distorted from the cubic symmetry. The ionic arrangement in these compounds is comparable to that of the cubic spinels. It can be described as the spinel structure elongated in the direction of the C-axis as exemplified by the hausmannite ( $Mn_3O_4$ ) structure. For ease of comparison of this distorted spinel with the cubic spinel, a larger unit cell is constructed based on the 'C' face diagonal of the original cell with the new lattice parameters  $a' = \sqrt{2}a$ , and  $c' = c$ . The volume of the new cell is twice that of the original body-centred cell, and it now contains eight molecules of  $A B_2 O_4$ . The axial ratio ( $c/a$ ) is usually expressed in terms of this pseudo-spinel cell parameters. The origin of the macroscopic distortion to low symmetry has been explained as the outcome of the Jahn-Teller (J-T) effect<sup>1</sup>.

The equilibrium cation distribution is influenced by a number of factors<sup>2</sup> such as the electrostatic and geometric factors, the bonding properties of the ion and its behaviour in a given crystal field of the anions. According to the crystal field theory<sup>3,4</sup> the  $Mn^{3+}$  ( $3d^4$ ) ions show a marked preference for the B-sites. On this basis, it is reasonable to expect a normal distribution of the cations in manganites as  $M^{2+}[Mn_2^{3+}]O_4$ , where  $M^{2+}$  is a divalent metal ion. But this necessarily be not always true. Certain cations may compete for the octahedral sites, and modify the supposedly normal distribution.  $Mn^{3+}$  ions at the B-sites are known to produce a large distortion to a tetragonal symmetry with  $c/a$  greater than 1 due to the J-T effect. But the bulk distortion is observable above a critical concentration (at least 25% of the B-sites occupied by the J-T ions).

The electronic properties of some of these oxidic spinels allow one to place them among the controlled valence semiconductors as described by Verwey<sup>5</sup>. The mechanism of electrical conduction involves an activated transfer process in which the charge carriers hop from site to site. One of the salient features of the primarily ionic oxides is that the lattice must contain the same cation in at least two adjoining valence states if the material is to be conducting. The distance between the A-sites or between the A- and B-sites is larger than the distance between the B-sites. Therefore, electron exchange between the ions in the B-sites plays the major role in the conduction mechanism. For example, the high conductivity of some manganites is thought of as due to electrons hopping from  $Mn^{3+}$  to  $Mn^{4+}$  ions in the B-sites.

TABLE 1—Mg Mn<sub>2</sub>O<sub>4</sub>—CRYSTALLOGRAPHIC DATA FOR Mg Mn<sub>2</sub>O<sub>4</sub> SAMPLES THAT WERE SUBJECTED TO DIFFERENT HEAT TREATMENTS.

DATA	Quenched from 950°C	Quenched from 750°C	Quenched from 550°C	Annealed
a (Å)	5.742 ±0.002	5.728 ±0.002	5.721 ±0.002	5.705 ±0.002
c (Å)	9.180 ±0.002	9.220 ±0.002	9.280 ±0.002	9.281 ±0.002
c/a expressed in terms of the pseudo— spinel cell parameters	1.130	1.139	1.147	1.150
Degree of inversion	37.10	28.00	22.00	20.10
Oxygen parameters				
x	0.241	0.240	0.241	0.240
z	0.379	0.380	0.379	0.380
Thermal factor, B (Å <sup>2</sup> )	0.77	0.60	0.70	0.72
R—factor (%)	1.97	2.3	2.4	2.7

TABLE 2—Mg Mn<sub>2</sub>O<sub>4</sub>—COMPARISON OF THE X-RAY AND THE NEUTRON DIFFRACTION DATA

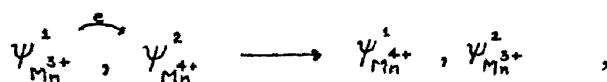
Parameters	X-ray results	Neutron results
c/a	1.15	1.15
Degree of inversion (%)	0-10.0	20.10
Oxygen parameters		
x	0.246	0.240
z	0.377	0.380
Thermal factor, B (Å <sup>2</sup> )	0.60	0.72
R—factor (%)	8.30	1.97
M <sub>Oct</sub> —O bond (long) (Å)	2.30	2.28
M <sub>Oct</sub> —O bond (short) (Å)	2.00	1.98
M <sub>Tet</sub> —O bond (Å)	1.918	1.910

the initial and final states are equivalent and, therefore, an electron transfer process is facilitated.

In a programme of studies on the structural and physical properties of the mixed valence oxides, we have prepared and studied a number of oxidic spinels. The present study deals with the structural properties of copper manganite, (CuMn<sub>2</sub>O<sub>4</sub>) and magnesium manganite (MgMn<sub>2</sub>O<sub>4</sub>).

For the determination of the cation ordering and related structural features of the compounds, the X-ray or the neutron diffraction technique<sup>6</sup> can be employed. It is well known that the X-ray scattering amplitude of an atom depends on its atomic number. This fact renders the location of the light atoms in the presence of heavier atoms difficult. Further, X-rays fail to differentiate the atoms whose atomic numbers are close to each other, except when its wavelength is proximate to the absorption discontinuity. Therefore, the structural investigation of the manganites, with X-rays as the probe, may lead to an indeterminacy in the determination of the ionic distribution. The nuclear scattering amplitudes of the atoms for neutrons, on the other hand, bears no relationship with the atomic number of the element. As a result the light atoms can scatter neutrons as efficiently as the heavier atoms, or two atoms whose atomic numbers are close to each other can have significantly different scattering amplitudes. In order to highlight these useful features of neutrons, the

In the mechanism,



scattering amplitudes of some selected elements for X-rays as well as for neutrons are given below.

Element	Scattering amplitudes ( $10^{-18}$ cm)		
	Neutron	X-rays	
		$\left(\frac{\sin \theta}{\lambda}\right) = 0.0$	$\left(\frac{\sin \theta}{\lambda}\right) = 0.5 \text{ \AA}^{-1}$
O	0.575	2.25	0.62
Mg	0.516	3.38	1.35
Mn	-0.37	7.0	3.1
Cu	0.76	8.2	3.8
Zn	0.57	8.5	3.9

Another distinctive feature is that while the X-ray scattering amplitudes are always positive, the nuclear scattering amplitudes can even be negative. The fortuitous circumstance that manganese has got a negative scattering amplitude for neutrons make the problem more amenable to the neutron diffraction technique. The choice of the neutron diffraction technique is, therefore, dictated by its specificity and superiority over the conventional X-ray diffraction technique.

### Experimental

The compounds were prepared by the standard ceramic technique in air starting from the pure oxides. Stoichiometric quantities were initially mixed in a stainless steel ball-mill for about six hours. The homogeneous mixture was then pressed into compacts and pre-fired at  $600^\circ$  for about six hours. The mass was then reground and again mixed in the ball-mill before being pressed into pellets under a pressure of 6000-7000 psi. The pellets were in the shape of circular discs of 18 mm diameter and 2 mm thick. These were finally sintered and the complete formation of the spinel was checked from the X-ray powder diffraction patterns.

Copper manganite was rather difficult to prepare. Only those samples that were quenched from a narrow temperature range between  $850^\circ$ - $920^\circ$ , gave a single phase compound unattended by other parasite phases.

In the preparation of  $\text{MgMn}_2\text{O}_4$  it was found that 48 hours of sintering at  $950^\circ$  gave a single phase

spinel. Several samples of the compound quenched after different thermal treatment were taken up for investigations.

Chemical analysis of these samples was carried out for the total metal ions. The compounds were found to be stoichiometric to the extent of more than 99.3 percent. The lattice constants were calculated from the d-values obtained from the X-ray diffraction traces using the  $\text{CuK}_\alpha$  radiation.

The neutron diffraction experiments were carried out in the Cirrus Reactor at the Bhabha Atomic Centre, Trombay. The analysis is based on the unpolarized neutron diffraction patterns taken at room temperature. The wavelength of the neutrons employed was 1.24 Å.

The neutron diffraction intensity  $I_{hkl}$  of a Bragg peak for a polycrystalline sample can be written as<sup>6</sup>

$$I_{hkl} \propto |F_{hkl}|^2 J_{hkl} \frac{1}{\sin \theta \cdot \sin 2\theta} \exp \left[ -2B \left( \frac{\sin \theta}{\lambda} \right)^2 \right] A(\theta)$$

where the symbols have their usual significance. The structure factor  $F_{hkl}$  is given by

$$F_{hkl} = b_A \sum_A \exp 2\pi i (hX_A + kY_A + lZ_A) + b_B \sum_B \exp 2\pi i (hX_B + kY_B + lZ_B) + b_O \sum_O \exp 2\pi i (hX_O + kY_O + lZ_O),$$

where  $b_A$  and  $b_B$  are the neutron scattering amplitudes of A and B metals,  $b_O$  that of oxygen, and  $X_A, Y_A, Z_A$  etc., are the atomic co-ordinates.

The final refinement of the structural parameters was carried out with the aid of a computer programme based on the method of least squares.

The R-factor has been calculated from the expression,

$$R = \frac{\sum \left| \sqrt{I_{\text{calc}}} - \sqrt{I_{\text{obs}}} \right|}{\sum \left| \sqrt{I_{\text{obs}}} \right|} \times 100$$

### Results and Discussion

#### Copper Manganite :

The distribution of the metal ions in the spinel  $\text{CuMn}_2\text{O}_4$  has been studied by several workers using

the X-ray<sup>7-9</sup> and the neutron diffraction techniques<sup>10-11</sup>. Nevertheless, one finds little agreement in the results reported by them. The valence states of Cu and Mn ions have also been a subject of much controversy. It has variously been attributed to have the cation distribution as

- (a)  $\text{Cu}^{2+}[\text{Mn}^{3+}\text{Mn}^{3+}]\text{O}_4^{2-}$ , (b)  $\text{Cu}^{1+}[\text{Mn}^{3+}\text{Mn}^{4+}]\text{O}_4^{2-}$   
 (c)  $\text{Cu}^{2+}[\text{Mn}^{2+}\text{Mn}^{4+}]\text{O}_4^{2-}$  or  $\text{Mn}^{2+}[\text{Cu}^{2+}\text{Mn}^{4+}]\text{O}_4^{2-}$

In the present study these aspects have been analysed by independent methods.

$\text{CuMn}_2\text{O}_4$  was found to be a cubic spinel with the cell edge  $a_0 = 8.327 \pm 0.002 \text{ \AA}$ . The least squares refinement of the neutron intensity data gave the following values for the structural parameters

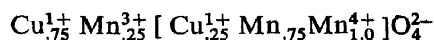
- (i) The degree of inversion = 24.8 percent.  
 (ii) The oxygen parameter,  $u = 0.2629$ .

The distribution of the metal ions in the compound can, therefore, be represented as  $\text{Cu}_{.75}\text{Mn}_{.25}[\text{Cu}_{.25}\text{Mn}_{1.75}]\text{O}_4$ . These results compare well with the recent neutron diffraction data by Buhl<sup>11</sup> as far as the distribution of the metal ions is concerned. However, his results indicate that the compound possesses a tetragonal symmetry with an axial ratio  $c/a = 1.03$ . In contrast with these, the neutron diffraction experiment by Zsalavskii et al.<sup>10</sup> indicates that copper manganite is a cubic spinel which is 16 percent inverted.

The neutron diffraction data, therefore, invariably point out that  $\text{CuMn}_2\text{O}_4$  is not a normal spinel but to a certain extent inverted. Even when the ionic distribution is fairly known, it remains a difficult task to assign the correct valence states to the metal ions, as both Cu and Mn ions are capable of existing in different valence states. Therefore, one can write down a number of ionic formulae to satisfy the charge neutrality conditions. All the same, these ionic configurations must also be compatible with the bonding characteristics, stability and site preference energies of the ions concerned. These factors enable one to cut down the number of models that have to be considered. The choice narrows down basically to two models, one in which the  $\text{Cu}^{1+}\text{-Mn}^{4+}$  pairs are envisaged to be more stable and the other one in which the combination of  $\text{Cu}^{2+}\text{-Mn}^{3+}$  ions is supposed to be more tenable.

The high electrical conductivity coupled with the low activation energy for conduction in  $\text{CuMn}_2\text{O}_4$

have led a number of authors<sup>12,13</sup> to postulate an ionic configuration  $\text{Cu}^{1+}[\text{Mn}^{3+}\text{Mn}^{4+}]\text{O}_4^{2-}$  in which all the copper ions are in the  $\text{Cu}^{1+}$  state and the manganese ions in  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  states. This readily explains the absence of a tetragonal distortion as the proportion of  $\text{Mn}^{3+}$  ions now falls short of the critical concentration necessary to bring a bulk distortion. On the assumption that all the copper ions are in the monovalent state, one may write the ionic formula



This involves the supposal that the following electron exchange,  $\text{Cu}^{2+} + \text{Mn}^{3+} \rightarrow \text{Cu}^{1+} + \text{Mn}^{4+}$ , takes place. On the basis of the free-ion chemistry such an interaction seems energetically unfavourable as it requires an energy of about 30 eV. However, it should be admitted that a certain amount of energy stabilization can be achieved by placing  $\text{Mn}^{4+}$  ions in a strong octahedral field. Similarly, at the tetrahedral sites  $\text{Cu}^{1+}$  ions can easily form stable  $sp^3$  hybrid orbitals. Yet the energy gained by placing  $\text{Cu}^{1+}$  ions at the tetrahedral sites and  $\text{Mn}^{4+}$  ions at the octahedral sites is too meagre to justify the reaction  $\text{Cu}^{2+} + \text{Mn}^{3+} \rightarrow \text{Cu}^{1+} + \text{Mn}^{4+}$ . Another valid objection to the above proposal is the observed value of the lattice constant which is too small to accommodate all the  $\text{Cu}^{1+}$  ( $r_{\text{Cu}} \approx 1.02 \text{ \AA}$ ) ions. Further, the X-ray absorption edge measurements by Miller<sup>14</sup> contradicts the hypothesis that the copper ions are present in the monovalent state.

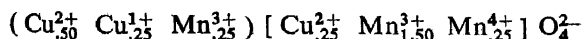
We go back to the alternative proposal wherein copper and manganese ions are allowed to maintain the same valence state, which they had in the parent oxides, namely  $\text{Cu}^{2+}$  and  $\text{Mn}^{3+}$  respectively. The ionic configuration could then be represented as  $\text{Cu}_{.75}^{2+} \text{Mn}_{.25}^{3+} [\text{Cu}_{.25}^{2+} \text{Mn}_{1.75}^{3+}] \text{O}_4$ . Both the metal ions  $\text{Cu}^{2+}$  ( $d^9$ ) and  $\text{Mn}^{3+}$  ( $d^4$ ) can gain a certain amount of energy stabilization in either sites by virtue of their electronic configurations, and therefore, the existence of  $\text{Cu}^{2+}\text{-Mn}^{3+}$  pairs does not defy the concept of site preference or energy considerations. For the calculated octahedral site preference<sup>3,4,15</sup> follows the order  $\text{Cr}^{3+} > \text{Ni}^{2+} > \text{Mn}^{3+} > \text{Cu}^{2+}$ .

The formula given above, however, has a few drawbacks. It cannot explain the observed high conductivity of the compound, which necessitates the presence of the same ion in two different valence states either at the octahedral or the tetrahedral sites. It also fails to explain the absence of a J-T distortion

despite the presence of two types of the distorting ions  $Mn^{3+}(d^4)$  and  $Cu^{2+}(d^9)$ . The idea<sup>16,17</sup> that the J-T distortion due to  $Cu^{2+}$  ions at the A-sites tend to compensate statistically the opposing distortion due to  $Mn^{3+}$  ions at the B-sites seems physically improbable.

The strength of the J-T distortion depends on the type of cations present in the lattice. No suitable theory has yet been formulated to describe the combined effect of the J-T ions. It is just possible that a good deal of stabilization may be achieved dynamically. We presume that static J-T effects give way to a dynamic one when competing J-T ions are present in the lattice. In this case the electron configuration adjusts itself to the instantaneous configuration of the neighbouring ligands, and the experimental probe sees only the time—average overall cubic symmetry of the lattice. Irrespective of the metal ion distribution, the symmetry of  $CuMn_2O_4$  remains cubic, even though it involves a certain amount extra strain on the lattice.

If one assumes that only  $Cu^{2+}$  and  $Mn^{3+}$  are present in the lattice, then the high conductivity of  $CuMn_2O_4$  remains unexplained. Invariably the electrical conduction in  $CuMn_2O_4$  must take place by the hopping of the charge carriers. Therefore small amount of  $Mn^{4+}$  ions ought to be present in the system. The presence of  $Mn^{4+}$  ions in turn should produce an equivalent amount of  $Cu^{1+}$  ions in order to keep up the charge balance. The only way to place these ions without violating the concept of site preference is to allow  $Cu^{1+}$  ions to co-exist at the A-sites alongwith  $Cu^{2+}$  ions, and  $Mn^{4+}$  ions to co-exist with  $Mn^{3+}$  ions at the B-sites. The ionic formula could thus be written as



We assume that the amount of  $Mn^{4+}$  ions retained in the system is also related to the degree of inversion. The presence of  $Cu^{2+}$  ions at the B-sites creates an equivalent amount of  $Mn^{4+}$  ions at the B-sites. Similarly  $Mn^{3+}$  ions at the A-sites induce an equivalent amount of  $Cu^{2+}$  ions to pass on to the  $Cu^{1+}$  state.

It can be visualized that the hopping of charge carriers can be operative at both sites. An electron transfer from  $Mn^{3+}$  ions to  $Mn^{4+}$  ions at the B-sites leads basically to a p-type conduction. Similarly it is also feasible for an electron transfer mechanism to take place at the A-sites between  $Cu^{2+}$  and  $Cu^{1+}$

ions. This however gives rise to an n-type conduction. The observed values of the Seebeck coefficient ( $20\mu V/^\circ C$ ) in the range  $100-250^\circ$  may be the average effects of these two types of conduction. The formula is also in accordance with Miller's experimental observation in which it is seen that majority of Cu ions are in the  $2^+$  state. Further support for the given ionic formula comes from the X-ray absorption edge measurements of manganese in a number of manganites by Padalia *et al.*<sup>18</sup> These experiments clearly show that the majority of the manganese ions are in the  $3^+$  state.

#### *Magnesium Manganite :*

The X-ray structural investigations by Irani *et al.*<sup>19</sup> on  $MgMn_2O_4$  have shown that there is a significant modification of the cation distribution at temperatures above  $800^\circ$ . At elevated temperatures  $Mg^{2+}$  ions migrate from the tetrahedral to the octahedral sites of the spinel lattice. This idea has also been suggested by Rosenberg and Nicolau<sup>20</sup>. The present attempt is to study the process of the cation migration in  $MgMn_2O_4$  by the neutron diffraction method. Different samples were prepared by varying the heat treatment in each case. The analysis of the neutron diffraction patterns of each sample was conducted in a conventional manner. The relevant crystallographic data obtained are reproduced in Table 1.

The results confirm the migration of the  $Mg^{2+}$  ions in the spinel lattice of  $MgMn_2O_4$ . From Table 1, it can be seen that below  $550^\circ$  the change in the ionic distribution is barely noticeable. However, above  $550^\circ$  significant migration takes place resulting in a variation of the ionic distribution with rise in temperature.

The activation energy of the cation migration has been calculated from the values of the degree of inversion at various temperatures using the relation,

$$\frac{(1 - \lambda)(1 - 2\lambda)}{2\lambda^2} = \exp(-\Delta E/kT),$$

where  $\lambda$  is the fraction of the B cations in A-sites. We make a valid assumption that the quenched samples represent the 'frozen in' ionic distribution stable at that particular temperature. It is found that the value of the activation energy ( $\Delta E$ ) of the ionic migration works out to be about 0.290 eV. However, this value is comparatively larger than

0.14 eV. found for  $\text{CuFe}_2\text{O}_4$  and  $\text{MgFe}_2\text{O}_4$  by Bertaut<sup>21</sup> and Pauthenet<sup>22</sup>. The large activation energy of the cation migration in  $\text{MgMn}_2\text{O}_4$  must be due to the strong stabilization of the  $\text{Mn}^{3+}$  ions in the octahedral sites.

*Comparison of the X-ray and the neutron diffraction results in  $\text{MgMn}_2\text{O}_4$  :*

In the study of  $\text{CuMn}_2\text{O}_4$ , because of the more favourable difference in the neutron scattering amplitudes of the ions, the neutron diffraction method should yield a more reliable information about the ionic distribution as well as about the position of the light atom oxygen in the lattice. Therefore, no comparison with the X-ray diffraction results needs to be made. In  $\text{MgMn}_2\text{O}_4$  one has a different situation where the X-ray scattering amplitudes of the ions are fairly far apart and a reasonable estimate of the ionic ordering as well as the position of the oxygen ions can be made.

The data obtained from the X-ray and the neutron diffraction analysis of the annealed sample of  $\text{MgMn}_2\text{O}_4$  are given in Table 2. It can be seen that the neutron results are less ambiguous and are characterized by a low R-factor. On the basis of the X-ray data, on the other hand, it is not easy to make a definitive choice between a structure that is normal and one that is 10 percent inverted. Besides, the R-factors were also found to be comparatively high. One can also perceive that the thermal factor B, obtained from the neutron analysis, tends to be a shade higher than that obtained from X-rays. The slight difference in the values of the bond lengths are also worth noting.

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