

ELECTRICAL AND MAGNETIC PROPERTIES
OF
SOME BINARY SPINELS

COMPUTERISED

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BY
SHIVARAM GANAPATI SHET, M.Sc.,
NATIONAL CHEMICAL LABORATORY,
POONA-8.

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S. G. Shet

National Chemical Laboratory,
Poona-8.

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CHAPTER - I

INTRODUCTION

1.1. GENERAL

In view of their great technical importance in electronics and electrical engineering, the ferrites have been subjected to an intensive study during the last twenty years and this has lead to deeper understanding of the electronic and magnetic interactions in such insulators. However, similar studies on other related spinels such as manganites, chromites, etc. have been initiated only recently and a lot remains to be done. The manganites are particularly complicated because of the fact that:

- (1) Manganese can exist as $Mn^{2+}(d^5)$, $Mn^{3+}(d^4)$ or $Mn^{4+}(d^3)$ ion.
- (2) The ions can be present either at the tetrahedral (A) or octahedral (B) sites of the spinel structure, and
- (3) Mn^{3+} ion causes a strong Jahn-Teller distortion leading to a tetragonal distortion of the crystal symmetry.

The present work is devoted mainly to the experimental study of structural, magnetic and electrical properties of manganites with a view to understand the nature of interactions in these spinels. The manganites chosen have the general formula Me_3O_4 where Me is a consolidated symbol representing all the metal ions in the compound. Obviously, the total charge on these three cations is 8^+ . These compounds crystallize in the cubic spinel or the tetragonal hausmanite structure.

Some of the compounds are specifically chosen such that all the tetrahedral sites are occupied exclusively by diamagnetic ions. This facilitates the study of 90° superexchange interactions between the manganese ions at the octahedral (B) sites without any interference from the otherwise stronger A-B interactions. ZnMn_2O_4 a simple example of this type, has already been studied and is known to show temperature independent antiferromagnetism due to the negative B-B interaction. The tetragonal distortion leads to an anisotropic exchange interaction giving rise to temperature independence of the antiferromagnetic susceptibility. In the present work this study has been extended to ZnMn_2O_4 - ZnFe_2O_4 and ZnMn_2O_4 - ZnCr_2O_4 system with a view to see the effect of a systematic replacement of d^4 by d^5 and d^3 ions respectively on the magnetic and structural properties of the spinels. Magnetic measurements have also been carried out on manganites containing transitional metal ions at (A) as well as at (B) sites. The results give an idea of the nature and strength of the A-B interactions.

As is well known, the tetragonal hausmanite structure is stable when the fraction of octahedral sites occupied by the Mn^{3+} ions exceeds a certain critical fraction x_c . The value of x_c was generally found to be around 0.60. Recently, some exceptions were observed and values as low as 0.30 were reported. We have, therefore, investigated the crystal distortion in numbers of manganites with a view to understand the factors which control the tetragonal to cubic transformation in these manganites.

The thesis is divided into four chapters. The first chapter describes the spinel structure followed by a historical survey of the work done on the structural, magnetic and electrical properties of manganites. The second chapter contains a description of the experimental methods used in these investigations. The third chapter covers the experimental results and finally in the chapter on "Discussion" we attempt some possible interpretations on the experimental results.

1.2. CRYSTAL STRUCTURE OF MANGANITES

As mentioned above, the manganites have the general formula Me_3O_4 where Me stands for a mixture of two or more cations. The total charge of the cations in the formula unit is 8^+ . In simple compounds we generally have only two cations, in which case, we can write the formula as XY_2O_4 . In manganites, generally X is a divalent ion and Y is Mn^{3+} . Such spinels are called 2-3 spinels. Solid solutions of these manganites with other spinels are also possible leading to homogeneous single phase compounds of a wide variety.

Manganites crystallize either in the cubic spinel or in the tetragonal hausmanite structure. In what follows, we give a brief description of these two structures:

Cubic spinel structure

The unit cell edge usually varies from compound to compound and is of the order of $8.3\text{\AA}$. The cubic space group is $Fd3m, O_h^7$ and the unit cell contains 8 molecules of XY_2O_4 . The atomic positions in the unit cell are given as:
 8 metal ions at 8(a) sites: 0,0,0; $1/4, 1/4, 1/4$ (+f.c.c.),
 16 metal ions at 16(d) sites:
 $5/8, 5/8, 5/8$; $5/8, 7/8, 7/8$; $7/8, 5/8, 7/8$; $7/8, 7/8, 5/8$ (+f.c.c.),

32 oxygen ions at 32(c) sites:

$$\begin{aligned} &u, u, u; \bar{u}, \bar{u}, \bar{u}; \bar{u}, u, \bar{u}; \bar{u}, \bar{u}, u; \\ &1/4-u, 1/4-u, 1/4-u; 1/4-u, 1/4+u, 1/4+u; \\ &1/4+u, 1/4-u, 1/4+u; 1/4+u, 1/4+u, 1/4-u; (+f.c.c.). \end{aligned}$$

The f.c.c. translations are:

$$+(0,0,0; 0,1/2,1/2; 1/2,0,1/2; 1/2,1/2,0).$$

The 8X and 16Y metal ions are distributed between 16 octahedral (d) and 8 tetrahedral sites (a) in the lattice. A 8(a) site is surrounded by four oxygen ions with tetrahedral arrangement and hence it is called a tetrahedral site. A 16(d) position is surrounded by six oxygen ions which form a regular octahedron and therefore it is called an octahedral site.

Tetragonal spinel structure

Some manganites such as Mn_3O_4 , $ZnMn_2O_4$, $MgMn_2O_4$ etc. do not show the cubic spinel structure, but crystallise in the form of tetragonal hausmannite structure at room temperature. The unit cell of the tetragonal structure contains 4 molecules of the formula unit. Usually $c \approx 9\text{\AA}$, $a \approx 5.5\text{\AA}$ and $c/a \approx 1.6$. The space group assigned to such spinels is $I_{41}^{19}/amd-D_{4h}^{19}$. The atomic coordinates in the unit cell are as follows:

4(a) position: $0,0,0; 0,1/2,1/4; + b.c.$

8(d) position: $0,1/4,5/8; 0,3/4,5/8; 1/4,0,3/8; 3/4,0,3/8;$
+ b.c.

and oxygen ions at 16(h) position:

$$0, \bar{x}, z; 0, x, z; 0, 1/2+x, 1/4-z; 0, 1/2-x, 1/4-z; \\ x, 0, \bar{z}; \bar{x}, 0, \bar{z}; x, 1/2, 1/4+z; \text{ and } \bar{x}, 1/2, 1/4+z + \text{b.c.}$$

The b.c. translations are $+0, 0, 0$ and $1/2, 1/2, 1/2$.

The body-centered tetragonal spinel can be changed into a larger face-centered tetragonal spinel on its 'c' face diagonals and the new parameters for this cell are $a' = a\sqrt{2} \approx 8A^{\circ}$ and $c' = c \approx 9A^{\circ}$. The volume of this new cell is double the original cell. The atomic positions are similar to those in a cubic spinel in case of tetragonally distorted spinel containing 8 molecules of Me_3O_4 . The metal ions in this tetragonal structure are distributed over the two types of sites. One type has the tetragonally distorted octahedral surrounding and the other type the tetragonally distorted tetrahedral surrounding. Each ion at the former set has six oxygen neighbours; four of which are in the plane defined by the axes $\underline{a}$ and $\underline{b}$ and the rest two oxygen ions along the normal to this plane. The four oxygen ions in the plane $\underline{a}-\underline{b}$ are closer to the metal ion than the remaining two oxygen ions by a factor a'/c' . The metal ions at the tetrahedral positions, however, have their four oxygen neighbours all at the same distance.

Cation distribution in spinels

The spinel (or hausmannite) structure can be described as an approximately close packed arrangement of oxygen ions with cations distributed among two kinds of sites viz.

tetrahedral (henceforth called A sites) and octahedral (henceforth called B sites), in the cubic as well as tetragonal structure. The 8X and 16Y ions can occupy the 8A and 16B sites in any proportion. Barth and Posnjak¹ (1932) have classified different spinels according to their cation distributions. If the 8X ions occupy the 8A sites and the 16Y ions in 16B sites, the structure is described as 'normal'. If the tetrahedral A sites are occupied by 8 of the 16Y ions with the remaining 8Y ions and the 8X ions distributed amongst the octahedral B sites the structure is described as 'inverted' spinel $Y(XY)O_4$. All the 8X and 16Y cations, if distributed randomly among the 8 tetrahedral and 16 octahedral sites give rise to the 'random' spinel.

The formula of a spinel is conveniently written by putting the cations situated at the octahedral sites inside square brackets, tetrahedral ions and oxygen ions outside the bracket on the left and right respectively. Thus $Cd[Mn_2]O_4$, $Zn[Mn_2]O_4$ are normal spinels, $Mn[MnNi]O_4$ is an inverse spinel and $Fe_xMn_{1-x}[Mn_{1+x}Fe_{1-x}]O_4$ is a random spinel.

The arrangement of the cations varies within certain limits. The variation in the distribution of cations in tetrahedral and octahedral positions causes a marked change in some of the physical properties. In other words, the magnetic, electric and other properties depend upon these arrangements of cations to a large extent. It is difficult to study the cation distributions of some transitional metal ions by X-ray

diffraction as these metals possess nearly equal scattering power. Neutron diffraction and magnetic measurements can often facilitate the determination of cation distribution.

Individual site preference of some cations

The distribution of the cations over the octahedral and tetrahedral sites is governed obviously by the consideration of minimization of the total energy. The primary contribution to the total energy comes from the coulomb and Born terms because of the ionic nature of the crystal. There are, however, additional terms such as energy lowering due to covalence, crystal field stabilization, etc. which though small in magnitude play decisive role in making one arrangement preferred over the other, because the larger terms are more or less equally balanced for the various alternative arrangements.

Theoretical calculations have been carried out by several workers^{4,5,6} and various ions have been arranged in a relative order depending on their preference for the octahedral site. This relative order matches fairly well with what one has been observing experimentally in a large number of spinels and it appears that this is more or less established.

In what follows, we review some relevant work done in this direction.

Transition metal ions such as Zn^{2+} , Cd^{2+} having a filled 3d shell form covalent bonds by sp^3 hybridization forming 4 bonds in tetrahedral directions. They, therefore,

prefer tetrahedral sites. The same holds good for In^{3+} and Ga^{3+} which have the same electronic configuration as Cd^{2+} and Zn^{2+} . Verwey and Häilmann²(1947) have shown that Fe^{3+} ion has a tetrahedral site preference. Direct evidence for such type of site preference for Fe^{3+} and Ga^{3+} has been given by Schulkes and Blasse³(1963). On the other hand, $\text{Cr}^{3+}(\text{d}^3)$ and $\text{Ni}^{2+}(\text{d}^8)$ prefer octahedral coordination because they can form $\text{d}^2 \text{sp}^3$ hybrid bonds.

Dunitz and Orgel⁴(1957) and McClure⁵(1957) have calculated site preference energies of transitional metal ions on the assumption that this preference is governed by the crystal field stabilization energy. They have assumed the bonds to be ionic and the calculation is based on one electron model. The degenerate set of five d orbitals of the ion, which is surrounded by six anions, splits into two levels; the upper doublet comprising $\text{d}_{x^2-y^2}$ and d_{z^2} orbitals, and lower triplet comprising d_{xy} , d_{xz} and d_{yz} . In the octahedral environment, the lower triplet is more stable than the upper doublet, whereas in the tetrahedral environment a similar splitting occurs, but here $\text{d}_{x^2-y^2}$, d_{z^2} have lower energy than the d_{xy} , d_{xz} and d_{yz} . The authors have computed the stabilization energies of these splitting by spectroscopic measurements. The difference between the energy values for octahedral and tetrahedral stabilization has been used by Dunitz and Orgel⁴(1957) and McClure⁵(1957) as a measure of the octahedral site preference and their results are shown in the Table No.1.

Table - 1

Stabilizations in terms of $\Delta/10$ for
transitional metal ions in crystal fields

<u>Ion</u>	<u>No. of d electrons</u>	<u>Stabiliza- tion in octahedral complex</u>	<u>Stabiliza- tion in tetrahedral complex</u>
Ti ³⁺ , V ⁴⁺	1	4	6
Ti ²⁺ , V ³⁺ , Cr ⁴⁺	2	8	12
V ²⁺ , Cr ³⁺ , Mn ⁴⁺	3	12	8*
Cr ²⁺ , Mn ³⁺ , Fe ⁴⁺	4	6*	4*
Mn ²⁺ , Fe ³⁺ , Co ⁴⁺	5	0	0
Fe ²⁺ , Co ³⁺ , Ni ⁴⁺	6	4	6
Co ²⁺ , Ni ³⁺	7	8	12
Ni ²⁺ , Cu ³⁺	8	12	8*
Cu ²⁺	9	6*	4*
Zn ²⁺	10	0	0

*These ions have additional Jahn-Teller stabilizations.

From the Table No. 1 it is seen that d^5 and d^{10} configurations have no site preference whereas d^3 and d^8 configurations have very large octahedral site preference. For ions with d^4 or d^9 configuration there is an additional stabilization due to the Jahn-Teller effect (to be discussed).

Octahedral stabilization can also be explained by using the ligand-field theory. The value of stabilization depends upon several factors, i.e. distance between the anions and cations, charge difference between cation and anions and also depends upon the surrounding neighbours, electron affinity of the anions and ionization potential of cations.

A more complete work on the octahedral site preference energy in spinels has been done by Miller⁶(1959). Site preference energies have been calculated which can be used to predict the ionic distributions. His values are shown in Table No.2.

Table - 2

Octahedral site preference energies for various cations. Values of P are in K.cal/g. atomic weight.

<u>Ion</u>	<u>P</u>	<u>Ion</u>	<u>P</u>	<u>Ion</u>	<u>P</u>	<u>Ion</u>	<u>P</u>
Li ⁺	-3.6	Mn ⁺⁺	-14.7	Zn ⁺⁺	-31.6	Cr ⁺³	16.6
Cu ⁺	-8.6	Fe ⁺⁺	- 9.9	Cd ⁺⁺	-29.1	Mn ⁺³	3.1
Ag ⁺	-19.6	Co ⁺⁺	-10.5	Al ⁺³	- 2.5	Fe ⁺³	-13.3
Mg ⁺⁺	-5.0	Ni ⁺⁺	9.0	Ti ⁺³	-21.9	Ga ⁺³	-15.4
Co ⁺⁺	-30.7	Cu ⁺⁺	-0.1	V ⁺³	-11.6	In ⁺³	-40.2

The cations with large value of P displace cations having a smaller value of P from octahedral spinel sites to tetrahedral sites.

Crystal structure and cation distributions in manganites

A lot of work has already been done on the crystal structure of manganites. The results obtained so far are tabulated in Table No. 3.

Table - 3

Structures of various manganites

Compound	Probable formula*	Lattice parameters			Structure	Ref.
		a	c	c/a		
CdMn_2O_4	$\text{Cd}^{2+}[\text{Mn}_2^{3+}]_4$	8.22	9.87	1.20	Tetragonal	64
ZnMn_2O_4	$\text{Zn}^{2+}[\text{Mn}_2^{3+}]_4$	8.1	9.24	1.14	"	64
		8.087	9.228	1.141	"	62
		8.092	9.244	1.142	"	66
		8.087	9.254	1.144	"	16
CuMn_2O_4	$\text{Cu}^{+1}[\text{Mn}^{3+}\text{Mn}^{4+}]_4$	8.33			Cubic	64
NiMn_2O_4	$\text{Mn}^{2+}[\text{NiMn}]_4$	8.37			Cubic	64
		8.38			Cubic	62
		8.39			Cubic	61
Mn_3O_4	$\text{Mn}^{2+}[\text{Mn}_2^{3+}]_4$	8.15	9.44	1.16	Tetragonal	64
		8.151	9.45	1.159	Tetragonal	62
		8.157	9.454	1.159	Tetragonal	66
CrMn_2O_4	$\text{Mn}^{2+}[\text{Cr}^{3+}\text{Mn}^{3+}]_4$	8.33	8.75	1.05	Tetragonal	62
ZnCrMnO_4	$\text{Zn}^{2+}[\text{Cr}^{3+}\text{Mn}^{3+}]_4$	8.25	8.62	1.04	Tetragonal	62
ZnFeMnO_4	$\text{Zn}^{2+}[\text{Fe}^{3+}\text{Mn}^{3+}]_4$	8.37			Cubic	65
		8.28	8.78	1.06	Tetragonal	53

ZnNiMnO_4	$\text{Zn}^{2+}[\text{Ni}^{2+}\text{Mn}^{4+}]_2\text{O}_4$	8.31	1.15	Cubic	62
GaNiMnO_4	$\text{Ga}^{3+}[\text{Ni}^{2+}\text{Mn}^{3+}]_2\text{O}_4$	8.38		Cubic	62
MgMn_2O_4	$\text{Mg}_{0.85}^{2+}\text{Mn}_{0.15}^{2+}[\text{Mg}_{0.15}^{2+}\text{Mn}_{1.85}^{3+}]\text{O}_4$	8.07	9.28	Tetragonal	64
LiMn_2O_4	$\text{Li}^+[\text{Mn}^{3+}\text{Mn}^{4+}]_2\text{O}_6$	8.246		Cubic	16
CoMn_2O_4	$\text{Co}^{2+}[\text{Mn}_2^{3+}]\text{O}_4$	8.10	9.31	Tetragonal	62
$\text{Zn}_{0.5}\text{Mg}_{0.5}\text{Mn}_2\text{O}_4$	$\text{Zn}_{0.5}\text{Mg}_{0.5}[\text{Mn}_2^{3+}]\text{O}_4$	8.095	9.278	Tetragonal	62
FeMn_2O_4	$\text{Mn}_{1-x}^{2+}\text{Fe}_x^{3+}[\text{Fe}_x^{2+}\text{Fe}_{1-2x}^{3+}\text{Mn}_{1+x}^{3+}]\text{O}_4$ ($0 < x < 0.33$)	8.31	8.85	Tetragonal	64
		8.49		Cubic	13
$\text{Zn}_{0.5}\text{Ge}_{0.5}\text{Mn}_2\text{O}_4$	$\text{Zn}_{0.5}^{2+}\text{Ge}_{0.5}^{4+}\text{Mn}_x^{2+}[\text{Ge}_x^{4+}\text{Mn}_{1-x}^{3+}]\text{O}_4$	8.37		Cubic	65
ZnCoMnO_4	$\text{Zn}^{2+}[\text{Co}^{2+}\text{Mn}^{4+}]\text{O}_4$	8.25		Cubic	62
GaMgMnO_4	$\text{Mg}_x^{2+}\text{Ga}_{1-x}^{3+}[\text{Mg}_{1-x}^{2+}\text{Ga}_x^{3+}\text{Mn}^{3+}]\text{O}_4$	8.35		Cubic	62
$\text{Mn}_{1.5}\text{FeTi}_{0.5}\text{O}_4$	$\text{Mn}^{2+}[\text{Ti}_{0.5}^{4+}\text{Fe}_{0.5}^{2+}\text{Fe}_{0.5}^{3+}\text{Mn}_{0.5}^{3+}]\text{O}_4$	8.6025		Cubic	63
$\text{ZnMg}_{0.5}\text{Ti}_{0.5}\text{MnO}_4$	$\text{Zn}^{2+}[\text{Mg}_{0.5}^{2+}\text{Ti}_{0.5}^{4+}\text{Mn}^{3+}]\text{O}_4$	8.397		Cubic	53

MnFeCrO_4	$\text{Mn}^{2+}[\text{Fe}^{3+}\text{Cr}^{3+}]_4\text{O}_4$	8.481	Cubic	63
$\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$	$\text{Cu}^+[\text{Mg}_{0.5}\text{Mn}_{1.5}^{4+}]_4\text{O}_4$	8.31	Cubic	58
$\text{CuNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$	$\text{Cu}^+[\text{Ni}_{0.5}\text{Mn}_{1.5}^{4+}]_4\text{O}_4$	8.31	Cubic	58
$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$	$\text{Li}^+[\text{Ni}_{0.5}\text{Mn}_{1.5}^{4+}]_4\text{O}_4$	8.17	Cubic	58
$\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$	$\text{Li}_{0.5}\text{Zn}_{0.5}[\text{Li}_{0.5}\text{Mn}_{1.5}^{4+}]_4\text{O}_4$	8.19	Cubic	58
CuCrMnO_4	No definite structure assigned.	8.31	Cubic	-

*Cations at the octahedral sites are put in the square bracket and those at the tetrahedral outside the bracket.

1.3. JAHN-TELLER DISTORTION IN MANGANITES

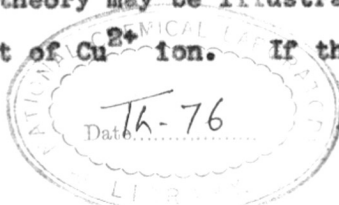
Goodenough and Loeb⁷(1955) explained the tetragonal distortion in oxidic spinels as arising due to the tendency of octahedral ions to form square coplanar, covalent bonds. If a cation forms four square, covalent dsp^2 bonds in an octahedral interstice of the spinel lattice, the steric constraints will permit covalent bonds to be formed in any one of the three biaxial planes of the site. At high temperatures there can be a resonance of the covalent bonds in three possible biaxial planes making six octahedrally directed bonds partially ionic and partially covalent. These bonds, therefore, become equal and the cubic symmetry is maintained. Below the transition temperatures the covalent bonds are frozen into one of the three biaxial planes and the octahedral site cation is bonded to the six near neighbour anions by four coplanar covalent bonds and two linear electrovalent bonds. Because of the overlap of the orbitals the four coplanar covalent bonds are shorter than electrovalent bonds and the octahedron becomes distorted from cubic to tetragonal symmetry with an axial ratio $c/a > 1$. If the octahedra have tetragonal symmetry the elastic energy of the crystal is minimized if the tetragonal axes are aligned parallel to one another. This produces a distortion of the bulk lattice from cubic to tetragonal symmetry with an axial ratio $c/a > 1$.

Dunitz and Orgel⁸(1957) have discussed the distortions from cubic symmetry in terms of the crystal field theory. When a transition metal ion is surrounded by six negative ions in a regular octahedral arrangement, the five d orbitals no longer have the same energy but are split into two groups, a lower triplet t_{2g} and an upper doublet e_g . This splitting is due to electrostatic repulsion between the d electrons and the surrounding negative ions. The e_g orbitals ($d_{x^2-y^2}$, d_{z^2}) point directly at these ions and are thus destabilized, whereas the t_{2g} orbitals (d_{xy} , d_{xz} and d_{yz}) point towards low field directions and are therefore stabilized.

In case of a cation located at a tetrahedral site, the set of d orbitals is split into a doublet e and a triplet t_2 orbital by the electrostatic repulsion between the d electrons and the four negative ions placed at the vertices of the regular tetrahedron. Dunitz and Orgel have shown that in many cases distortion is related in a simple fashion to the electronic configuration of the metal ion and may be considered to arise as a consequence of the well-known Jahn-Teller effect.

Jahn and Teller⁹(1937) have shown that if the electronic state of a non-linear molecule is degenerate the system is unstable and distortion to a lower symmetry takes place. Jahn-Teller's theory may be illustrated by taking a particular example, that of Cu^{2+} ion. If the Cu^{2+} ion is

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situated at the octahedral site the d electron configuration of the ion is $(t_{2g})^6 (e_g)^3$. It gives rise to a doubly degenerate ground state since two assignments of the e_g electrons, $(d_{z^2})^2 (d_{x^2-y^2})^1$ and $(d_{z^2})^1 (d_{x^2-y^2})^2$ are possible. Hence the regular octahedral arrangement according to the Jahn-Teller theorem is unstable. The system could be energetically stabilized if a distortion from regular octahedral symmetry takes place. There are various possible distortions which could remove the degeneracy. However, in case of Cu^{2+} and Mn^{3+} the tetragonal distortion with $c/a > 1$ is most commonly observed.

Opik and Pryce¹⁰ (1957) and Liehr and Ballhausen¹¹ (1958) have studied in detail the conditions which stabilize a particular distortion in preference to others.

The magnitude of Jahn-Teller distortion depends on the bonding and anti-bonding power of the degenerate electrons. It varies from one transitional metal ion to another. Van Vleck¹² (1939) has studied the distortions caused by d^1 and d^2 electrons and his results confirm the small distortions due to electrons from t_{2g} non-bonding orbitals.

Dunitz and Orgel⁸ have pointed out that according to the molecular orbital theory the t_{2g} electrons are non-bonding and e_g electrons are strongly anti-bonding. Accordingly, degeneracy of t_{2g} -electrons will produce only small distortion from octahedral symmetry and larger distortion is caused by the degeneracy of e_g electrons. This argument leads to the

conclusion that large distortions from octahedral symmetry should occur only for the configurations $(t_{2g})^3(e_g)^1$, $(t_{2g})^6(e_g)^1$ and $(t_{2g})^6(e_g)^3$, that is for four 3d electrons all unpaired (high spin Cr^{2+} , Mn^{3+}), for six 3d electrons paired in t_{2g} and one unpaired in e_g (low spin Co^{2+}) and for nine 3d electrons (Cu^{2+}).

The experimental results on manganites containing $Mn^{3+}(d^4)$ ions at octahedral sites confirm the above predictions given by Dunitz and Orgel⁴(1957). Table No. 4 reproduced from Dunitz and Orgel⁸(1957) for the various d electron configurations at the octahedral and tetrahedral sites, the type of Jahn-Teller distortion expected.

Finch et.al.¹³(1957) have studied the crystal distortion in case of spinels containing $Mn^{3+}(d^4)$ or $Cu^{2+}(d^9)$ ions at the octahedral sites. They found that the degree of distortion depends on the temperature and also on the number of distorting cations present at the octahedral sites. They have assumed three possible orientations of the elongated axis of each octahedron and that the long range distortion of the crystal depends on the net fraction of the elementary octahedra aligned parallel to the z axis. Thus they deduced that

$$\frac{\sigma}{\sigma_e} = S = \frac{\exp \frac{W}{RT} - \exp - \frac{W}{RT}}{\exp \frac{W}{RT} + \exp - \frac{W}{RT}}$$

where $\sigma = c/a - 1$,

$\sigma_e = \text{Constant.}$

Table - 4

Jahn-Teller distortions for d electrons

Ions	No. of d elec- trons	Octahed- ral configu- ration	Distor- tion	Tetra- hedral configu- ration	Distortion
Ti ³⁺	1	t_{2g}	Small	e	Small
V ³⁺	2	$(t_{2g})^2$	Small	$(e)^2$	0
V ²⁺ , Cr ³⁺ , Mo ³⁺	3	$(t_{2g})^3$	0	$(e)^2 t_2$	Large c/a > 1.
Cr ²⁺ , Mn ³⁺	4	$(t_{2g})^3 (e_g)^1$	Large	$(e)^2 (t_2)^2$	Large c/a < 1.
Mn ²⁺ , Fe ³⁺	5	$(t_{2g})^3 (e_g)^2$	0	$(e)^2 (t_2)$	0
Fe ²⁺ , Co ³⁺	6	$(t_{2g})^4 (e_g)^2$	Small	$(e)^3 (t_2)^3$	Small
Rh ³⁺ , Co ²⁺	7	$(t_{2g})^5 (e_g)^2$	Small	$(e)^4 (t_2)^3$	0
Ni ²⁺	8	$(t_{2g})^6 (e_g)^2$	0	$(e)^4 (t_2)^4$	Large c/a > 1.
Cu ²⁺	9	$(t_{2g})^6 (e_g)^3$	Large	$(e)^4 (t_2)^5$	Large c/a < 1.

The order-disorder process has been treated as a cooperative phenomenon in the sense that the energy (W) required to change the orientation of an octahedron from the right to wrong direction is proportional to the long range distortion present i.e. $W = W_0 \left(\frac{\sigma}{\sigma_c} \right) x$ where x is the fraction of octahedral sites occupied by the distorting cations. On this basis they have arrived at the following theoretical equations expressing distortion as a function of temperature (a) and the numbers of distorting cations (b) at the octahedral sites.

$$S = \tanh \left[\left(\frac{T_c}{T} \right) S \right] \quad \dots(a)$$

$$S = \tanh \left[\left(\frac{x}{x_c} \right) S \right] \quad \dots(b)$$

where x_c and T_c are constant. Experimental results collected on a large number of systems have been found to agree with these equations.

These authors, however, considered only one wrong direction whereas actually there are two such directions in the crystal; one parallel to the a and the other parallel to the b axis. When two wrong directions are taken into account the above equation gets slightly modified.

Wojtowicz¹⁴(1959) has also investigated the problem of tetragonal to cubic phase transformation theoretically. Interactions between the local Jahn-Teller distortions about neighbouring octahedral cations have been taken into account explicitly and the configuration energy of the system has been worked out in terms of occupation variable. Thus the temperature and composition dependence of long range distortion has been worked out. The phase transformation has been shown to be of first order.

Kanamori¹⁵(1960) has developed a very general theory for this type phase transformation from a different approach. In the theories of Finch, Sinha and Sinha¹³(1957) and of Wojtowicz¹⁴(1959), it is assumed that local distortion is

preserved even beyond the transition temperature and the cubic structure arises merely due to the randomisation of the g axis of the distorted octahedra. In Kanamori's theory this would correspond to the special case of high anisotropy energy giving rise to a first order transformation. In the absence of high anisotropy the transformation turns out to be of second order.

Wickham and Croft¹⁶ (1958) have studied several spinels containing manganese. Solid solutions in the system

- (1) $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$
- (2) $\text{Li}_{1-x}^{1+}\text{Zn}_x^{2+}[\text{Mn}_{1+x}^{3+}\text{Mn}_{1-x}^{4+}]\text{O}_4$
- (3) $\text{Zn}^{2+}\text{Ge}_{1-x}^{4+}[\text{Co}_{2-2x}^{2+}\text{Mn}_{2x}^{3+}]\text{O}_4$

have been formed and their magnetic and crystallographic properties studied. In all cases, they observed a tetragonal to cubic transformation as the Mn^{3+} ion concentration decreased below a critical fraction f_c . They found that the critical fraction of B sites occupied by Mn^{3+} ions is $0.6 < f_c < 0.65$.

Ohnishi and Teranishi¹⁷ (1961) have studied the cation distribution of copper ferrite-chromite series of the general formula $\text{Cu}_x\text{Fe}_{1-x}[\text{Cu}_{1-x}\text{Fe}_{1+x-t}\text{Cr}_t]\text{O}_4$ by X-ray diffraction method. Crystal distortion has been found to depend on the Cu ion distribution. Phase changes as a function of Cu ion concentration and temperature have been studied by them in detail. They have found that there is no distortion with $c/a > 1$ for $x > 0.2$ and no distortion with $c/a < 1$ for $x < 0.65$ i.e. for

bulk distortion with $c/a > 1$ copper ions more than 0.8 are required in the octahedral site and for the distortion with $c/a < 1$ copper ions more than 0.65 are required in tetrahedral sites.

Grenot and Huber¹⁸ (1967) have studied the temperature effect on the distribution of the metal atoms in the mixed $\text{MgGa}_{2-x}\text{Mn}_x\text{O}_4$ and $\text{MgCr}_{2-x}\text{Mn}_x\text{O}_4$ spinels of various compositions by X-ray and neutron scattering techniques. A continuous range of solid solutions was observed for both the series at temperatures above 850°C . On cooling, two phases (tetragonal and cubic) appeared when manganese concentration was high. The critical compositions at which the tetragonal phase appears had the same value of the ratio (octahedra (Mn)/to total Mn) for the two series.

Irani et.al.¹⁹ (1960) have studied the effect of chemical composition on tetrahedral to cubic transformations in the system Mn_3O_4 - MgAl_2O_4 and MgMn_2O_4 - MgAl_2O_4 by X-ray diffraction. From the X-ray intensity calculation the actual number of distorting Mn^{3+} ions in octahedral sites have been determined. They have thus found the exact fraction of Mn^{3+} ions required for the tetragonal distortion. In agreement with earlier workers they found that the transformation of tetragonal to cubic symmetry takes place even when there is an appreciable number of Mn^{3+} occupying the octahedral sites. This is due to the long range disorder

of the distorted octahedra by the introduction of the non-distorting cations through the formation of solid solutions, which separates these distorted octahedra thereby decreasing the mean interaction energy.

Irani et.al.²⁰ (1962) have also studied the effect of temperature on the structure of 'normal' manganites of Mn^{2+} , Zn^{2+} , Mg^{2+} and Co^{2+} with Mn^{3+} ions in octahedral sites by X-ray diffraction techniques. As said above tetragonal distortion is due to Mn^{3+} ions at octahedral sites by virtue of their d^4 electronic configuration which tend to distort each elementary octahedra. The observed tetragonal to cubic transformation at elevated temperature has been attributed to the randomization of direction of the individual distorted octahedra.

Robbins and Darcy⁷² (1966) have studied the effect of different cations on the ionic distribution and the cooperative Jahn-Teller distortion in spinels containing Cu^{2+} . They have found that the presence of Cu^{2+} on the B sites in compounds like $Zn(Cu_x Ge_x Mn_{2-2x})O_4$, $Zn(CuTi)O_4$ and $Ga(CuGa)O_4$ has no effect on the cooperative Jahn-Teller distortion down to $\sim 80^\circ K$.

They have also studied the ionic distributions in spinels like $CuGaM^{3+}O_4$ (where $M^{3+} = Al^{3+}, Ga^{3+}, Cr^{3+}, Mn^{3+}$), by X-ray diffraction techniques. From the ionic distributions they came to the conclusion that Jahn-Teller distortion and

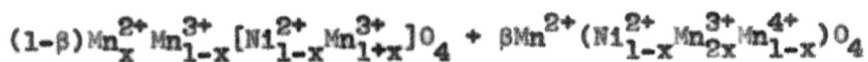
the site preference of Cu^{2+} in spinels strongly depends on the other cations present in the spinels.

Robbins and Baltzer⁷³(1965) have studied the ionic distributions and cooperative Jahn-Teller distortions in the systems $\text{ZnMn}_2\text{O}_4\text{-Cu}_2\text{GeO}_4$ and $\text{ZnMn}_2\text{O}_4\text{-ZnCuGeO}_4$ which contain both Cu^{2+} and Mn^{3+} ions. In the first system they have found that axial ratio c/a depends essentially on the Mn^{3+} content only and equal distribution of the Cu^{2+} ions over A and B sites give rise to neutralization of cooperative Jahn-Teller distortions. In the second system Jahn-Teller distortion has observed even for lower concentrations of Mn^{3+} as compared to the first system.

1.4. ELECTRICAL CONDUCTIVITY OF MANGANITES

Since many years, electrical conductivity of mixed oxides containing manganese oxides, has been studied by several workers^{24,25,26,31} because these materials are used in making thermistors. However, systematic studies on well characterised compounds have started only recently. The electrical conductivity in spinels is often useful in determining the valence state of the ions.

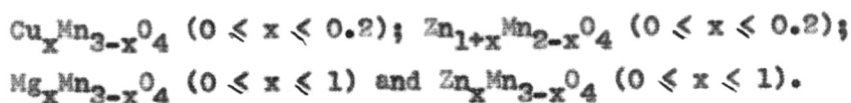
Larson et.al.²⁴ (1962) have prepared the complete range of solid solutions between nickel manganite NiMn_2O_4 and Mn_3O_4 and studied the crystal symmetry, electrical conductivity and low temperature magnetic properties. They have found that the compound $\text{Ni}_{1-x}\text{Mn}_{2+x}\text{O}_4$ shows cubic symmetry when x is less than 0.42 and tetragonal symmetry for values of x greater than 0.42. The compound shows n-type conduction for values of x less than 0.46 and p-type conduction for greater values and a sharp change in the low temperature magnetization is observed as the value of x increases from 0.36 to 0.42. On the basis of all these above studies they have assigned the following cation distribution configuration for the above series of compounds:



The electrical conductivity is interpreted as due to the transfer of electrons from Mn^{3+} ions to Mn^{4+} ions in the octahedral sites. The conductivity at A site is treated

as less likely because the A-A or A-B distances are too great to allow a charge transfer by the hopping mechanism according to which electron jumps from one cation to neighbouring cation.

Rosenberg et.al.²⁵ (1963) have studied the crystal symmetry and electrical conductivity as a function of composition and temperature of the tetragonal spinels having the general formulae



From the above studies they have proposed the cation distribution formulae for each system. They have also said that conductivity involves the hopping of electrons between octahedral site Mn^{3+} and Mn^{4+} ions.

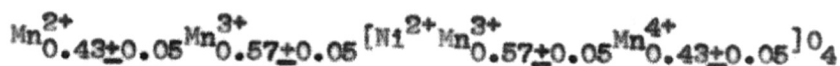
Jogalekar and Sinha²⁶ (1967) have prepared the series of compounds of the general formula $\text{ZnLi}_{2x}\text{Mn}_{2-2x}\text{O}_4$ and studied the electrical conductivity and thermoelectric coefficient as a function of temperature and have found that when $0 \leq x \leq 0.1$ the compounds are p-type and when $0.15 \leq x \leq 0.3$ the compounds show n-type conduction. They concluded that conduction is due to hopping of electrons from Mn^{3+} ions to the neighbouring Mn^{4+} ions at the octahedral sites. Another series of compounds $\text{Zn}_x\text{Cu}_{1-x}\text{Mn}_2\text{O}_4$ with $0 < x < 1$, show a p-type conductivity. Crystal structure studies reveal that when $x < 0.05$ the compounds have the cubic spinel structure and when $x > 0.25$

the compounds have the tetragonal symmetry and mixed phase is observed in the range $0.05 \leq x \leq 0.25$.

Ghare and Sinha²⁷ (1968) have synthesised a series of compounds of the general formula $Zn^{2+}(Ni_x^{2+} Mn_{2-2x}^{3+} Mn_x^{4+})O_4$ containing both Mn^{3+} and Mn^{4+} ions at the octahedral sites and have measured the conductivity as a function of temperature. They have found that energy of activation first decreases rapidly with increasing x in the range $0 < x < 0.3$ then slowly in the range $0.3 < x < 0.7$ and becomes constant after $x = 0.7$. Similarly, specific resistance first decreases with increasing x reaches minimum at $x = 0.7$ beyond which it starts increasing again. They have also suggested the hopping mechanism for conduction of electrons.

Sabane et.al.²⁸ (1966) have synthesised copper manganite by solid state reaction under controlled conditions and measured the conductivity as a function of temperature. They have observed that conductivity rises exponentially with temperature. Thermoelectric coefficient is constant in the temperature range $100-250^\circ C$ and has the value of $18 \pm 8 \mu v./^\circ C$. From these results and structural evidences they have come to the conclusion that conduction is due to electron exchange between Mn^{3+} and Mn^{4+} ions at the octahedral sites in the spinel structure. They have reported the ionic configuration of copper manganite as $Cu^+[Mn^{3+} Mn^{4+}]O_4$.

Sabane et.al.²⁹ (1967) have studied the electrical conductivity of nickel and copper manganites. They have observed that the resistivity increases with the decrease in oxygen partial pressure in case of nickel manganite whereas resistivity of copper manganite is independent of oxygen partial pressure. They have assigned the formula for nickel manganite as:



which explains the variation of resistance with oxygen partial pressure. They have given the ionic configuration for copper manganite as $\text{Cu}_{0.9}^{1+} \text{Cu}_{0.1}^{2+} [\text{Mn}_{1.1}^{3+} \text{Mn}_{0.9}^{4+}] \text{O}_4$.

Jogalekar and Sinha³⁰ (1967) have synthesised CuFeMnO_4 , CuCrMnO_4 , NiCrMnO_4 and studied the crystallographic and electrical properties to determine the correct valency states of Cu and Mn ions in manganite. All these compounds are cubic. They have measured the X-ray diffraction intensities to study the cation distribution in the compound. They have reported that conductivity increases exponentially with temperature. They have concluded that copper ions are present at the tetrahedral sites as Cu^{1+} .

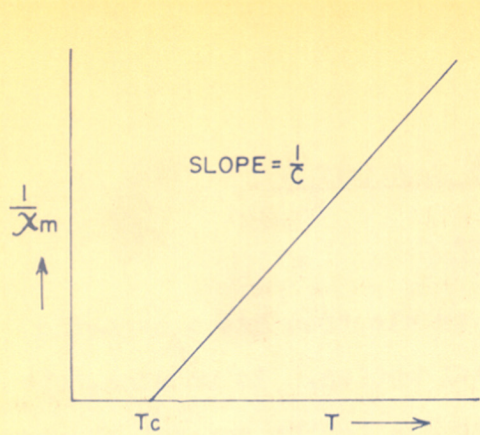
Simsa³¹ (1967) has studied the influence of Mn^{3+} ion clustering in octahedral sites of the spinel lattice on Seebeck voltage and electric conductivity. He has also furnished some information and indirect evidence on the degree of clustering of Mn^{3+} ions in octahedral positions by the measurements of electrical properties of manganese ferrites.

1.5. MAGNETIC PROPERTIES OF MANGANITES

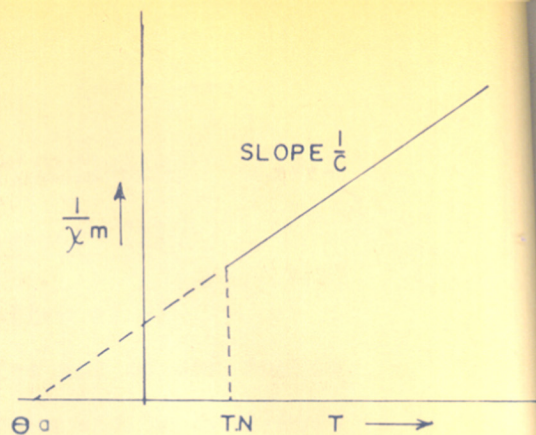
[1] General Principles

It is well-known that an electron has a magnetic moment due to its spin and orbital motion. In an atom, the resultant of the magnetic moments due to the several electrons may or may not be zero. If there is a net magnetic moment, we call such atoms or ions para-magnetic. Solids containing paramagnetic ions can, under certain conditions, get magnetically ordered. If the magnetic moment on each atom or ion is aligned parallel to one another, then the solid is called ferromagnetic. On the other hand, in certain solids we have half the atoms have their spins aligned in one direction and the other half in the opposite direction with zero resultant magnetic moment. Such solids are called antiferromagnetic. There is a third class of alignment in which case the spins on a fraction of atoms or ions point in one direction and the remaining ones in the opposite direction. However, the magnitude of the resultants are not equal so that there is a net resultant magnetic moment. This alignment is called ferrimagnetic. The ordered ferromagnetic, antiferromagnetic or ferrimagnetic materials transform to the disordered paramagnetic state at a transition temperature.

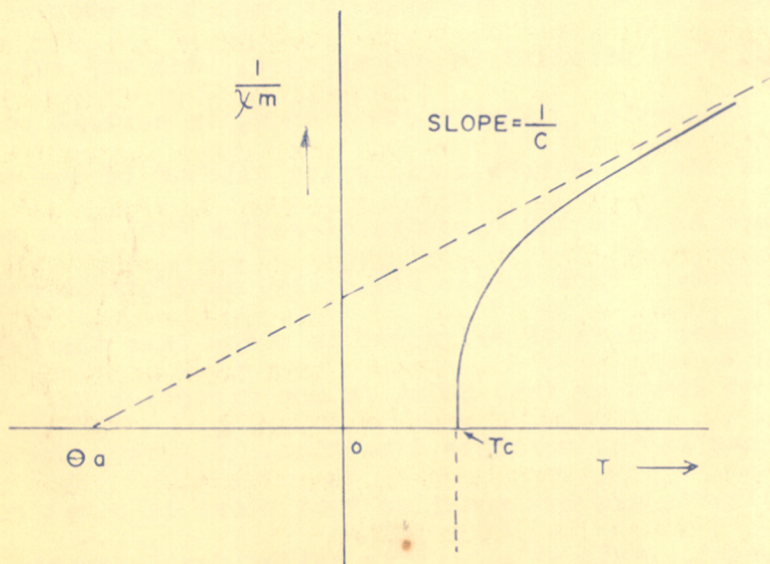
The relationship between magnetic susceptibility (χ) and temperature in the paramagnetic region for the three classes of materials are as follows:



(a)



(b)



(c)

FIG. No. 1. $\frac{1}{\chi_m}$ vs. T CURVES FOR (a) FERROMAGNETIC (b) ANTIFERROMAGNETIC (c) FERRIMAGNETIC MATERIALS.

$$\text{Ferrom} \quad \frac{1}{\chi_{\text{mole}}} = \frac{T}{C_{\text{mole}}} - \frac{\theta}{C_{\text{mole}}} \quad \dots(1)$$

$$\text{Antiferro} \quad \frac{1}{\chi_{\text{mole}}} = \frac{T}{C_{\text{mole}}} + \frac{\theta}{C_{\text{mole}}} \quad \dots(2)$$

$$\text{Ferri} \quad \frac{1}{\chi_{\text{mole}}} = \frac{T}{C_{\text{mole}}} + \frac{1}{\chi_0} - \frac{S}{T-\theta} \quad \dots(3)$$

Figure 1 gives a diagram for $1/\chi_r$ vs T plot for the three cases at temperatures above the transition temperature.

Eqⁿ 3 has been deduced by Neel³²(1948) assuming a sublattice model in which the magnetization of one sublattice is antiparallel to the other. We call such ferrimagnets as collinear ferrimagnets. Below the transition temperature T_c there would be a spontaneous magnetization M_s which is given as the vector sum of the magnetization of two antiparallel sublattices. Thus $M_s = |M_1 - M_2|$. The temperature dependence of M_s is the resultant of the temperature dependence of M_1 and M_2 . Depending on the relative variations in M_1 and M_2 , different types of variations in M_s are observed. Two typical cases are illustrated in Figure 2(a).

It has been shown by Yafet-Kittel³³(1952) that under certain conditions the collinear ferrimagnetic arrangement is not stable and non-collinear (angular) configurations may arise. In case of spinels, Yafet and Kittel have shown that the lattice can be subdivided into six spin sublattices; two for the tetrahedral sites A_1, A_2 and four for the octahedral lattice B_1, B_2, B_3 and B_4 , so that there are six independent spin directions

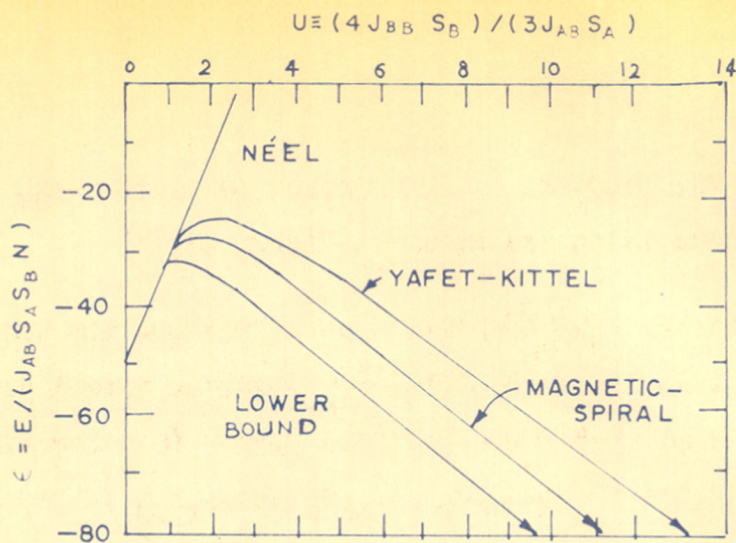


FIG No 2(c) NORMALISED ENERGY Vs. RELATIVE INTERACTION STRENGTHS FOR THREE SPIN CONFIGURATIONS IN CUBIC SPINELS (After Kaplan ; *et al.*,³⁴)

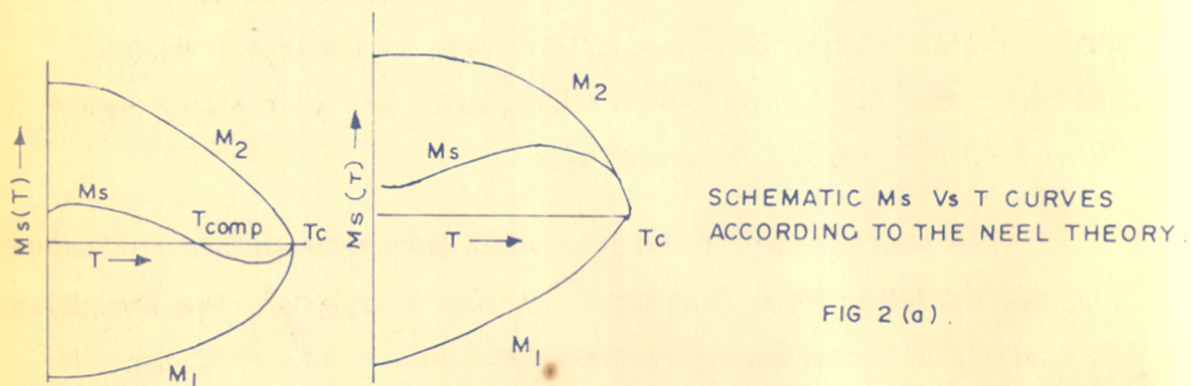


FIG 2 (a) .

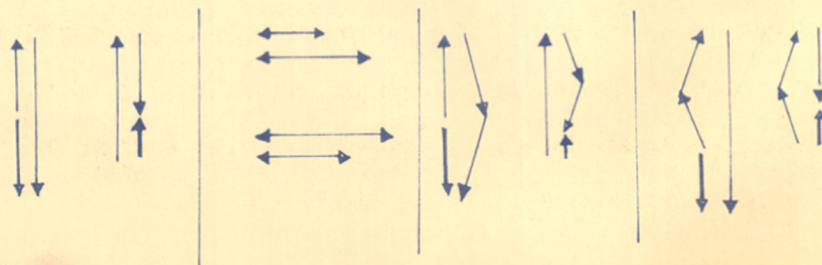


FIG No. 2b FOUR DIFFERENT THEORETICALLY POSSIBLE ORIENTATIONS OF THE MOMENTS IN THE SUBLATTICES 'A' AND 'B' FOR DIFFERENT RATIOS BETWEEN J_{AA} , J_{AB} AND J_{BB} INTERACTIONS.

allowed in the crystal. They arrived at stable spin configurations which are shown in Figure 2(b).

Kaplan et.al.³⁴ (1961) have calculated the relative stability of Neel, Yafet-Kittel and magnetic spiral arrangements. They have shown that the normalized energy is a function of a single parameter $u = (4J_{BB}S_B)/3J_{AB}S_A$ where J_{BB} is the B-B exchange constants and J_{AB} is the A-B exchange constant. S_A and S_B being the spin angular momentum vector at the A and B sites respectively. The results of their calculations for cubic spinel lattice are shown in Figure 2(c). It can be seen that the Neel configuration is stable only for small values of u . For higher values of u i.e. when B-B interaction becomes sufficiently large Neel's configuration is no longer stable. It turns out that spiral spin arrangement has much lower energy than that of a Neel, Yafet-Kittel.

These calculations have also been extended to tetragonal spinels by Kaplan and coworkers³⁴ (1961). However, the distortion requires four exchange parameters, even if A-A interactions are neglected. These four parameters are J_{AB} , $J_{AB'}$, J_{BB} and $J_{BB'}$. Energy then becomes a function of three parameters. The authors have given the ground state spin configuration for various regions in the space described by these parameters. Regions where Neel, Yafet-Kittel and spiral structures are stable are marked out in their diagram.

Sinha and Sinha³⁵ (1962) have made a theoretical study on antiferromagnetism in some normal spinels. They have selected the spinels such that the cations located at tetrahedral sites are diamagnetic while those at octahedral sites are paramagnetic. By making use of the molecular field approximation they found that the most stable arrangement is one in which each $[110]$ and $[\bar{1}\bar{1}0]$ row is antiferromagnetically ordered with the spin vectors pointing along these directions. Magnetic susceptibility independent of temperature is predicted by this arrangement. Experimental results on ZnMn_2O_4 confirm these conclusions.

Gennes³⁶ (1960) has studied theoretically the double exchange phenomena with magnetic compounds of mixed valency. He has shown that double exchange phenomena give rise to distortion of the ground state spin arrangement. Since electron transfer lowers the energy to the first order in the distortion angles, distortion would correspond to a uniform canting of the spin sublattices if the Zener carriers are mobile. On the other hand, bound carriers are expected to give a non-homogeneous distortion even though the average effect will be the same as above. He has found that canted arrangements are stable upto certain temperature, above this temperature the system will behave as antiferromagnetic or ferromagnetic depending upon the relative amount of mobile electrons.

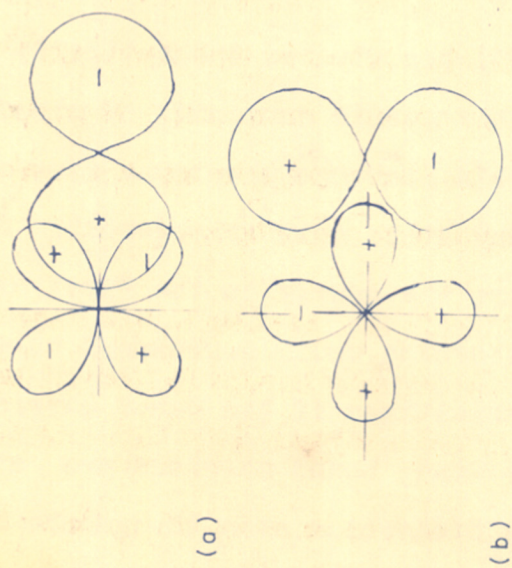


FIG. 3 (a) SYMMETRY RELATIONS BETWEEN (a) t_{2g} AND $p\sigma$ ORBITALS, (b) e_g AND $p\sigma$ ORBITALS.

The theories so far discussed have only considered the nature of magnetic ordering where exchange parameters J_{ij} has been introduced merely as constants. The various mechanisms which determine the sign and the magnitude of J_{ij} constitute a separate theoretical problem which has been investigated by several workers. It is now accepted that the predominant interaction between two magnetic ion in spinels is of super exchange type where the anion plays the role of intermediary. This type of interaction was first proposed by Kramers³⁷(1934). The theory of superexchange based on Kramers idea was first developed by Anderson⁴⁰(1950). This has been followed by theories of Slater³⁸(1953), Goodenough and Loeb⁷(1955), Goodenough³⁹(1955), Anderson and Hasegawa⁴¹(1954) and Kanamori⁴²(1959). It is clear from these theories that there are several mechanisms which contribute to the exchange coupling and they are all of comparable magnitude.

Goodenough⁶⁸(1963) has reviewed and summarized different principal contribution to superexchange interactions and in what follows, we present a brief abstract from his work.

The various mechanisms can be illustrated with the help of Figure 3(a).

It is clear from the Figure 3(a) that σ orbital of the anion is orthogonal to the t_{2g} orbital of the cation but not to the e_g orbital. On the other hand, p_{π} anion orbitals are orthogonal to e_g orbitals of the cation but not to the t_{2g} orbitals. Therefore, electron transfer or partial covalence can take place between $p_{\sigma} - e_g$ (σ transfer) and $p_{\pi} - t_{2g}$ (π transfer).

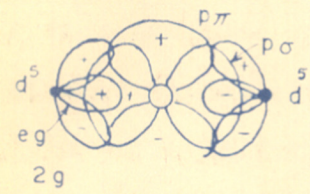
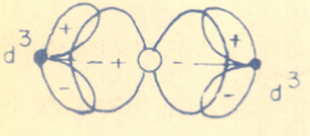
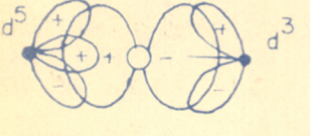
CASE	OUTER-ELECTRON CONFIGURATION	CORRELATION SUPER EXCHANGE		DELOCALIZATION SUPER EXCHANGE		SUM	STRENGTH °K (OXIDES)
		$p \sigma$	$p \pi$	$p \sigma$	$p \pi$		
1		STRONG ↑ ↓	WEAK ↑ ↓	STRONG ↑ ↓	WEAK ↑ ↓	↑ ↓	~ 750
2		WEAK TO MODERATE ↑ ↓	WEAK ↑ ↓	—	WEAK ↑ ↓	↑ ↓	≤ 300
3		MODERATE ↑ ↑	WEAK ↑ ↓	MODERATE ↑ ↑	WEAK ↑ ↓	↑ ↑	~ 400

FIG No 3 (b) THREE POSSIBLE 180° CATION-ANION-CATION INTERACTIONS BETWEEN OCTAHEDRAL-SITE CATIONS. (Goodenough⁶⁸)

There are three principal contributions to the superexchange viz: (1) correlation effect, (2) delocalization effect, (3) polarization effect.

(1) Correlation effect arises due to simultaneous covalent bond formation by coupling of the two anion electrons with the two cations on the two sides. This can lead either to a ferromagnetic or an antiferromagnetic coupling between two cations depending on their ionic configuration as can be seen from three typical examples given in Figure 3(b).

(2) In the delocalization mechanism, the electron is assumed to go from one cation to the other via the oxygen ion. This again depends on the nature of the cation orbitals and the degree of the overlap of the cation and the anion orbitals. If the cations on both sides have half filled orbitals, then the coupling is antiferromagnetic; on the other hand, if we have half filled orbital on one side and a completely full or a completely empty orbital on the other side, then the interaction is ferromagnetic. For the last case, as the e_g orbitals are empty on both sides, the interaction takes place only through π bonding which is expected to be much weaker.

(3) Anion polarization effect is very much weaker than the correlation and the delocalization effects and hence may be neglected.

Examples stated above are all for collinear metal-oxygen-metal arrangement. There are examples of 90° cation-anion-cation configuration in many solids. In this case the direct exchange interaction is likely to be pronounced because

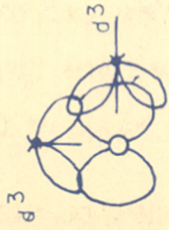
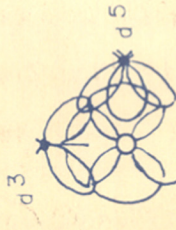
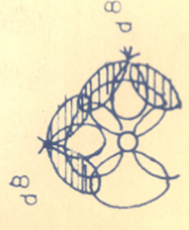
CASE	OUTER-ELECTRON CONFIGURATION	DELOCALIZATION SUPEREX				CORRELATION SUPEREX			OXIDES	SUM CHLORIDES
		$t_{2g} - \uparrow$	$e_g - \uparrow$	$e_g - \uparrow$	$e_g - \uparrow$	via s	via $p\sigma, p\pi$	via $p\sigma, p\sigma'$		
1		$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\left[\begin{array}{c} \uparrow \uparrow \end{array} \right]$	$\uparrow \downarrow$ $\sim 200^\circ K$	$\uparrow \downarrow$ $\sim 50^\circ K$
2		$\uparrow \downarrow$	$\uparrow \uparrow$	—	—	$\uparrow \downarrow$	$\left[\begin{array}{c} \uparrow \uparrow \end{array} \right]$	$\left[\left[\begin{array}{c} \uparrow \uparrow \end{array} \right] \right]$	$\uparrow \downarrow$ $\sim 300^\circ K$	$\uparrow \uparrow$ $\sim 50^\circ K$
3		$\uparrow \downarrow$	$(\uparrow \downarrow)$	$\left[\begin{array}{c} \uparrow \uparrow \end{array} \right]$	$\left[\begin{array}{c} \uparrow \uparrow \end{array} \right]$	$\uparrow \uparrow$	$(\uparrow \downarrow)$	$\left[\left[\begin{array}{c} \uparrow \downarrow \end{array} \right] \right]$	$\uparrow \downarrow$ $\sim 100^\circ K$	?
4		—	$\left[\begin{array}{c} \uparrow \uparrow \end{array} \right]$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	—	$\left[\begin{array}{c} \uparrow \uparrow \end{array} \right]$	$\uparrow \downarrow$ AND $\uparrow \uparrow$	$\uparrow \uparrow$ $\sim 50^\circ K$

FIG. 4 FOUR ILLUSTRATIONS OF SUPEREXCHANGE INTERACTIONS (Cooper, 1968)

of the direct overlap of t_{2g} orbitals of the two cations. Delocalization superexchange can, however, also occur between e_g orbitals via the intermediate anion orbitals. As far as correlation superexchange is concerned, the interaction can take place by means of the following three sets of anion electrons:

- 1) Anion S electrons.
- 2) Two p electrons of the same orbitals.
- 3) Two p electrons from different p orbitals.

The interaction via the S electrons is supposed to be weaker because of the smaller radial extension of the s orbitals. The interaction via p electrons belonging to different p orbitals is also expected to be weaker than that via the two electrons from the same p orbitals, unless the t_{2g} orbitals are more than half filled. Four illustrative 90° interactions are shown in the Figure 4. In addition to the 180° or 90° cation-anion-cation angles, there are other intermediate angles observed in many solids. For example, in spinel the angle between the tetrahedral cation and octahedral cation via the intermediate oxygen ion is only 125° . No detailed calculations for intermediate angles seem to have been done, but it is expected that the interaction would vary in a regular way as the angle is changed from 180° to 90° .

Possibilities of cation-anion-anion-cation superexchange interactions have also been considered by several

workers. Blasse⁴³(1963) has proposed an exchange mechanism involving $\text{Co}^{2+}-\text{O}^{2-}-\text{Rh}^{3+}-\text{O}^{2-}-\text{Co}^{2+}$. Mays⁴⁴(1963) had earlier assumed similar type of exchange in LiMnPO_4 through chains of $\text{MnO}-\text{P}-\text{O}-\text{Mn}$. Bertaut⁴⁵(1964) proposes even more distant interactions.

[2] Historical survey

Magnetic susceptibility of Mn_3O_4 has been studied by Honda and Sone⁴⁷(1914) at 20°C who found the value of χ to be 55.8×10^{-6} . Moore *et.al.*⁴⁸(1950) have studied the magnetic susceptibility of this compound at low temperatures and got the values: χ $298^\circ\text{K} = 54.2 \times 10^{-6}$, χ $193^\circ\text{K} = 66.6 \times 10^{-6}$ and at χ $88^\circ\text{K} = 126 \times 10^{-6}$. Borovik *et.al.*⁴⁹(1957) measured the magnetic susceptibility of Mn_3O_4 at the temperature range of 20° 300°C and they observed that the compounds become ferrimagnetic below 42.5°K and the temperature dependence of magnetic susceptibility above the Curie temperature is described by the formula

$$1/\chi = T/C + 1/\chi_0 - \frac{\sigma}{T-\phi}$$

where χ = Magnetic susceptibility.

T = Absolute temperature

χ_0 , σ , ϕ and C are constants.

Jacobs⁵⁰(1959) has studied the compounds of the formula $\text{MO} \cdot \text{Mn}_2\text{O}_3$ where M is Mn , Co , Zn and Mg and mixtures. He has reported magnetization curves at 4.2°K in pulsed fields upto 140 kilo-oersteds. Field dependent susceptibility has

been observed in these compounds. The results suggest the presence of triangular Yafet-Kittel type alignment. The author has also determined the strength of the B-B interaction. The spontaneous moment of Mn_3O_4 is 1.56 ± 0.04 Bohr magneton per molecule with the B site moments subdivided into groups at angles.

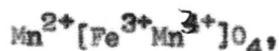
Recently, Jacobs and Kouvel⁵¹ (1961) studied the magnetic properties of Mn_3O_4 containing partial to nearly complete substitution of diamagnetic Zn^{2+} or Mg^{2+} ions in the tetrahedral sites. They have observed the unidirectional anisotropy from the hysteresis loops displaced along the field axis when the materials are cooled to low temperatures in magnetic field of several kilo-oersteds. This unidirectional behaviour is stable to reverse field pulses of 140 kilo-oersteds. An exchange anisotropy model is proposed involving interactions between ferrimagnetic and nearly antiferromagnetic regions brought about by the random distribution of the diamagnetic ions among the tetrahedral sites and the consequent magnetic inhomogeneity.

Wickham and Croft¹⁶ (1958) have studied several spinels containing manganese. In case of $\text{Co}_{3-x}\text{Mn}_x\text{O}_4$ they have concluded from the saturation magnetisation and Curie temperature data that the cubic materials show Neel-type magnetic coupling between Co^{2+} ions on tetrahedral sites and Mn^{3+} ions on octahedral sites. The number of Mn^{3+} ions on octahedral sites increases through the composition range ($0. \leq x \leq 1.2$) and hence the number of A-B interactions increases producing

a constantly rising Curie temperature which reaches maximum at 191°K at $x = 1.2$. An abrupt change in the magnetization curve occurs for this value of x . Further, appreciable magnetic moment appears again for values of x greater than 2.1 reaching a maximum of $1.4 \mu\beta/\text{molecule}$ for pure Mn_3O_4 .

Sabane⁵² (1960) has measured the paramagnetic susceptibility of CdMn_2O_4 , ZnMn_2O_4 , MgMn_2O_4 , Mn_3O_4 , CoMn_2O_4 , NiMn_2O_4 , CuMn_2O_4 at various temperatures. In most of the cases, Curie-Weiss law is not obeyed. In case of CdMn_2O_4 the results agree with four free spins per manganese ions, which indicates that manganese is present as Mn^{3+} . MgMn_2O_4 and ZnMn_2O_4 show temperature independent paramagnetic susceptibility. The ferrimagnetism of the rest of the compounds has been explained on the basis of the Neel's theory and Yafet-Kittel's modifications.

O'Keeffe⁵³ (1961) has reported the magnetic and crystallographic results for some spinels in which A sites are occupied solely by Zn^{2+} , or $\text{Zn}^{2+} + \text{Ge}^{4+}$. The amount of Mn^{3+} ions required on octahedral sites to produce tetragonal distortion in spinels depends upon the nature of other ions present. He has extended his assumptions to predictions of valencies and distributions in FeMn_2O_4 , CuMn_2O_4 and $\text{XMn}_3\text{O}_4 + (1-x)\text{NiMn}_2\text{O}_4$. The structures proposed are:



$\text{Cu}^{2+}[\text{Mn}_2^{3+}]\text{O}_4$ and $\text{Mn}_x^{2+}\text{Mn}_{1-x}^{3+}[\text{Ni}_{1-x}^{2+}\text{Mn}_{1+x}^{3+}]\text{O}_4$ respectively.

Blasse⁵⁴(1963) has synthesised new oxidic spinels containing tetravalent manganese viz. $\text{LiMe}^{3+}\text{Mn}^{4+}_2\text{O}_4$ (Me = Al, Cr, Fe, Co, Ga, Rh) and $\text{LiMe}^{2+}_{0.5}\text{Mn}^{4+}_{1.5}\text{O}_4$ (Me = Mg, Co, Ni, Cu, Zn). The magnetic susceptibility has been determined as a function of temperature. From the susceptibility vs temperature curves of these compounds, information about $90^\circ \text{Mn}^{4+} - \text{Mn}^{4+}$, B-B interaction has been obtained. It is found to be weak and negative where Mn^{4+} ions are the only paramagnetic ion in the octahedral sites and with diamagnetic ions on tetrahedral sites.

Rosenberg and Nicolae⁵⁵(1964) have studied the magnetic susceptibility of spinels $\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$, $\text{Cd}_x\text{Mn}_{3-x}\text{O}_4$ (with $0.2 \leq x \leq 1.0$) and also the normal and inverted MgMn_2O_4 . From the linear region of the $(1/\chi, T)$ curves, Curie constants have been calculated which agree with the formula based on the spin-only moments of the Mn^{2+} and Mn^{3+} ions. They have assigned the cation distribution as $\text{D}_x\text{Mn}^{2+}_{1-x}[\text{Mn}^{3+}_2]_0_4$ where D is Zn or Cd. For higher values of x (i.e. > 0.8) they have observed only a small variation of magnetic susceptibility with temperature in region lower than $150-200^\circ\text{K}$. In case of samples with $0 < x < 0.7$, $1/\chi$ curves similar to Neel hyperbola are observed over the whole investigated temperature range. The Curie point is less than 75°K .

Jogalekar⁵⁶(1965) has synthesised the system $\text{Zn}[\text{Li}^{1+}_x\text{Mn}^{3+}_{2-6x}\text{Mn}^{4+}_{4x}]_0_4$ for various values of x and measured the paramagnetic susceptibility as a function of temperature.

Compounds in which the number of Mn^{4+} ions ($x \leq 0.1$) is small become paramagnetic and obey Curie-Weiss law and the compounds in which Mn^{3+} and Mn^{4+} ion concentrations are nearly equal ($0.15 \leq x \leq 0.25$) obey Neel's equation.

Baltzer and Lopatin²² (1964) have done magnetic and crystallographic measurements on compounds CuMn_2O_4 , ZnCrMnO_4 , LiMn_2O_4 , CuCrMnO_4 , ZnCr_2O_4 , LiCrMnO_4 , $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{CuMnO}_4$ and GaCuMnO_4 . They have reported that CuMn_2O_4 , CuCrMnO_4 become ferrimagnetic at low temperatures and found that Cu^{2+} ions occupy tetrahedral lattice completely in CuMn_2O_4 , CuCrMnO_4 and GaCuMnO_4 and partially in $\text{Zn}_{0.5}\text{Ge}_{0.5}\text{CuMnO}_4$.

Dey and Anderson⁵⁷ (1965) have studied the magnetic susceptibility of cadmium manganites $(\text{Cd}_x^{2+}\text{Mn}_{1-x}^{2+})\text{Mn}_2^{3+}\text{O}_4$ between 4.2°K and 1000°K as a function of field and temperature. They have observed that all the samples except $x = 1$ become ferrimagnetic at low temperature and show three transition temperatures. First transition corresponds to paramagnetic antiferromagnetic ordering which appears to be of canted type. They suggest that the susceptibility is independent of temperature between the first and second transitions assuming that the B-site spins are all antiferromagnetically ordered in low-anisotropy planes. Between the second transition and the Curie temperature there are evidences of the absence of long range order and magnetic property is due to the local clusters of canted or spiral antiferromagnets.

Blasse⁷⁹ (1965) has reported the crystallographic and magnetic properties of a number of compounds with spinel

structure. He has found that the Curie constants in $\text{ZnMn}_t\text{Fe}_{2-t}\text{O}_4$ system are too low as compared with the spin only values. He concludes that this is due to cluster formation and the amount of Mn^{3+} ions on B sites necessary to give macroscopic tetragonal distortion is very low in $\text{ZnMn}_t\text{Fe}_{2-t}\text{O}_4$ and very high in $\text{Li}_{0.5}\text{Mn}_t\text{Fe}_{2.5-t}\text{O}_4$ and $\text{Li}_{0.5}\text{Al}_{2.5-t}\text{Mn}_t\text{O}_4$. This value of distortion is explained partly on short range orders and partly on oxygen-anion polarization.

Blasse⁵⁸ (1966) has studied the magnetic properties of number of oxygen spinels containing Mn^{4+} ions. Some of the compounds such as $\text{CuMg}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiZn}_{0.5}\text{Mn}_{1.5}\text{O}_4$ are ferromagnetic and others such as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, ZnNiMnO_4 are ferrimagnetic due to crystallographic order of paramagnetic ions on octahedral sites. He concluded that the 90° $\text{Mn}^{4+}-\text{O}^{2-}-\text{Mn}^{4+}$ interaction is ferromagnetic and the 90° $\text{Ni}^{2+}-\text{O}^{2-}-\text{Mn}^{4+}$ interaction is antiferromagnetic.

In case of CuCrMnO_4 saturation is not obtained in fields upto 30 k.o.e. which probably indicates non-collinear spin arrangements. He has reported that at low temperatures, the cation distribution is approximately $\text{Cu}^+(\text{Cr}^{3+}\text{Mn}^{4+})\text{O}_4$ but the long-range magnetic order on B-sites is not easy to achieve as there is no crystallographic order.

Ghare and Sinha²⁷ (1968) have synthesised a series of compounds containing both Mn^{3+} and Mn^{4+} of the general formula $\text{Zn}^{2+}(\text{Ni}_x^{2+}\text{Mn}_{2-2x}^{3+}\text{Mn}_x^{4+})\text{O}_4$ where $x = 0.1, 0.3, 0.5, 0.7, 0.8, 0.9$.

They have measured the paramagnetic susceptibility by Gouy method in the temperature range 100°K to about 340°K , all compounds show ferrimagnetic property.

Heikes et.al.⁵⁹ (1961) have studied the magnetic properties of lithium substituted manganese selenide at various temperatures. At low temperature the hole which is introduced by the Li^+ is loosely bound to Li^+ itself. So in the region around Li ion, double exchange causes the local distortions of the spin system. These clusters can overlap sufficiently if the Li concentration increases so that magnetic field induces an appreciable magnetic moment.

Jonker and Van Santen⁶⁰ (1950) have synthesised the system $\text{LaMnO}_3\text{-CaMnO}_3$ and $\text{LaMnO}_4\text{-SrMnO}_3$ and studied its magnetic, structural and electric properties. They have observed that these compounds have perovskite structure and they are good conductors of electricity and are ferrimagnetic. They have proposed a positive $\text{Mn}^{3+}\text{-Mn}^{4+}$ exchange interaction. The crystallographic and magnetic properties of the system $(\text{NiFe}_2\text{O}_4)_{1-x}(\text{NiMn}_2\text{O}_4)_x$ have been studied by Baltzer and White⁶¹ (1958). The cubic spinel structure is obtained through out the system with the lattice parameter increasing monotonically with x from 8.34 to 8.39Å. It is found that in the range $0 \leq x \leq 0.5$ that manganese progressively replaces

iron on six coordinated sites whereas in the range $0.5 \leq x \leq 1$ progressively replaces iron on the four coordinated sites. The authors concluded that their magnetic moment measurements indicate that all of the manganese is trivalent in the range $0 \leq x \leq 0.5$ and that in the range $0.5 \leq x \leq 1$ the manganese is divalent and quadrivalent on the four and six coordinated sites respectively. The authors have found NiMn_2O_4 becomes ferrimagnetic at approximately 100°K .

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CHAPTER - II

EXPERIMENTAL TECHNIQUES

2.1.

PREPARATION OF COMPOUNDS

Manganites of the general formula

(1) $\text{Zn}(\text{Cr}_x\text{Mn}_{1-x})_2\text{O}_4$, (2) $\text{Ni}(\text{Cr}_x\text{Mn}_{1-x})_2\text{O}_4$, (3) $\text{Cu}(\text{Cr}_x\text{Mn}_{1-x})_2\text{O}_4$, (4) $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$ and (5) $\text{Zn}(\text{Fe}_x\text{Mn}_{1-x})_2\text{O}_4$, where x varies from 0.1 to 0.9 have been synthesised. The compounds have been prepared by reacting appropriate mixtures at elevated temperatures. Finely divided spectroscopically pure compounds are taken and mixed together in appropriate proportions by grinding under alcohol for about two hours in an agate mortar and pestle to ensure the formation of homogeneous mixture. After removal of alcohol completely by evaporation, this mixture of oxides is then heated in a platinum crucible at about 1000°C for about five hours in oxygen atmosphere. The temperature of the electric furnace could be controlled within $\pm 5^\circ\text{C}$. After heating for five hours, the compound is allowed to cool slowly in the same atmosphere and taken out and reground in the same manner for several hours. The sample is then heated again in oxygen atmosphere at about $1250\text{--}1300^\circ\text{C}$ for about four to five hours. When the reaction is complete, the sample is allowed to cool very slowly in the oxygen atmosphere. The product thus obtained is then analysed by X-ray diffraction using a 14 cm. Debye Scherrer camera and $\text{Fe-K}\alpha$ ($\lambda = 1.93597\text{\AA}$) radiation filtered through a manganese foil. The heating is continued till no diffraction lines due to unreacted oxides are observed.

In case of chromium containing compounds the temperature required for the completion of the reaction is more than 1300°C and are reacted more than two times by repeated grinding. In most cases, the X-ray diffraction pattern shows homogeneous single phase compounds. In some cases however, it was not possible to form a homogeneous compounds even after repeated heating. These will be mentioned at appropriate places when the results are described. In case of copper chromium-manganites $\text{Cu}[\text{Cr}_x\text{Mn}_{1-x}]_2\text{O}_4$ where $x = 0.1$ to 0.5 the reaction has been carried out at low temperatures at 950°C for about 100 hours in an oxygen atmosphere and finally the compounds have been quenched and analysed by X-ray diffraction.

Preparation of pellets

The pellets are then prepared by the standard ceramic technique of powdering, mixing, grinding and sintering, etc. The compounds obtained after reaction are finely ground in an automatic grinder for about 5 hours to obtain a particle size of less than forty microns. About 1 cc. of 2% polyvinyl acetate in acetone is then added to about one gram of the powder and mixed nicely by grinding with excess of acetone for about half an hour. The paste thus formed is dried and again ground for about 15 minutes to form a powder. The powder is pressed in a die of 1 cm. diameter by means of a Carver laboratory hydraulic press fitted with a calibrated pressure gauge. The pressure applied is usually 5000 p.s.i.

The pellet is normally of 1 cm. diameter and 0.2 to 0.3 cm. in thickness. The pellets thus obtained are slowly heated in oxygen atmosphere at the rate of 100°C per hour, when the binder is burnt completely at about 800°C . The temperature of the furnace is then increased gradually to the sintering temperature i.e. at about $1300\text{--}1350^{\circ}\text{C}$. The pellets are allowed to remain at that temperature for about 3 hours after which the furnace is switched. The oxygen atmosphere is maintained until the furnace is cooled to room temperature. Polyvinyl acetate is found to be the most convenient binder for these series of compounds and dense crack free pellets are easily obtained.

Electrical conductivity

The electrical conductivity of the above sintered pellets has been studied as a function of temperature. A suitable furnace and a sample holder has been constructed.

The furnace is constructed by winding a standard resistor Kanthal wire on a silica tube of one inch inner diameter and a length of one foot, so as to obtain a constant temperature zone of about six inches in length. This assembly is fixed in a box made up of asbestos cement sheets lagged by asbestos powder in order to avoid heat transfer. The temperature of the furnace can be controlled to $\pm 2^{\circ}\text{C}$ by making use of automatic temperature controller. Power is fed to the furnace through a suitable voltage stabilizer and a variac to control the current.

The sample holder is constructed out of 1/2 inch diameter silica tube with one end closed by a flat silica plate. A slot is made just above the closed end to give an opening of about 1" x 1/4". The pellet is sandwiched between two platinum foils and placed on the bottom of the silica tube. The spring is placed in such a way that it does not come across in the heating zone but remains out of the furnace. Calibrated chromel-alumel thermocouple is placed very close to the pellet. The platinum wires fused to the platinum foils are insulated and taken out of the silica tube.

The two end faces of the pellet are made conducting by applying platinum paste. This type of contact gives low resistance and high reproducibility. Electric conductivity as a function of temperature is measured on EICO electric volt-OHM meter Model 214. The temperature is measured by the help of Kaycee potentiometer and a lamp and scale arrangement which can measure the e.m.f. to an accuracy of 5μ v.

Conductivity has been measured at various temperatures from room temperature upto 350°C . The temperature of the furnace is increased slowly at different intervals and allowed to attain equilibrium. The resistance of the pellet is then measured at that temperature. Resistance at room temperature of the pellet is of the order of 10^6 ohms. and falls to about 10^2 at nearly 350°C .

Electric conductivity measurements have also been done at low temperature in case of the system $\text{Cu}(\text{Cr}_x\text{Mn}_{1-x})_2\text{O}_4$ where $x = 0.2$ to 0.5 which usually shows very low resistance of the order of 30-70 ohms. Hence conductivity has been measured at temperatures down to liquid nitrogen temperature by using various fixed temperature baths such as liquid nitrogen, solid alcohol in equilibrium with liquid alcohol at its freezing point; solid CO_2 , ice, etc. The sample along with the sample holder has been kept in vacuum in order to avoid the condensation of moisture on the pellet. Copper constantan thermocouple is used to measure low temperatures.

2.2. MEASUREMENT OF THERMOELECTRIC COEFFICIENT

When a semiconductor is heated at one end with respect to other the charge carrier move from hot zone to cold zone. If these carriers are electrons, the hot portion would get positively charged and the cold portion negatively charged due to this movement and a voltage difference would develop. This voltage difference is known as thermo-e.m.f. The opposite type of polarity would develop if the holes are charge carriers. Thus the sign of thermo-e.m.f. can be used to determine the nature of charge carriers. For this measurement, the sample in the form of a long pellet is mounted on a hot plate heated electrically. The temperature of this hot plate is controlled by regulating the voltage supply through a voltage stabilizer and a variac.

The pellet is placed on silica plate and held in position by suitable phosphor bronze spring. Two platinum foils have been put in contact with the two faces of the pellet and two calibrated chromel-alumel thermocouples are also kept in close contact with the two faces. The hot plate is allowed to attain steady temperature for a sufficiently long time after which the temperatures on the two faces are measured by means of two thermocouples. The voltage difference developed between two faces is also measured on a sensitive Kaycee potentiometer. The temperature of the hot plate is then raised and the whole operation is repeated to get thermal-e.m.f. at different temperatures.

2.3. X-RAY EXAMINATION

X-ray powder diffraction technique has been employed to check the completion of the reaction and to determine the crystal structure of the compounds formed. The samples have been filled in thin glass capillaries and Debye-Scherrer powder patterns have been taken on a Philips X-ray machine using Fe-K α radiation ($\lambda = 1.9359 \text{ \AA}$) filtered through a manganese foil in a 14 cm. camera. The d values have been obtained from the powder diffraction data and lattice parameters have been calculated from the observed d values. The patterns have been indexed as cubic or tetragonal with the help of the standard charts. The cation distribution in some compounds has been determined by visually estimating the intensities of different diffraction lines and compared with those calculated for different cation distribution. Details of intensities calculation are given later.

2.4. MAGNETIC SUSCEPTIBILITY

Magnetic susceptibility of our samples has been measured by Gouy method. This method is based on the fact that if a cylindrical sample is suspended between the two poles of the magnet so that one end of the sample is in the region of large field intensity and the other end of the sample in the region of very low field intensity, then the force exerted on the sample along its length is given by:

$$f = 1/2 (K_1 - K_2)(H_1^2 - H_2^2)A$$

where K_1 = volume susceptibility of sample, K_2 - volume susceptibility of the surroundings, H_1 = maximum field intensity at one end of sample, H_2 = minimum field intensity at the other end of the sample, A = area of cross-section of the sample.

If the length of the sample is large the $H_2 = 0$. Furthermore, the volume susceptibility of the surroundings can be taken to be very small and can be neglected. Hence the equation can be simplified to:

$$f = 1/2 K_1 H_1^2 A = g \Delta W$$

where g is gravitational constant and ΔW is the change in weight of the substance due to the application of field.

A small flat face electromagnet of one square inch cross-sectional area with a gap between the two magnetic

pole pieces of about 3.5 cms. has been used. The magnet has been attached to a variable stabilized power supply of 0-200 volts DC and 0-50 amperes current. A steady magnetic field of about 5000 oersteds is obtained by passing a current of 20 amps. through the coils of the magnet. Same constant field is maintained for all measurements at all temperatures. The weight of the specimen as well as the change in weight are measured by a Mettler make single pan balance which can read weights with a 0.05 milligram accuracy.

The sample holder is a cylindrical pyrex glass tube of 20 cms. length with a uniform internal diameter of 3 mm. The tube is filled with a finely powdered sample upto the fixed mark (about 13 cms. above the bottom) and is suspended from the arm of the microbalance. A silver chain is used for suspending the tube. One end of the sample is kept exactly at the centre of the pole pieces and the other end is at nearly zero field. The specimen tube is surrounded in a glass chamber which is again kept in the special type of pyrex Dewar flask arranged in the centre of the pole pieces. When the measurements are carried out at low temperatures dry nitrogen gas is passed continuously to avoid condensation of moisture over the specimen tube.

The susceptibility has been measured at various temperatures. The desired temperature is obtained by using suitable baths. The low temperature baths are liquid nitrogen, solid alcohol at its freezing point, solid carbon

dioxide and ice. High temperatures are obtained by making use of a specially designed platinum furnace. The temperature is measured by using a calibrated copper-constantan thermocouple and a portable potentiometer which can read upto the accuracy of 5μ volts.

Magnetic force acting on the sample is:

$$f = 1/2 K_1 H_1^2 A = g \Delta W \text{ from which the relation:}$$

$$\frac{\chi_1 W_1}{\chi_2 W_2} = \frac{\Delta W_1}{\Delta W_2} \text{ can be easily obtained where:}$$

χ_1 = Magnetic susceptibility per gm. of sub.1.

χ_2 = Magnetic susceptibility per gm. of sub.2.

W_1 = Wt. of the substance 1.

W_2 = Wt. of the substance 2.

ΔW_1 = Change in wt. of the substance 1 in the magnetic field.

ΔW_2 = Change in wt. of the substance 2 in the magnetic field.

$$\text{Hence: } \chi_2 = \left[\chi_1 \frac{W_1}{\Delta W_1} \right] \left[\frac{\Delta W_2}{W_2} \right].$$

If the magnetic susceptibility of the compounds are measured under the identical conditions and the value of susceptibility of one of the compound is known, the susceptibility of the other compound can easily be obtained from the above relation, if

$$\frac{\chi_1 W_1}{\Delta W_1} = A, \quad \chi_2 = A \frac{\Delta W_2}{W_2}$$

A = tube constant for the magnetic set up.

The tube constant is found out with the aid of analar grade copper-sulphate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ whose susceptibility is known to be equal to:

$$\chi_{\text{gm.}} = 6.24 \times 10^{-6} \text{ at } 300^\circ\text{K.}$$

By using this constant, magnetic susceptibility of specpure Mn_3O_4 has been determined at various temperatures. The values for Mn_3O_4 at various temperatures have been found to be in agreement with those of reported by Moore et.al.⁴⁸ (1950).

Thus the same tube has been used throughout the experiment and the susceptibility of the unknown substances have been determined knowing the change in wt. of the unknown sample under identical conditions at various temperatures.

CHAPTER - III
EXPERIMENTAL RESULTS

3.1. X-RAY RESULTS

The X-ray powder diffraction patterns have been taken on a Philips X-ray machine using a 14 cm. Debye-Scherrer camera. Fe-K α radiation ($\lambda = 1.9359\text{\AA}$) filtered through a manganese foil has been used in all cases. The d values have been calculated and the indexing of the patterns has been done with the help of the standard log d charts.

The unit cell dimensions, 'a' of the cubic samples has been calculated by making use of the formula

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

The mean value of 'a' has been found out from the d values of all the reflections. The values of $1/d^2$ have then been calculated for each reflection and compared with the $1/d^2$ values experimentally observed. It is found that the calculated values agree well with the experimental values.

In case of tetragonal patterns, first an approximate value of 'a' is calculated from the reflection of the type 'hko'. This value of 'a' is used to determine an approximate value of 'c' from the equation

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

taking various hkl reflections with high values of 'l'. The mean value of 'c' thus found out is taken and a fresh value of 'a' is

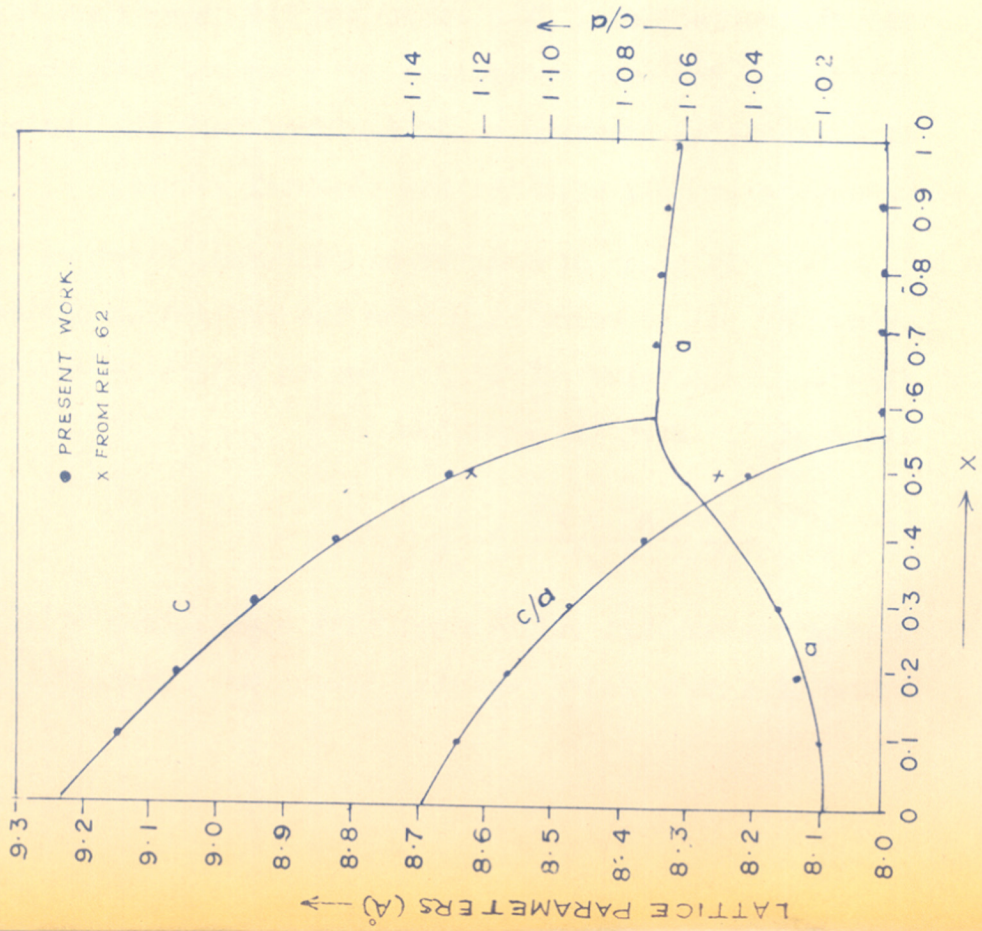


FIG. No. 5 CELL EDGES AND C/a RATIO FOR THE
SYSTEM $\text{ZnCr}_2\text{Mn}_{2-2x}\text{O}_4$

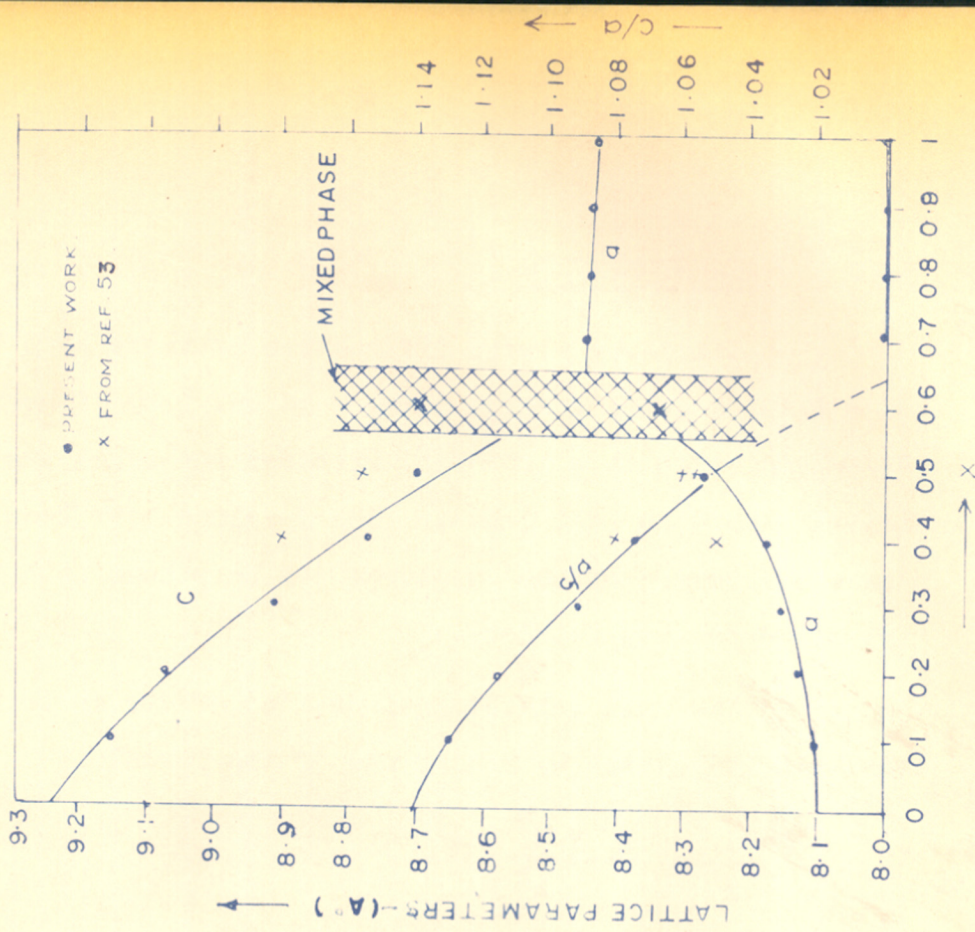


FIG. No. 6 CELL EDGES AND C/a RATIO FOR THE
SYSTEM $\text{ZnFe}_2\text{Mn}_{2-2x}\text{O}_4$

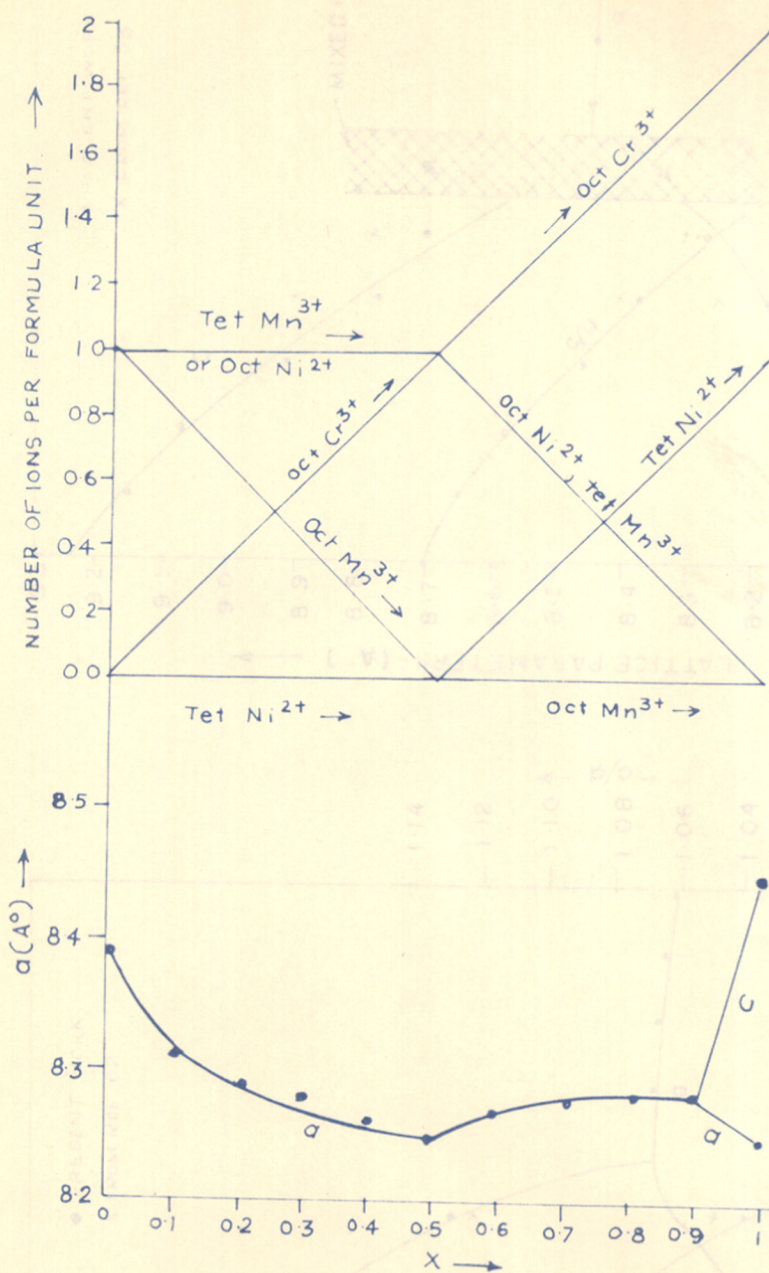


FIG No.7. CELL EDGES AS A FUNCTION OF COMPOSITION
FOR THE SYSTEM $\text{NiCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$

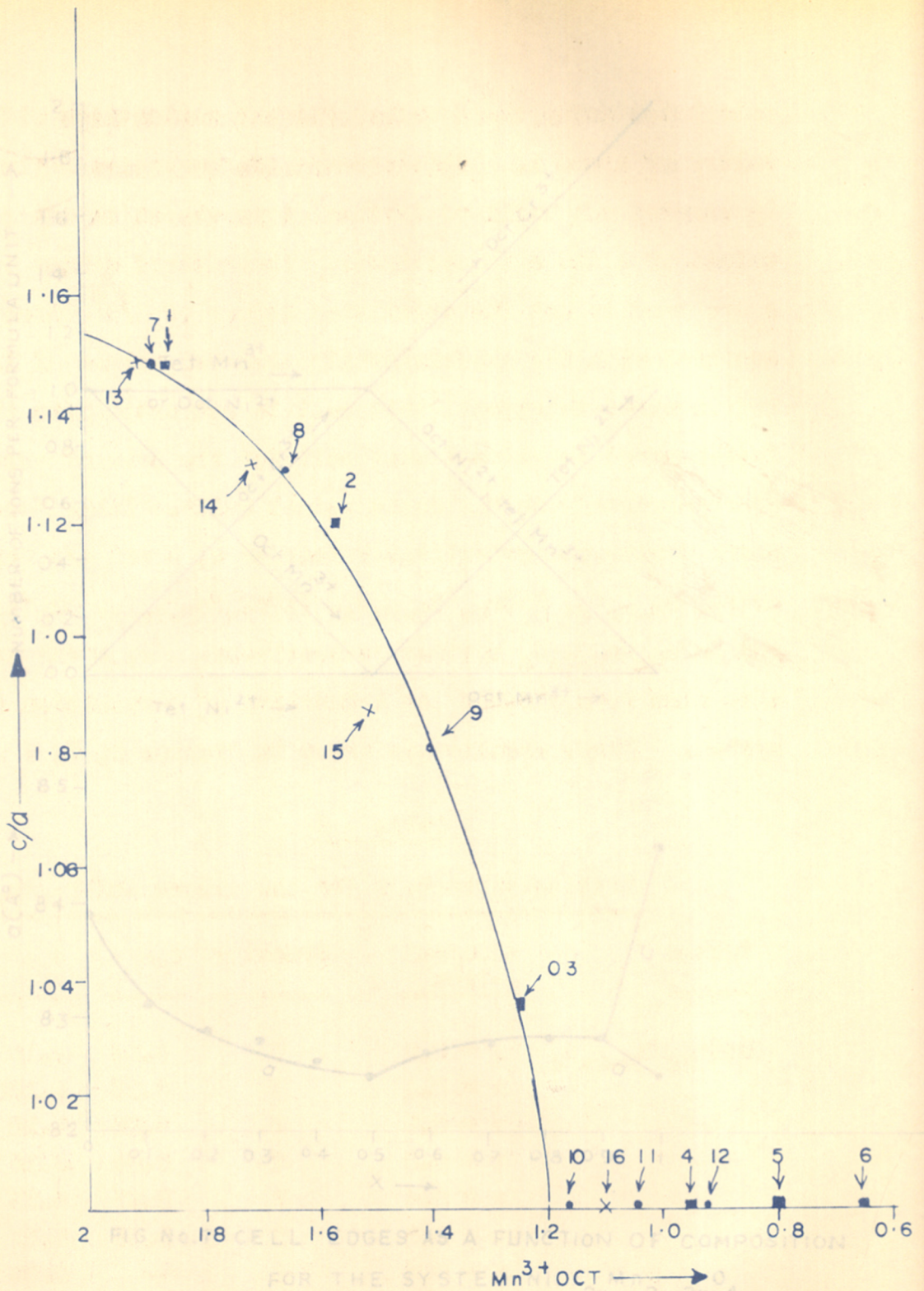


FIG.No 8 C/Q RATIO FOR THE SYSTEM $Zn_x Ni_y Mn_{3-x-y} O_4$
(Numbers according to the serial number in table No 25)

calculated using the 'd' values for hkl reflections with high values of h and k. This process of successive refinement is carried out until no further improvement in the calculated values of 'a' and 'c' is obtained. These final values of 'a' and 'c' are used to get the calculated values of $1/d^2$ which are compared with the experimentally observed values of $1/d^2$. The body centred tetragonal unit cell is converted into the bigger face-centred tetragonal unit cell for the sake of convenience of comparison with the cubic spinel cells. Table Nos. 5, 6, 7, 8 and 9 give the calculated values of c, a and c/a for $\text{ZnCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$, $\text{NiCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$, $\text{CuCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$, $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$, and $\text{ZnFe}_{2x}\text{Mn}_{2-2x}\text{O}_4$ systems respectively. c, a and c/a values have also been plotted as a function of composition for each system. These results are shown in Figures 5, 6, 7 and 8.

Table - 5

Lattice parameters for the system $\text{Zn}(\text{Cr}_{2x}\text{Mn}_{2-x})\text{O}_4$

<u>System</u>	<u>Composi- -tion</u>	<u>Symmetry</u>	<u>c_{Ao}</u>	<u>a_{Ao}</u>	<u>c/a</u>
$\text{ZnCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$	x = 0.0	T	9.24	8.10	1.14
	x = 0.1	T	9.15	8.105	1.129
	x = 0.2	T	9.06	8.13	1.114
	x = 0.3	T	8.94	8.16	1.095
	x = 0.4	T	8.82	8.23	1.072
	x = 0.5	T	8.65	8.31	1.041
	x = 0.6	C	-	8.34	1.00
	x = 0.7	C	-	8.35	1.00
	x = 0.8	C	-	8.33	1.00
	x = 0.9	C	-	8.325	1.00
	x = 1.0	C	-	8.31	1.00

Table - 6Lattice parameters for the system $\text{Ni}(\text{Cr}_{2x}\text{Mn}_{2-2x})\text{O}_4$

System	Composition	Symmetry	c_{Ao}	a_{Ao}	c/a
$\text{NiCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$	x = 0.0	C	8.39	8.39	1.00
	x = 0.1	C		8.31	1.00
	x = 0.2	C		8.29	1.00
	x = 0.3	C		8.28	1.00
	x = 0.4	C		8.26	1.00
	x = 0.5	C		8.25	1.00
	x = 0.6	C		8.27	1.00
	x = 0.7	C		8.28	1.00
	x = 0.8	C		8.28	1.00
	x = 0.9	C		8.28	1.00
	x = 1.0	T	8.454	8.258	1.025

Table - 7Lattice parameters for the system $\text{CuCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$

System	Composition	Symmetry	c_{Ao}	a_{Ao}	c/a
$\text{CuCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$	x = 0.0	C	-	8.33	1.00
	x = 0.1	C	-	8.346	1.00
	x = 0.2	C	-	8.347	1.00
	x = 0.3	C	-	8.347	1.00
	x = 0.4	C	-	8.352	1.00
	x = 0.5	C	-	8.35	1.00
	x = 0.6	T + C	-	-	-
	x = 0.7	T + C	-	-	-
	x = 0.8	T	7.93	8.328	0.952
	x = 0.9	T	7.83	8.42	0.930
	x = 1.0	T	7.788	8.532	0.912

Table - 8

Lattice parameters for the system $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$

Composition	Symmetry	a_{AO}	a_{AO}	c/a
$\text{Zn}_{0.75}\text{Ni}_{0.075}\text{Mn}_{2.175}\text{O}_4$	T	9.312	8.107	1.148
$\text{Zn}_{0.75}\text{Ni}_{0.225}\text{Mn}_{2.025}\text{O}_4$	T	9.128	8.150	1.12
$\text{Zn}_{0.75}\text{Ni}_{0.375}\text{Mn}_{1.875}\text{O}_4$	T	8.518	8.23	1.035
$\text{Zn}_{0.75}\text{Ni}_{0.525}\text{Mn}_{1.725}\text{O}_4$	C	-	8.287	1.00
$\text{Zn}_{0.75}\text{Ni}_{0.60}\text{Mn}_{1.65}\text{O}_4$	C	-	8.29	1.00
$\text{Zn}_{0.75}\text{Ni}_{0.675}\text{Mn}_{1.575}\text{O}_4$	C	-	8.262	1.00
$\text{Zn}_{0.6}\text{Ni}_{0.06}\text{Mn}_{2.34}\text{O}_4$	T	9.321	8.113	1.148
$\text{Zn}_{0.6}\text{Ni}_{0.18}\text{Mn}_{2.22}\text{O}_4$	T	9.161	8.11	1.129
$\text{Zn}_{0.6}\text{Ni}_{0.3}\text{Mn}_{2.1}\text{O}_4$	T	8.93	8.27	1.08
$\text{Zn}_{0.6}\text{Ni}_{0.42}\text{Mn}_{1.98}\text{O}_4$	C	-	8.272	1.00
$\text{Zn}_{0.6}\text{Ni}_{0.48}\text{Mn}_{1.92}\text{O}_4$	C	-	8.28	1.00
$\text{Zn}_{0.6}\text{Ni}_{0.54}\text{Mn}_{1.86}\text{O}_4$	C	-	8.29	1.00
$\text{Zn}_{0.5}\text{Ni}_{0.05}\text{Mn}_{2.45}\text{O}_4$	T	9.32	8.115	1.148
$\text{Zn}_{0.5}\text{Ni}_{0.15}\text{Mn}_{2.35}\text{O}_4$	T	9.21	8.15	1.13
$\text{Zn}_{0.5}\text{Ni}_{0.25}\text{Mn}_{2.25}\text{O}_4$	T	9.05	8.28	1.087
$\text{Zn}_{0.5}\text{Ni}_{0.45}\text{Mn}_{2.05}\text{O}_4$	C	-	8.305	1.00

Table - 9

Lattice parameters for the system $\text{ZnFe}_{2x}\text{Mn}_{2-2x}\text{O}_4$

System	Composition	Symmetry	c_{A0}	a_{A0}	c/a
$\text{ZnFe}_{2x}\text{Mn}_{2-2x}\text{O}_4$	x = 0.0	T	9.24	8.10	1.14
	x = 0.1	T	9.16	8.10	1.131
	x = 0.2	T	9.07	8.13	1.115
	x = 0.3	T	8.9	8.15	1.091
	x = 0.4	T	8.77	8.17	1.074
	x = 0.5	T	8.7	8.25	1.054
	x = 0.6	T + C	-	-	-
	x = 0.7	C	-	8.44	1.00
	x = 0.8	C	-	8.43	1.00
	x = 0.9	C	-	8.43	1.00
	x = 1.0	C	-	8.42	1.00

In a few compounds from the system $\text{NiCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$, intensity calculation has also been done in order to study the cation distribution. The calculated and observed intensities have been given in Table Nos. 10 to 13.

The compounds $\text{ZnCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$ with x = 0.1, 0.2, 0.3, 0.4 and 0.5 are found to be isomorphous with the tetragonal hausmannite Mn_3O_4 structure (space group $I_{41}/\text{amd}-D_{4h}^{19}$). A trace of cubic spinel seems to be present in case of compound x = 0.5. The compounds with x = 0.6, 0.7, 0.8 and 0.9 are isomorphous with cubic spinels (space group $\text{Fd}3m-O_h^7$).

It is well established that both zinc manganite spinel and zinc chromite are normal spinels. The octahedral site preference energies of ions calculated by Miller⁶(1959) show that zinc ions prefer strongly the tetrahedral sites, whereas Mn^{3+} , Mn^{4+} and Cr^{3+} ions have a stronger preference for octahedral sites. Therefore, we can say that in compounds $ZnCr_{2x}Mn_{2-2x}O_4$, the tetrahedral sites are occupied by the Zn^{2+} ions and octahedral sites are occupied by chromium and manganese ions. So the formula can be written as $Zn[Cr_{2x}Mn_{2-2x}]O_4$.

It is well known that the tetragonal distortion is due to the presence of Mn^{3+} ions with the d^4 electron configuration at the octahedral sites. As the Mn^{3+} ion concentration decreases, c/a decreases and finally at a critical concentration the structure becomes cubic. Critical composition for this system is $[Mn^{3+}_{oct}] = 1.0$ i.e. $x_c = 0.5$. This value is lower than the value of 1.2 ($x_c = 0.6$) found by Finch, Sinha and Sinha¹³ (1957) for many manganites.

In case of the system $NiCr_{2x}Mn_{2-2x}O_4$ all the compounds with $0 \leq x \leq 0.9$ are cubic spinels. Pure nickel chromite (i.e. $x = 1$) is known to be tetragonal at room temperature. The variation of 'a' with composition is known shown in Figure 7. An inflexion in the value of 'a' can be seen at $x = 0.5$. This corresponds to an inflexion in the cation distribution as can be seen from a plot of various cation concentrations at the octahedral and the tetrahedral

sites given in the same figure. The cation distribution has been arrived at on the basis of intensity calculation given below.

It is known that NiMn_2O_4 is inverse spinel, whereas NiCr_2O_4 is a normal spinel. According to the well known octahedral site preference energies, Cr^{3+} ions have the strongest octahedral preference and are always found at these sites. It is, therefore, reasonable to assume that they are present at the octahedral sites. Ni^{2+} and Mn^{3+} ions, on the other hand, have a comparable value for the octahedral preference. In pure nickel manganite the Ni^{2+} ions displace the Mn^{3+} ions from the octahedral sites, but one cannot be sure that this would be so in presence of Cr^{3+} ions. For example, when Cr^{3+} ions are present, the oxygen ion parameter u , may be having a value favourable to 3^+ ions at the octahedral site enabling the Mn^{3+} ions to displace the Ni^{2+} ions from the octahedral sites.

Placing all the Cr^{3+} ions at the octahedral sites and leaving the distribution of other cations unsettled, the molecular formula becomes $\text{Ni}_a^{2+}\text{Mn}_{1-a}^{3+}[\text{Cr}_{2x}^{3+}\text{Mn}_{1-2x+a}^{3+}\text{Ni}_{1-a}^{2+}]_4\text{O}_4$. The X-ray intensities have been calculated for the various compounds (i.e. the various values of x) using different cation distributions (i.e. different values of a).

Reflection intensities have been calculated by using the formula:

$$I_{hkl} \propto F^2 \times p \times \frac{1 + \cos^2 2\theta}{\cos \theta \sin^2 \theta}$$

where $|F|$ denotes the structure factor, p the multiplicity factor and the remaining part comprises the combined Lorentz and polarization factors. We have not done the corrections for the absorption and thermal vibrations. The structure factor $|F|$ for each of the reflections was calculated by making use of the ionic scattering power of these different ions, $f_{Ni^{2+}}$, $f_{Mn^{3+}}$, $f_{Cr^{3+}}$, $f_{O^{2-}}$ for different cation distributions in the lattice. The ionic scattering factor ' f ' for these different ions has been computed from the standard values given in the international tables for the determination of crystal structures Vol. II, 1935. The scattering power for the tetrahedral cation (f_A) and that for the octahedral cation (f_B) are:

$$f_A = a f_{Ni^{2+}} + b f_{Mn^{3+}}$$

$$f_B = \frac{2x f_{Cr^{3+}} + (1-2x+a) f_{Mn^{3+}} + (1-a) f_{Ni^{2+}}}{2}$$

Intensities have been calculated for all reflections observed by taking oxygen parameter as $u = 0.375$ (this value of u has been refined later). Reflections 220, 400 and 422 are fairly sensitive to the cation distribution. The ratios of intensities of reflections I_{220}/I_{422} , I_{422}/I_{400} were obtained for the various values of ' a '. The value of ' a ' has been fixed by comparing the calculated ratios with the corresponding ratios of the observed reflection intensities which are obtained by the automatic recording diffractometer using Fe-K α radiation.

After fixing the value of 'a' we proceed to determine value of oxygen parameter u. The reflection most sensitive to change in the value of 'u' is 111. We calculate the intensity of 111 reflection for different values of u, and find out the value which gives the best match. This new value of u is taken and the intensity of 220, 400, 422, reflections are recalculated. This process of refinement is continued till the value of 'a' and 'u' continue to change. Taking the final value of 'a' and 'u', we calculate the intensities for all the observed reflections. Results are presented in Table Nos. 10 to 13.

From these results it is clear that in nickel chromite-manganite also, Ni^{2+} ions have a stronger preference for the octahedral sites than the Mn^{3+} ions. It is, therefore, reasonable to conclude that in case of $0 < x \leq 0.5$ all the Cr^{3+} and Ni^{2+} ions are in octahedral sites and Mn^{3+} ions are in tetrahedral and octahedral sites. This is also supported by the fact that the structure is cubic and not tetragonal. If the octahedral sites left vacant by the Cr^{3+} ions were all occupied by Mn^{3+} then the structure should have been tetragonal.

The cation distribution for the complete series is given in Table No. 14.

Table - 10

Observed and calculated intensities for
 $\text{NiCr}_{1.2}\text{Mn}_{0.8}\text{O}_4$

hkl	Intensity Obs.	Intensity Cal.	Oxygen parameter
111	5	7	-
220	40	39	u = 0.387
311	100	100	
222	10	4	
400	30	32	
422	10	9	
511,333	50	36	
440	70	61	

Table - 11

Observed and calculated intensities for
 $\text{NiCr}_{1.4}\text{Mn}_{0.6}\text{O}_4$

hkl	Intensity Obs.	Intensity Cal.	Oxygen parameter
111	10	10	
220	40	41	u = 0.390
311	100	100	
222	10	4	
400	25	30	
422	10	10	
511,333	50	36	
440	70	60	

Table - 12

Observed and calculated intensities for
 $\text{NiCr}_{1.6}\text{Mn}_{0.4}\text{O}_4$

<u>hkl</u>	<u>Intensity Obs.</u>	<u>Intensity Cal.</u>	<u>Oxygen parameter</u>
111	10	10	
220	40	44	u = 0.390
311	100	100	
222	5	3	
400	30	28	
422	15	10	
511, 333	50	36	
440	70	60	

Table - 13

Observed and calculated intensities for
 $\text{NiCr}_{1.8}\text{Mn}_{0.2}\text{O}_4$

<u>hkl</u>	<u>Intensity Obs.</u>	<u>Intensity Cal.</u>	<u>Oxygen parameter</u>
111	15	12	
220	40	40	u = 0.393
311	100	100	
222	15	16	
400	30	24	
422	15	12	
511, 333	50	45	
440	70	54	

Table - 14

Cation distribution for the system $\text{NiCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$

Composition	Formula
$x = 0.1$	$\text{Mn}_{1.0}^{3+}[\text{Cr}_{0.2}^{3+}\text{Ni}_{1.0}^{2+}\text{Mn}_{0.8}^{3+}]_4\text{O}_4$
$x = 0.2$	$\text{Mn}_{1.0}^{3+}[\text{Cr}_{0.4}^{3+}\text{Ni}_{1.0}^{2+}\text{Mn}_{0.6}^{3+}]_4\text{O}_4$
$x = 0.3$	$\text{Mn}_{1.0}^{3+}[\text{Cr}_{0.6}^{3+}\text{Ni}_{1.0}^{2+}\text{Mn}_{0.4}^{3+}]_4\text{O}_4$
$x = 0.4$	$\text{Mn}_{1.0}^{3+}[\text{Cr}_{0.8}^{3+}\text{Ni}_{1.0}^{2+}\text{Mn}_{0.2}^{3+}]_4\text{O}_4$
$x = 0.5$	$\text{Mn}_{1.0}^{3+}[\text{Cr}_{1.0}^{3+}\text{Ni}_{1.0}^{2+}]_4\text{O}_4$
$x = 0.6$	$\text{Mn}_{0.8}^{3+}\text{Ni}_{0.2}^{2+}[\text{Cr}_{1.2}^{3+}\text{Ni}_{0.8}^{2+}]_4\text{O}_4$
$x = 0.7$	$\text{Mn}_{0.6}^{3+}\text{Ni}_{0.4}^{2+}[\text{Cr}_{1.4}^{3+}\text{Ni}_{0.6}^{2+}]_4\text{O}_4$
$x = 0.8$	$\text{Mn}_{0.4}^{3+}\text{Ni}_{0.6}^{2+}[\text{Cr}_{1.6}^{3+}\text{Ni}_{0.4}^{2+}]_4\text{O}_4$
$x = 0.9$	$\text{Mn}_{0.2}^{3+}\text{Ni}_{0.8}^{2+}[\text{Cr}_{1.8}^{3+}\text{Ni}_{0.2}^{2+}]_4\text{O}_4$
$x = 1.0$	$\text{Ni}_{1.0}^{2+}[\text{Cr}_{2.0}^{3+}]_4\text{O}_4$

It may be noted that there is no tetragonal distortion at $x = 0.5$, although the tetrahedral sites are occupied by the Mn^{3+} ions which are expected to cause a strong Jahn-Teller distortion with $c/a < 1$.

In the series $\text{CuCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$ compounds with $x = 0.1, 0.2, 0.3, 0.4$ and 0.5 and have the cubic spinel structure and those with 0.8 and 0.9 crystallize in the tetragonal hausmannite structure with $c/a < 1$. Delorme⁷¹(1956)

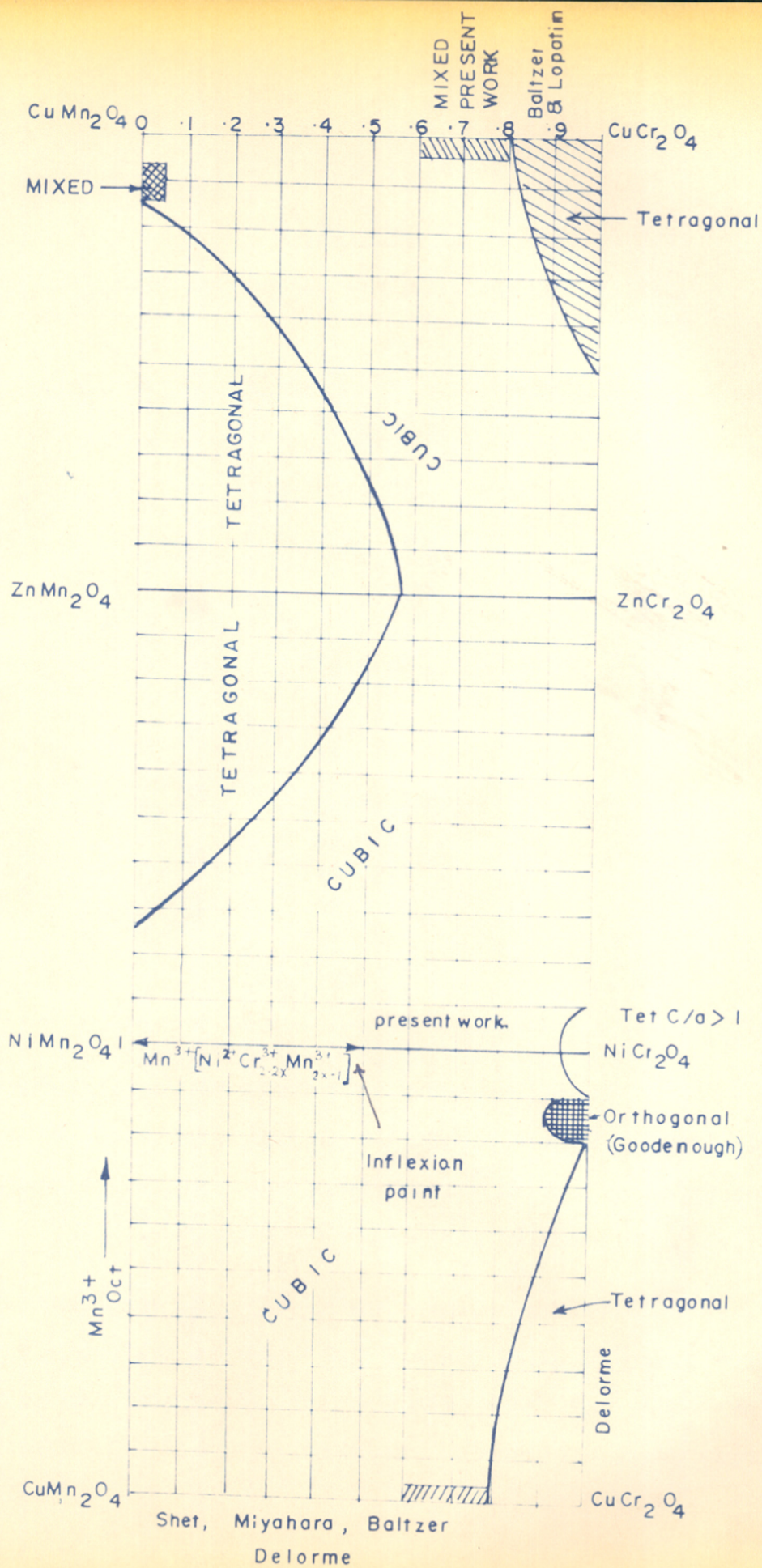


FIG.No.9 SCHEMATIC PHASE DIAGRAM FOR $(\text{Cu-Zn-Ni})(\text{Cr-Mn})_2\text{O}_4$ SYSTEM

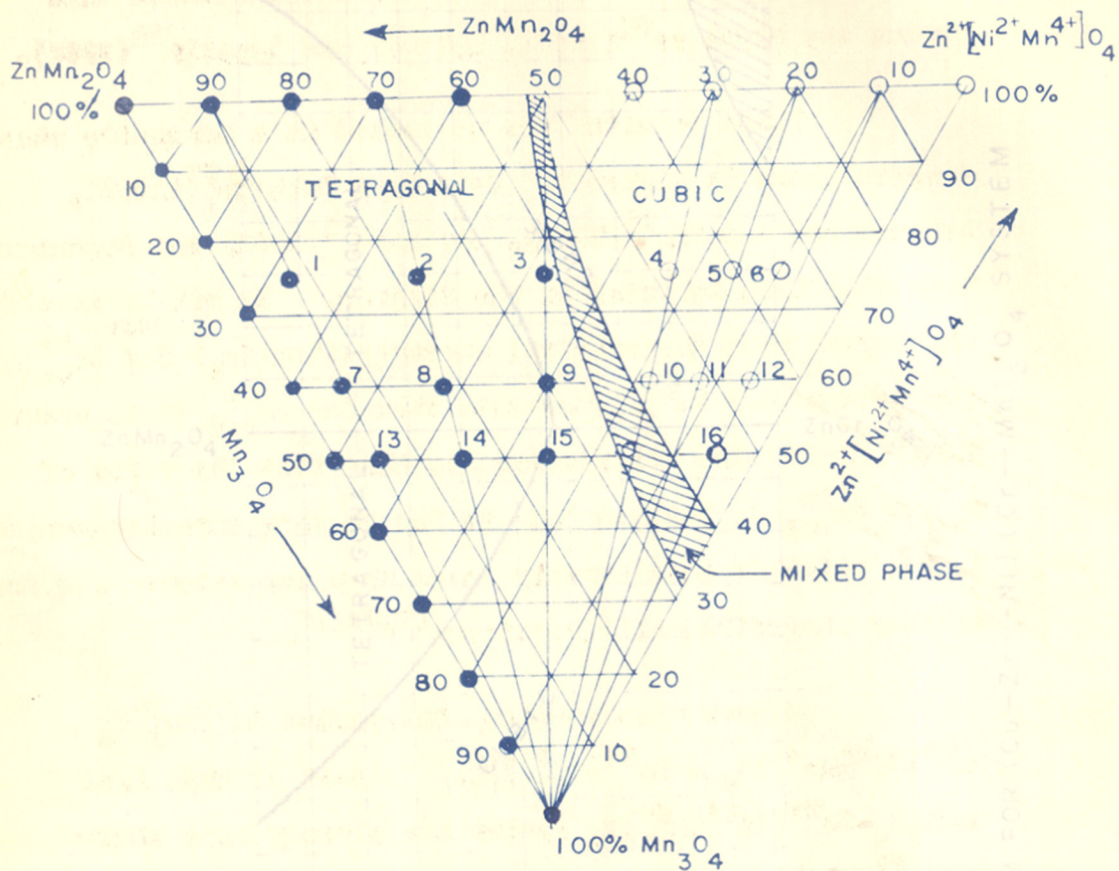


FIG. No. 10. SCHEMATIC PHASE DIAGRAM FOR THE SYSTEM $\text{ZnMn}_2\text{O}_4 - \text{Zn}^{2+}[\text{Ni}^{2+}\text{Mn}^{4+}]\text{O}_4 - \text{Mn}_3\text{O}_4$

has also studied this series. Others who studied this system are Miyahara²¹(1962), Baltzer and Lopatin²²(1964).

These results are presented in a schematic phase diagram shown in Figure 9. Data from Delorme⁷¹(1956), Baltzer and Lopatin²²(1964), Miyahara²¹(1962) and Goodenough⁷⁸ have also been included in the diagram. It can be seen from the figure that the critical concentration (x_c) for Ni_{tet}^{2+} lie between 0.9 to 1.0, whereas that for Cu_{tet}^{2+} it is around 0.5. It is also interesting to find that the value of x_c for Mn_{oct}^{3+} is between 0.3 to 0.4 in this chromite-manganite series which is considerably lower than the values 0.60 found in other manganite solid solutions^{13,22,16}.

We have also studied the system $Zn^{2+}Mn_2^{3+}O_4 - Zn^{2+}[Ni^{2+}Mn^{4+}]O_4 - Mn^{2+}[Mn_2^{3+}]O_4$. A part of this i.e. $ZnMn_2O_4 - Zn^{2+}[Ni^{2+}Mn^{4+}]O_4$ system has already been studied by Ghare²⁷(1968). Results are presented schematically in Figure 10. These compounds can be represented by the general formula $Zn_xNi_yMn_{3-x-y}O_4$. Compounds with $x = 0.75$ and $y = 0.075, 0.225$ and 0.375 are tetragonal, whereas $x = 0.75$ and $y = 0.525, 0.60$ and 0.675 , are cubic. When $x = 0.6$ and $y = 0.06, 0.18, 0.3$ the compounds are tetragonal and when $x = 0.6$ and $y = 0.42, 0.48, 0.54$ the compounds have the cubic spinel structure. When $x = 0.5$ and $y = 0.05, 0.15, 0.25$, the compound has the tetragonal structure, whereas the compound having $x = 0.05$ and $y = 0.45$ is cubic.

In the system $\text{ZnFe}_{2x}\text{Mn}_{2-2x}\text{O}_4$ compositions with $x = 0.1, 0.2, 0.3, 0.4, 0.5$ and 0.6 , crystallize in tetragonal hausmannite phase. Faint lines due to cubic spinel structure are also observed for the compound $x = 0.6$. The compounds with $x = 0.7, 0.8, 0.9$, are cubic and there is no trace of any tetragonal phase. These investigations are also done by Blasse⁷⁹ (1965), and O'Keeffe⁵³ (1961). Once again, we find that in this system also the value of the critical concentration (x_c) of the $\text{Mn}_{\text{Oct}}^{3+}$ ion required to bring about the tetragonal distortion is only 0.3 .

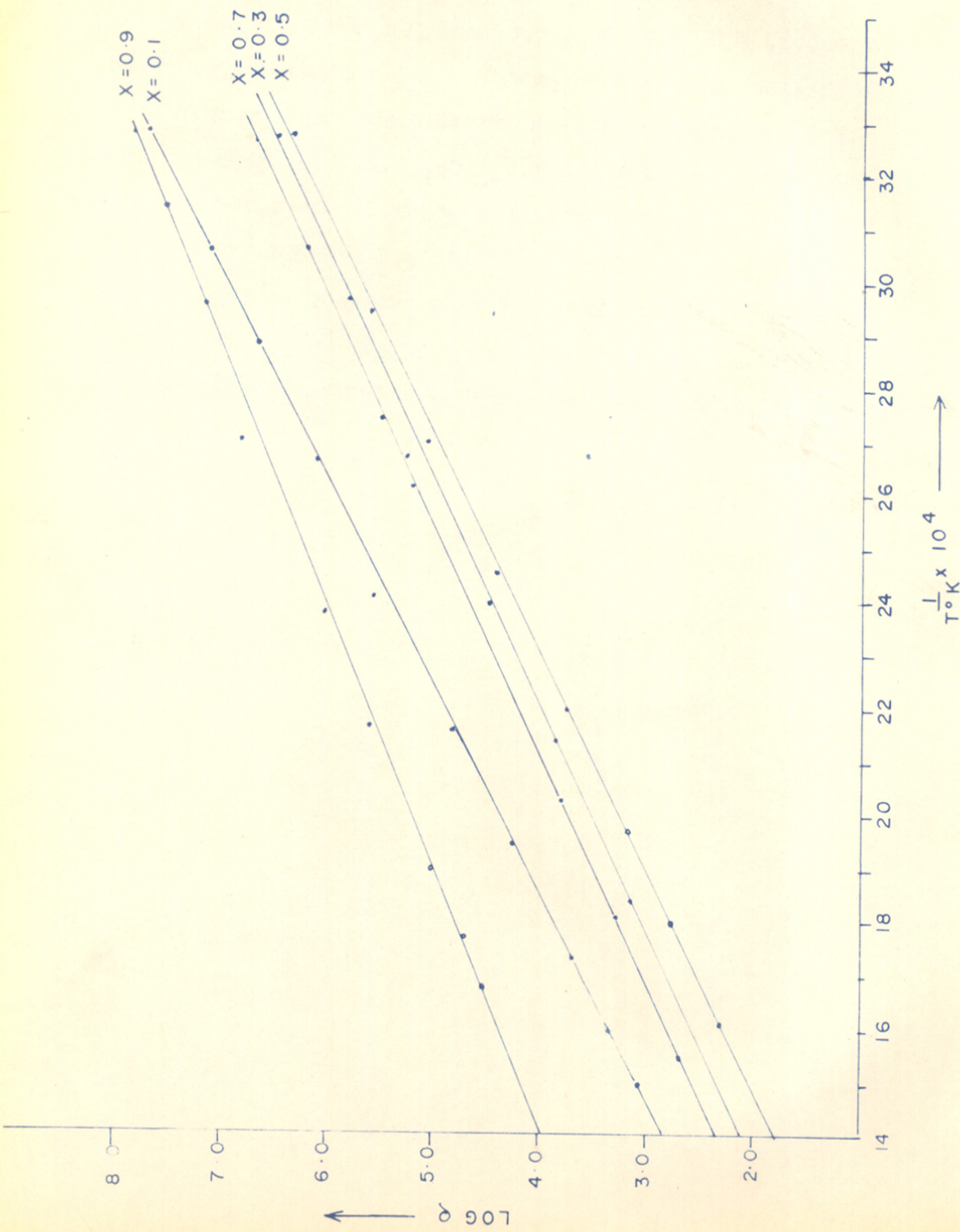


FIG. No. 11. PLOTS OF $\log Q$ AS A FUNCTION OF RECIPROCAL TEMPERATURE FOR THE SYSTEM $Zn-Cr-Mn-O$

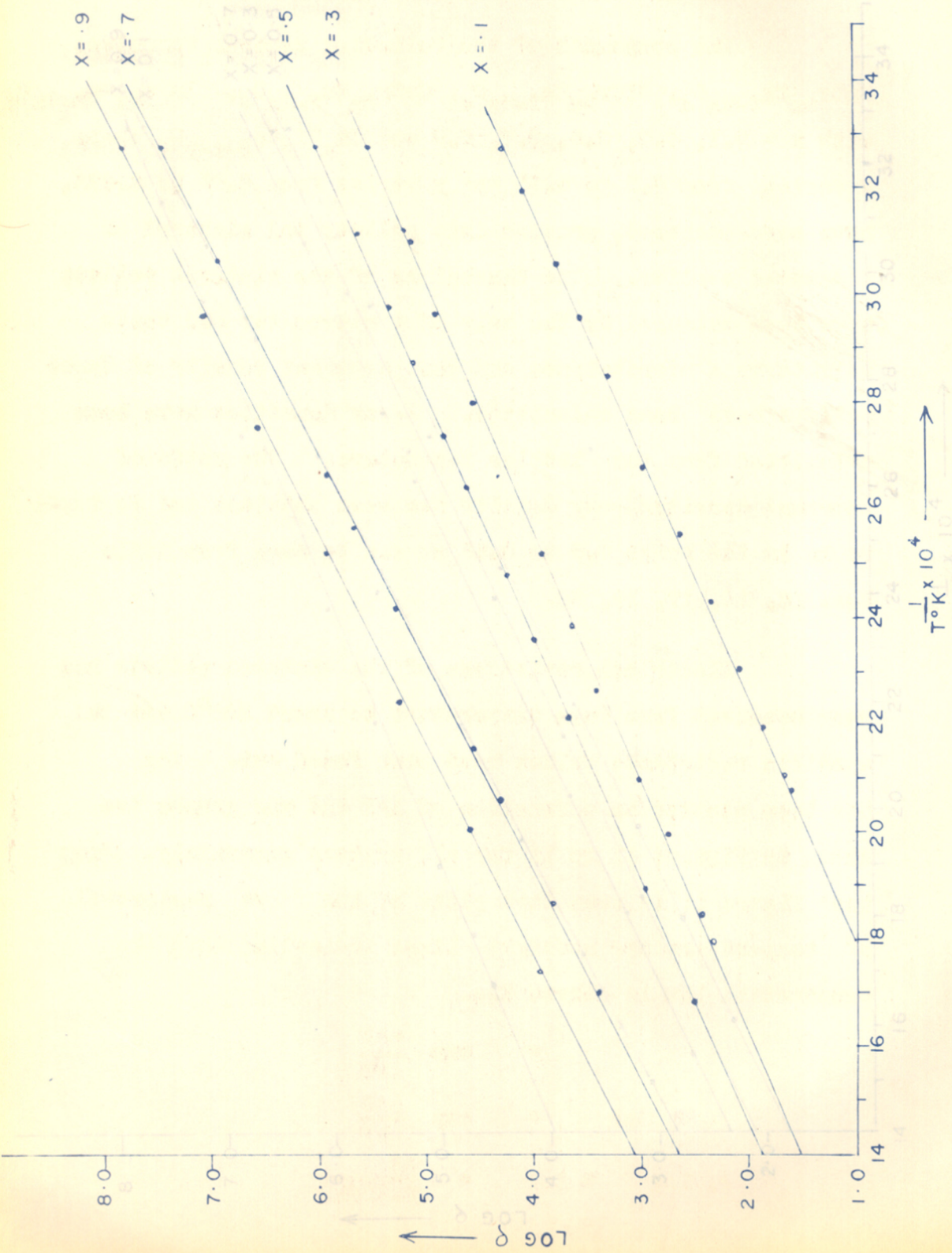


FIG.No 12. PLOTS OF LOG Q AS A FUNCTION OF RECIPROCAL TEMPERATURE FOR THE SYSTEM $\text{NiCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$

3.2. ELECTRICAL CONDUCTIVITY MEASUREMENTS

The compounds of the following general formulae:
 $\text{ZnCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$, $\text{NiCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$, $\text{CuCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$, $\text{ZnFe}_{2x}\text{Mn}_{2-2x}\text{O}_4$
 with $x = 0.1, 0.3, 0.5, 0.7, 0.9$ and $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$ where
 x varies from 0.5 to 0.75 and y varies from 0.05 to 0.675,
 have been prepared, pressed into pellets and sintered as
 discussed earlier. The dimensions of the sintered pellets
 have been measured by the help of a micrometer and their
 weights on a microbalance and the apparent density of these
 pellets have been calculated. X-ray densities have been
 calculated from the lattice parameters. The ratio of
 apparent density/X-ray density has been obtained and is found
 to be in the range 0.5 to 0.85 as can be seen from Table
 Nos. 15, 16, 17, 19, 20.

Electrical resistance of the sintered pellets has
 been measured from room temperature to about 300°C and the
 specific resistance values have been found out. $\log \rho$
 has been plotted as a function of $1/T$ and the graphs are
 shown in Figures 11 to 18 for all systems separately. From
 the figure it is seen that plots of $\log \rho$ vs reciprocal
 of temperature are straight lines indicating that the
 exponential law is obeyed i.e.

$$\begin{aligned}\sigma &= \sigma_0 \exp \frac{-\Delta E}{kT} \\ \text{or } \rho &= \rho_0 \exp \frac{\Delta E}{kT} \\ \therefore \log \rho &= \log \rho_0 + \frac{\Delta E}{2.303kT}\end{aligned}$$

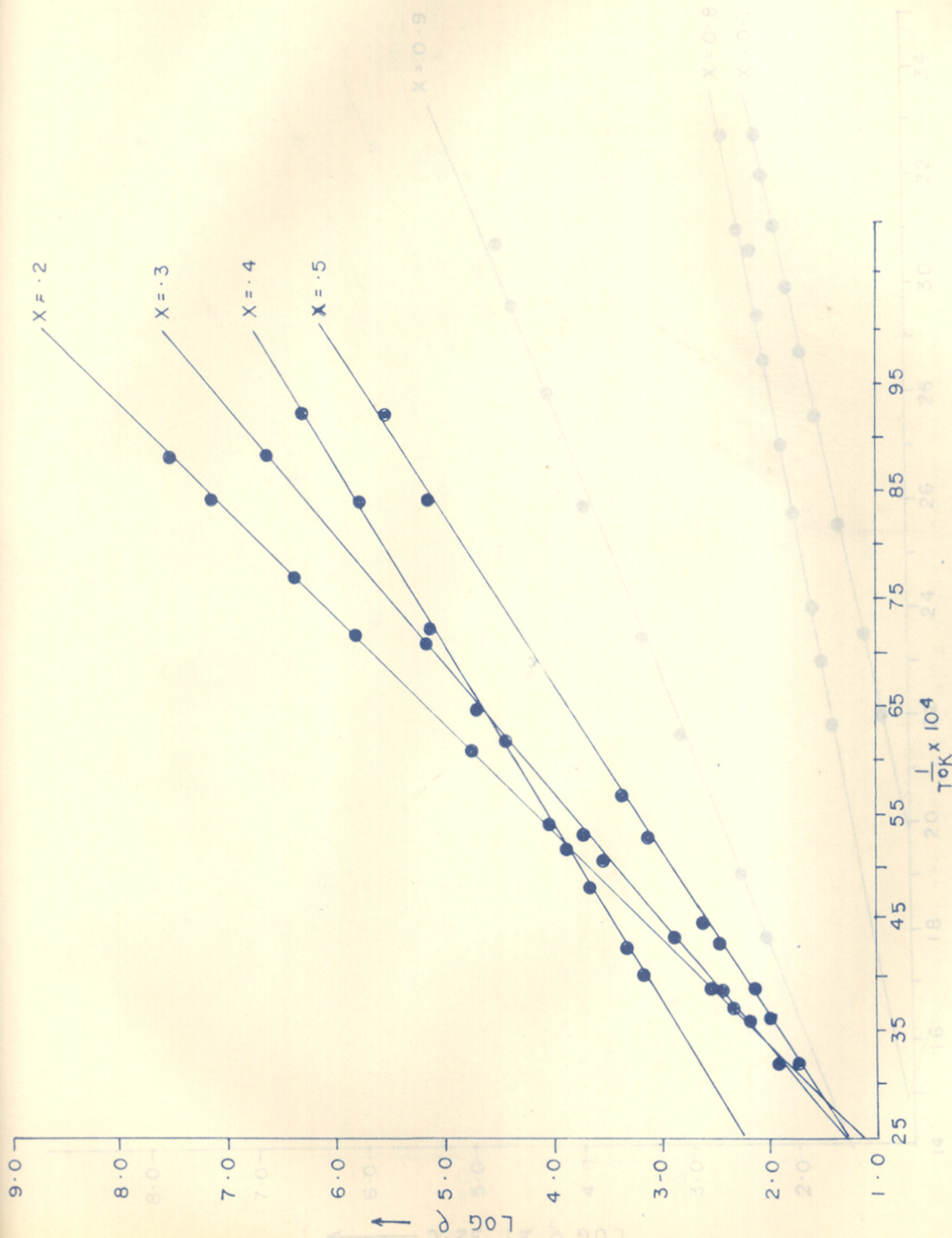


FIG. 13 PLOTS OF $\log Q$ AS A FUNCTION OF RECIPROCAL TEMPERATURE FOR THE SYSTEM $\text{CuCr}_{2-x}\text{Mn}_x\text{O}_4$

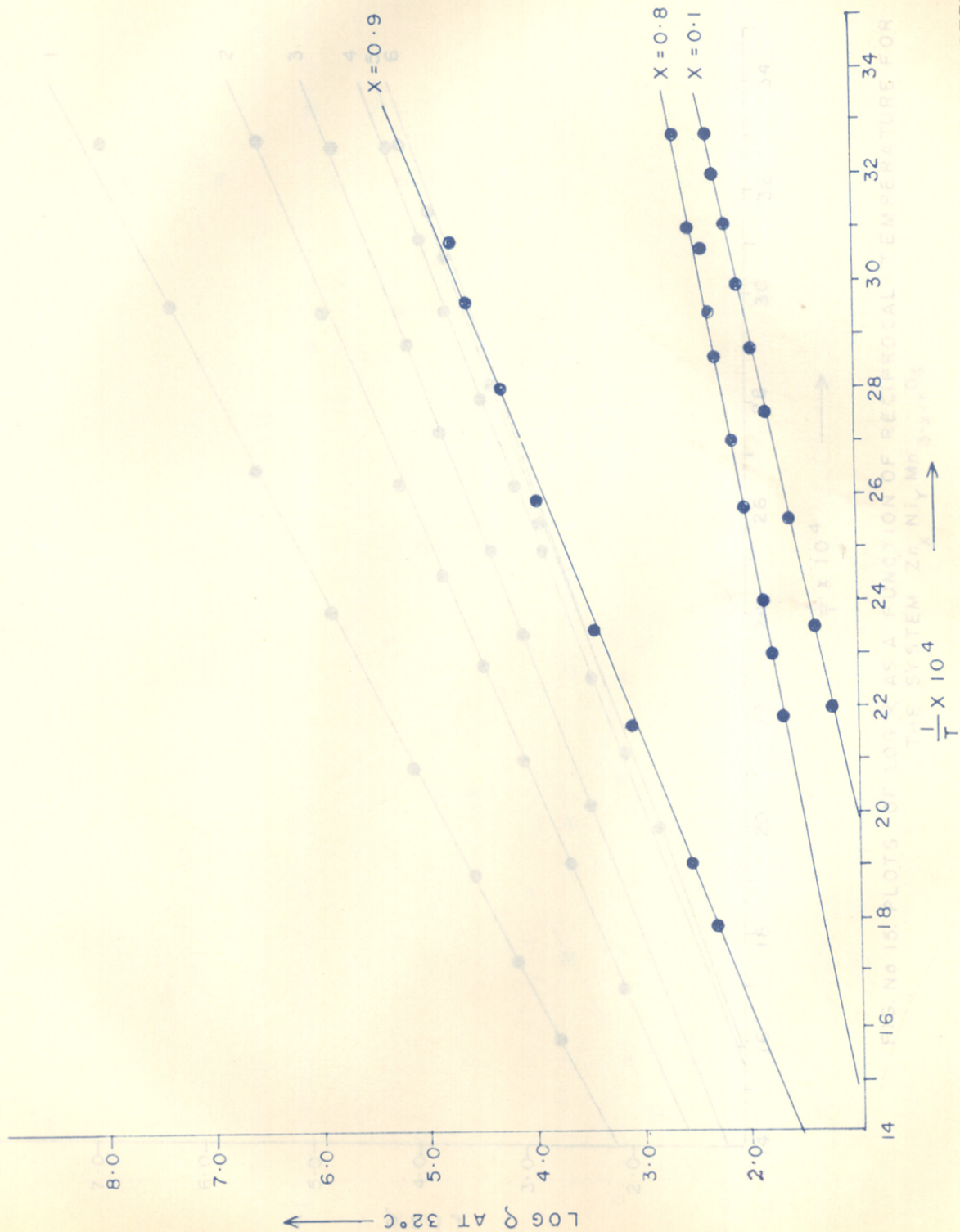


FIG.14. PLOTS OF $\log Q$ AS A FUNCTION OF RECIPROCAL TEMPERATURE FOR THE SYSTEM $\text{CuCr}_2\text{Mn}_{2-2x}\text{O}_4$

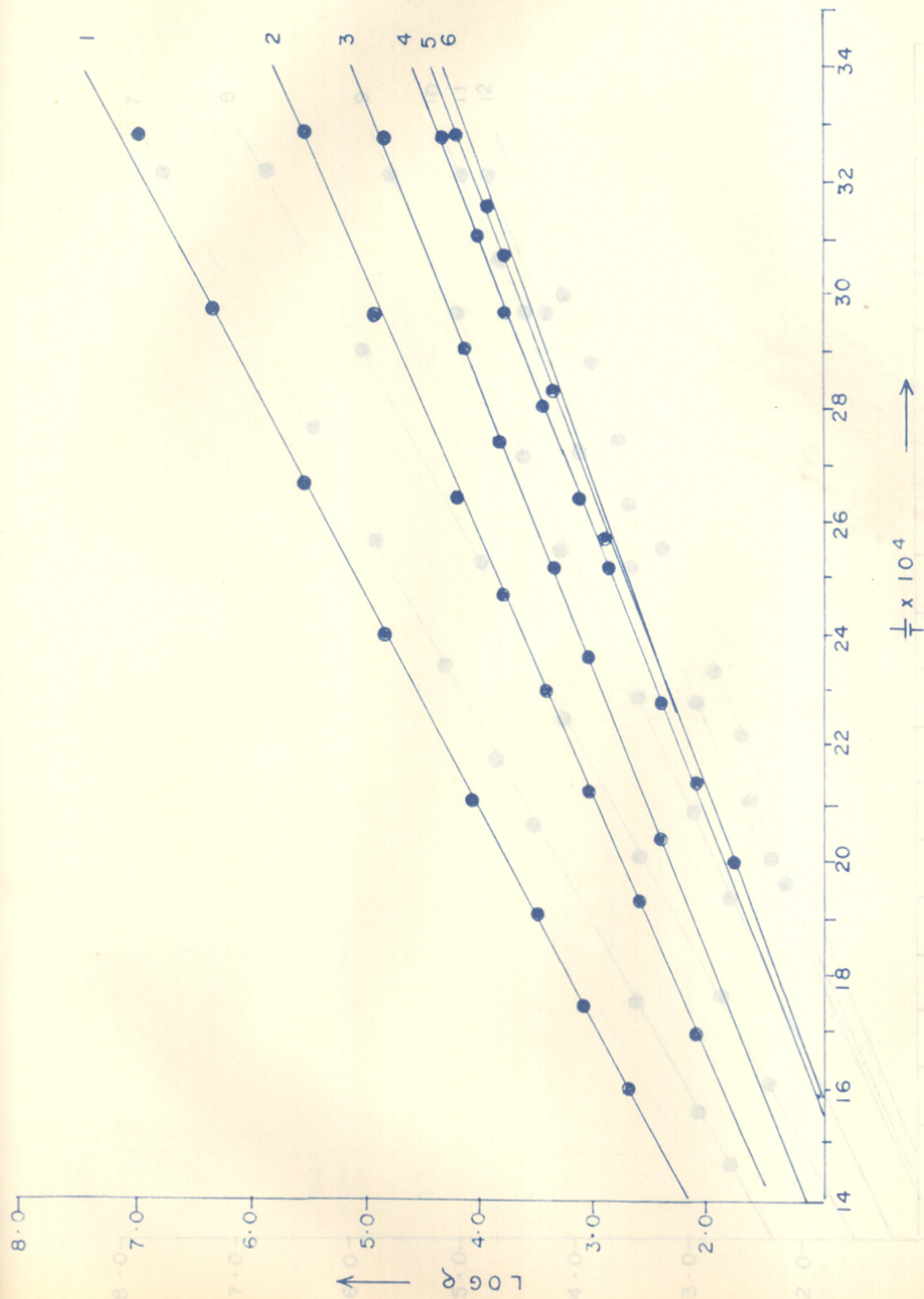


FIG. No 15. PLOTS OF $\log Q$ AS A FUNCTION OF RECIPROCAL TEMPERATURE FOR THE SYSTEM $Zn_x Ni_y Mn_{3-x-y}O_4$

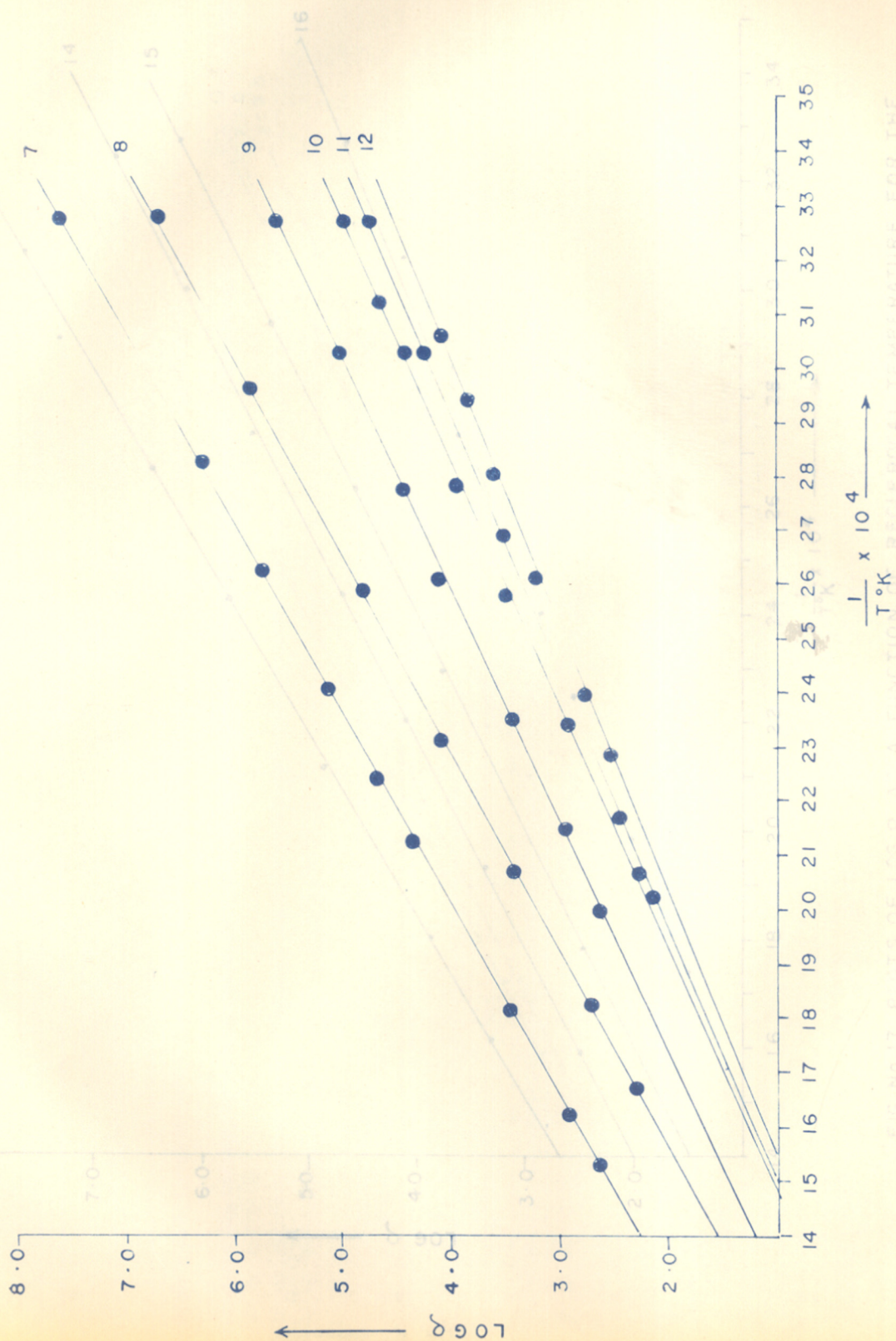


FIG No. 16 PLOTS OF $\log Q$ AS A FUNCTION OF RECIPROCAL TEMPERATURE FOR THE SYSTEM $Zn_x Ni_y Mn_{3-x-y}O_4$

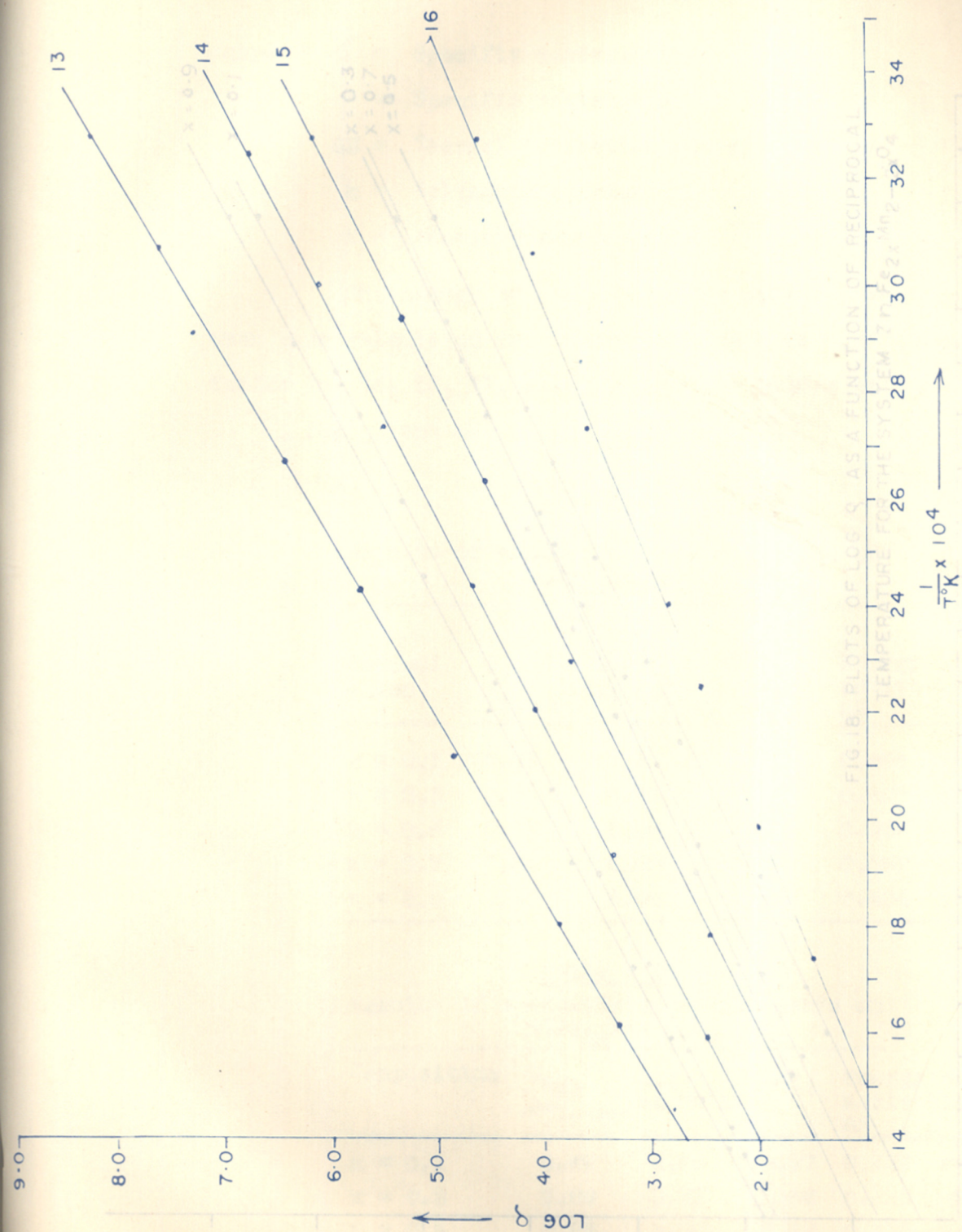
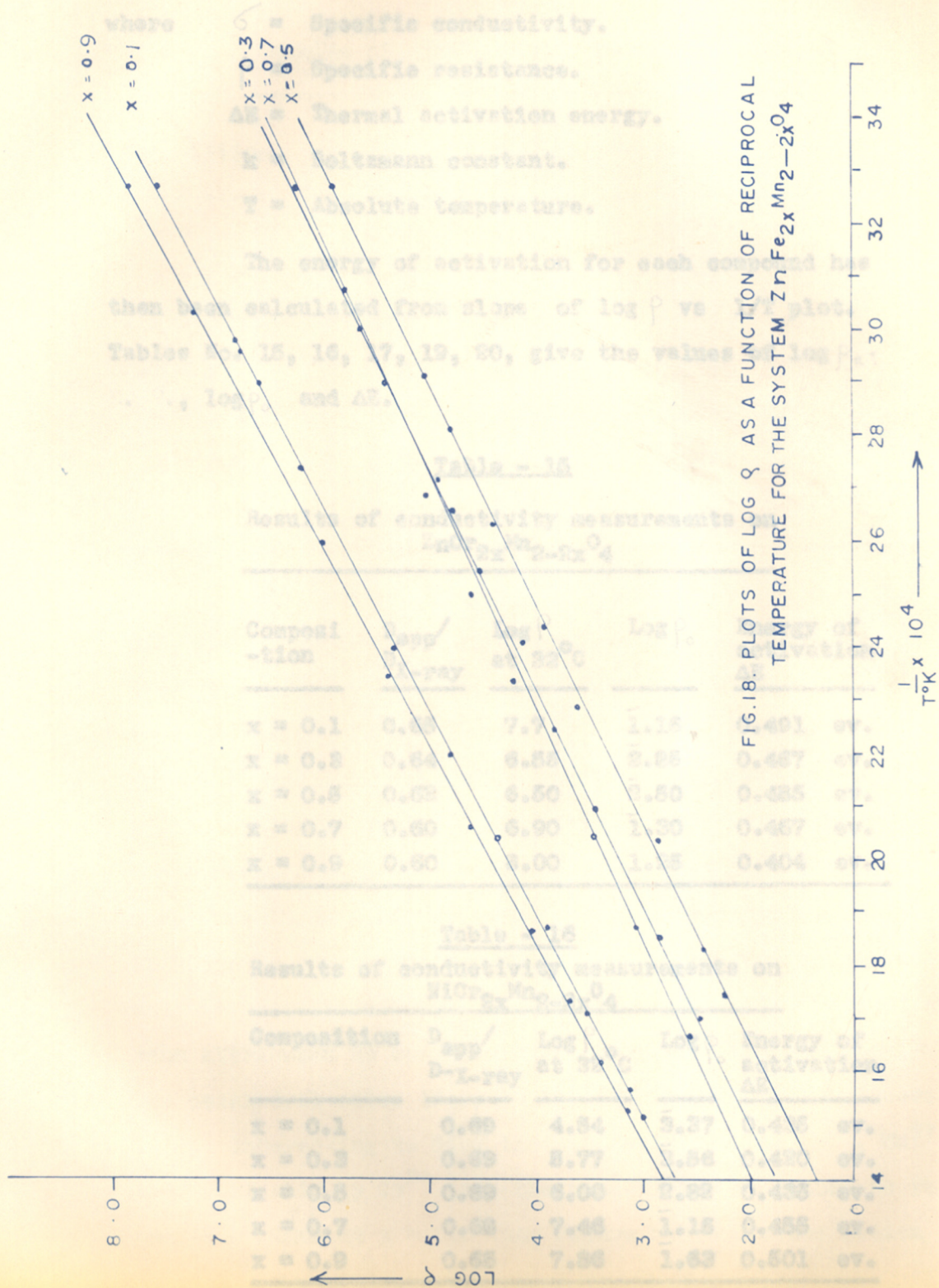


FIG. No. 17. PLOTS OF $\log Q$ AS A FUNCTION OF RECIPROCAL TEMPERATURE FOR THE SYSTEM $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$

FIG. No. 18. PLOTS OF $\log Q$ AS A FUNCTION OF RECIPROCAL TEMPERATURE FOR THE SYSTEM $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$



where σ = Specific conductivity.
 ρ = Specific resistance.
 ΔE = Thermal activation energy.
 k = Boltzmann constant.
 T = Absolute temperature.

The energy of activation for each compound has then been calculated from slope of $\log \rho$ vs $1/T$ plot. Tables No. 15, 16, 17, 19, 20, give the values of $\log \rho_{R.T}$, $\log \rho_0$, and ΔE .

Table - 15

Results of conductivity measurements on
 $ZnCr_{2x}Mn_{2-2x}O_4$

Composi- -tion	$D_{app}/$ D_{X-ray}	$\log \rho$ at 32°C	$\log \rho_0$	Energy of activation ΔE
$x = 0.1$	0.65	7.7	1.16	0.491 ev.
$x = 0.3$	0.64	6.55	2.85	0.467 ev.
$x = 0.5$	0.62	6.50	2.50	0.435 ev.
$x = 0.7$	0.60	6.90	1.30	0.467 ev.
$x = 0.9$	0.60	8.00	1.25	0.404 ev.

Table - 16

Results of conductivity measurements on
 $NiCr_{2x}Mn_{2-2x}O_4$

Composition	$D_{app}/$ D_{X-ray}	$\log \rho$ at 32°C	$\log \rho_0$	Energy of activation ΔE
$x = 0.1$	0.69	4.54	3.37	0.435 ev.
$x = 0.3$	0.69	5.77	3.56	0.420 ev.
$x = 0.5$	0.69	6.00	2.82	0.435 ev.
$x = 0.7$	0.68	7.46	1.15	0.455 ev.
$x = 0.9$	0.65	7.86	1.63	0.501 ev.

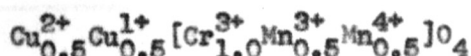
Table - 17

Results of conductivity measurements on
 $\text{CuCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$

Composition	$D_{\text{app}}/D_{\text{x-ray}}$	$\log \rho$ at 32°	Energy of activation ΔE
x = 0.1	0.80	2.350	0.2100 ev.
x = 0.2	0.81	2.099	0.1980 ev.
x = 0.3	0.82	2.183	0.1624 ev.
x = 0.4	0.79	2.228	0.1188 ev.
x = 0.5	0.79	1.696	0.1287 ev.
x = 0.8	0.70	2.70	0.1782 ev.
x = 0.9	0.65	5.20	0.384 ev.

In case of $\text{CuCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$ with x = 0.2, 0.3, 0.4, 0.5, the measurement of electrical conductivity has been done from 90°K to 300°K as the resistance at room temperature is very small. The plot of $\log \rho$ vs $1/T$ is shown in Figure 13 and the activation energy is calculated from the slope of $\log \rho$ vs $1/T$ plot. This graph is also observed to be straight line. It may be noted that most of the compounds in this series have very low resistance. CuMn_2O_4 is known to have a resistance of 10-50 Ω at room temperature and the activation energy of 0.25 ev. These low values have been attributed to the coexistence of Mn^{3+} and Mn^{4+} ions at the octahedral sites (formula $\text{Cu}^{1+}[\text{Mn}^{3+} + \text{Mn}^{4+}]_2\text{O}_4$). However, it is interesting to find that on replacing the Mn^{3+} , Mn^{4+} ions partially by Cr^{3+} ions the resistivity continues to fall and is minimum at x = 0.5 (see Figure 21) where the cation

distribution is expected to be:



This observation raises the possibility that tetrahedral cations also take part in conduction process, at least in spinels containing copper ions at the tetrahedral sites. In the compound under consideration the tetrahedral site is occupied by the Cu^{2+} and Cu^{1+} ions in equal proportion which increases the electron transfer probability. This point would be taken up again under discussion.

The thermoelectric coefficient (S) of these compounds have also been measured at temperatures (mean) from 70° to 100°C . All the compounds are of p-type and the value of ST is very small indicating that the Fermi level is very close to the conduction level. The values are summarised in Table 18.

Table - 18

Thermoelectric coefficients of $\text{Cu}[\text{Cr}_{2x}\text{Mn}_{2-2x}\text{O}_4]$

Composition	Values of ST at different temperatures			
	343°K	353°K	363°K	373°K
x = 0.1	0.0106	0.012	0.0125	0.0129
x = 0.2	0.0164	0.0165	0.0153	0.0148
x = 0.3	0.0093	0.0094	0.0096	0.0098
x = 0.4	0.0092	0.0094	0.0097	0.0099
x = 0.5	0.0040	0.0045	0.0048	0.0051
x = 0.6	0.0070	0.0064	0.0057	0.0052
x = 0.7	0.0042	0.0048	0.0038	0.0037
x = 0.8	0.0033	0.0032	0.0025	0.0022

Table - 19

Results of conductivity measurements on $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$

Composition	$\frac{D_{\text{app}}}{D_{\text{x-ray}}}$	$\log \rho$ at 32°C	$\log \rho$	Energy of activation ΔE	
$\text{Zn}_{0.75}\text{Ni}_{0.075}\text{Mn}_{2.175}\text{O}_4$	0.65	7.25	2.45	0.528	ev.
$\text{Zn}_{0.75}\text{Ni}_{0.225}\text{Mn}_{2.025}\text{O}_4$	0.70	5.92	2.73	0.456	ev.
$\text{Zn}_{0.75}\text{Ni}_{0.375}\text{Mn}_{1.875}\text{O}_4$	0.76	5.02	2.89	0.410	ev.
$\text{Zn}_{0.75}\text{Ni}_{0.525}\text{Mn}_{1.725}\text{O}_4$	0.80	4.47	2.12	0.396	ev.
$\text{Zn}_{0.75}\text{Ni}_{0.6}\text{Mn}_{1.65}\text{O}_4$	0.82	4.31	3.86	0.3802	ev.
$\text{Zn}_{0.75}\text{Ni}_{0.675}\text{Mn}_{1.575}\text{O}_4$	0.85	4.24	3.16	0.3664	ev.
$\text{Zn}_{0.6}\text{Ni}_{0.06}\text{Mn}_{2.34}\text{O}_4$	0.65	7.62	2.34	0.5564	ev.
$\text{Zn}_{0.6}\text{Ni}_{0.18}\text{Mn}_{2.22}\text{O}_4$	0.67	6.79	3.81	0.5347	ev.
$\text{Zn}_{0.6}\text{Ni}_{0.3}\text{Mn}_{2.1}\text{O}_4$	0.70	5.66	2.11	0.4654	ev.
$\text{Zn}_{0.6}\text{Ni}_{0.42}\text{Mn}_{1.98}\text{O}_4$	0.75	5.07	3.82	0.4376	ev.
$\text{Zn}_{0.6}\text{Ni}_{0.48}\text{Mn}_{1.92}\text{O}_4$	0.81	4.93	2.012	0.4158	ev.
$\text{Zn}_{0.6}\text{Ni}_{0.54}\text{Mn}_{1.86}\text{O}_4$	0.78	4.58	2.001	0.396	ev.
$\text{Zn}_{0.5}\text{Ni}_{0.05}\text{Mn}_{2.45}\text{O}_4$	0.72	8.27	3.23	0.5841	ev.
$\text{Zn}_{0.5}\text{Ni}_{0.15}\text{Mn}_{2.35}\text{O}_4$	0.67	6.87	2.40	0.5109	ev.
$\text{Zn}_{0.5}\text{Ni}_{0.25}\text{Mn}_{2.25}\text{O}_4$	0.75	6.10	3.91	0.4950	ev.
$\text{Zn}_{0.5}\text{Ni}_{0.45}\text{Mn}_{2.05}\text{O}_4$	0.81	4.70	3.96	0.4150	ev.

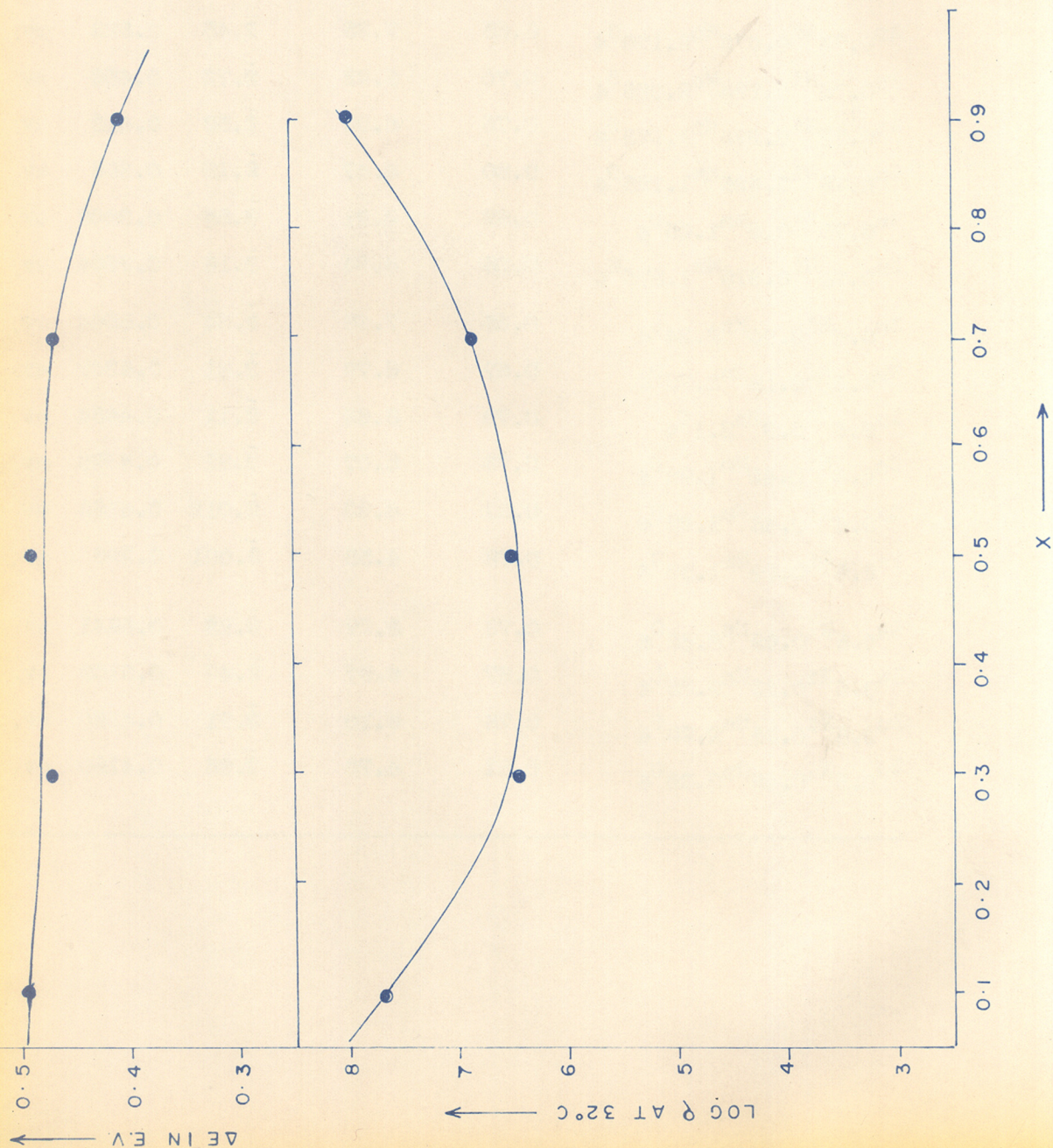


FIG. No. 19 PLOTS OF ΔE AND $\log \rho$ AS A FUNCTION OF COMPOSITION FOR $ZnCr_{2x}Mn_{2-2x}O_4$

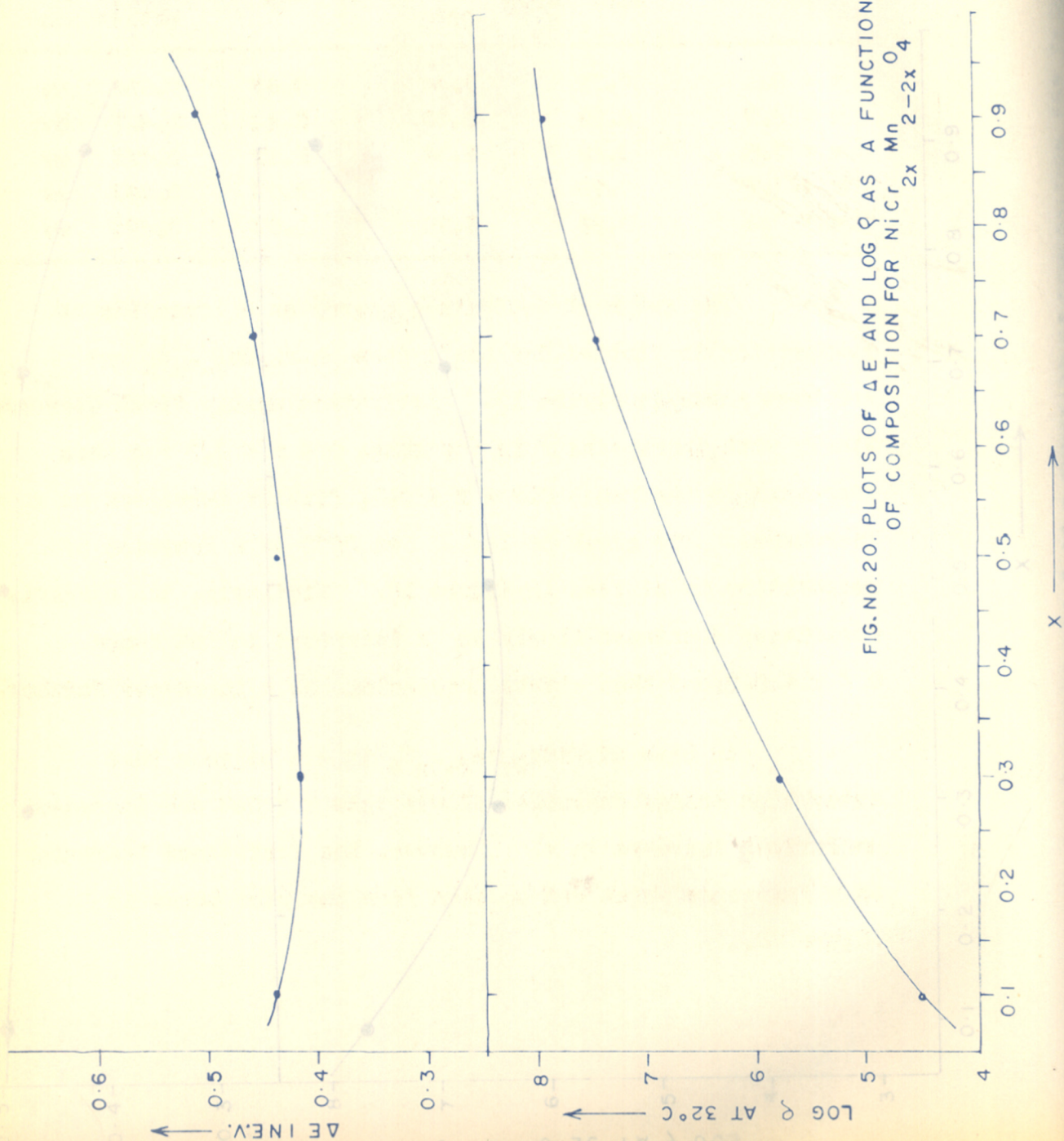


FIG. No. 20. PLOTS OF ΔE AND $\log Q$ AS A FUNCTION OF COMPOSITION FOR $\text{NiCr}_{2x}\text{O}_{4-2x}$

Table - 20

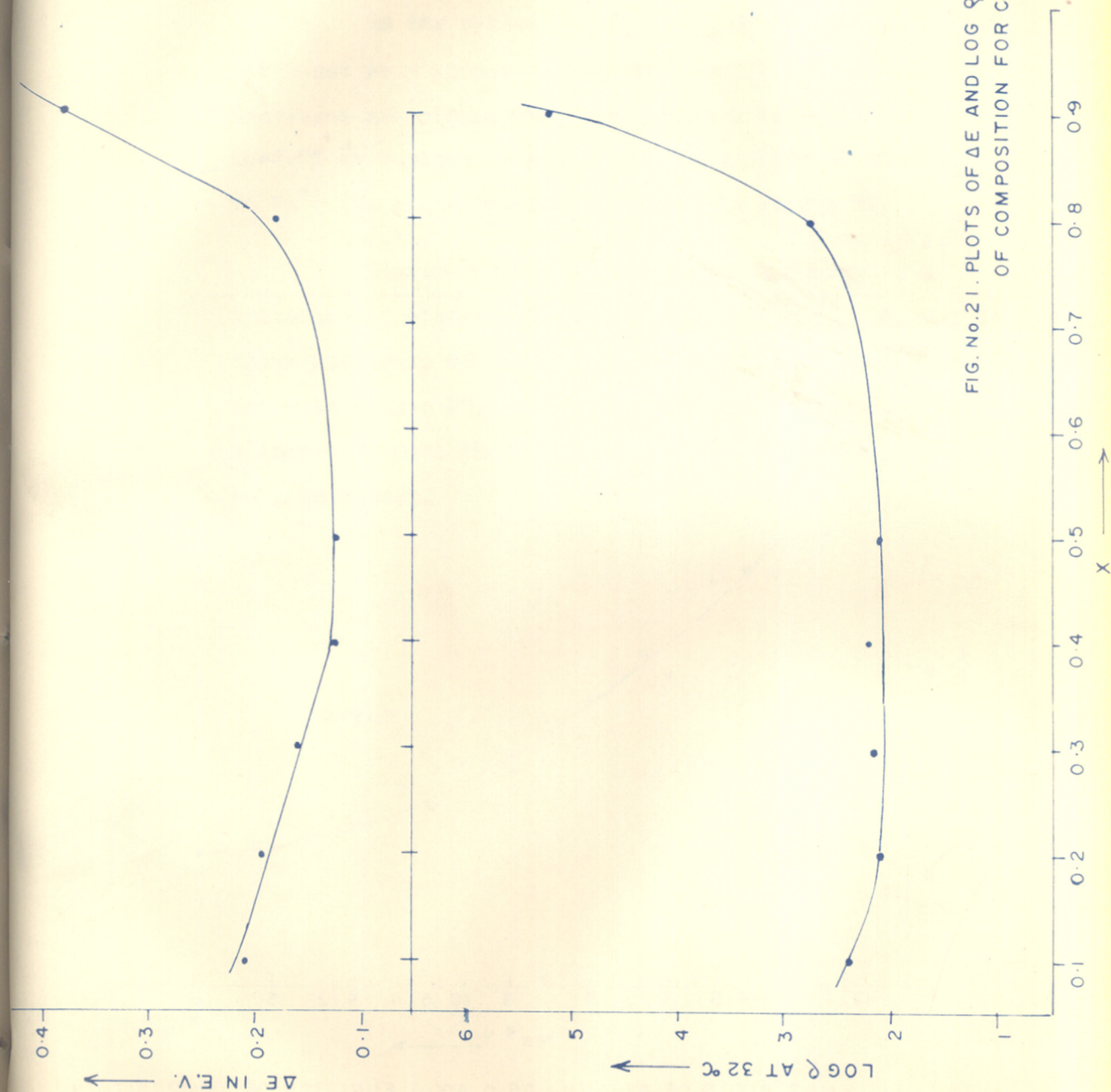
Results of conductivity measurements on
 $\text{ZnFe}_{2x}\text{Mn}_{2-2x}\text{O}_4$

Composition	$D_{\text{app}}/D_{\text{X-ray}}$	$\log \rho$ at 32°C	at	$\log \rho_0$	Energy of activation
$x = 0.1$	0.70	7.44		3.65	0.505 ev.
$x = 0.3$	0.68	6.30		2.44	0.481 ev.
$x = 0.5$	0.68	5.94		2.17	0.475 ev.
$x = 0.7$	0.76	6.12		2.73	0.447 ev.
$x = 0.9$	0.85	7.79		1.07	0.424 ev.

The graph of activation energy as a function of composition is plotted for the system $\text{ZnCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$ and has been shown in Figure 19. Activation energy first decreases slowly with increasing x in the range $0 < x < 0.3$ and then increases in the range $0.3 < x < 0.5$, finally decreases as x increases. The graph of $\log \rho$ at 32°C as a function of composition is plotted in Figure 19. Similarly, the specific resistance decreases slowly as x increases in the range $0 < x < 0.3$ and then starts increasing as x increases further.

In case of $\text{NiCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$ it can be seen that activation energy decreases slowly upto $x = 0.3$ and increases on further increase in x . However, the resistance increases as x increases which can be seen from the plot shown in Figure 20.

FIG. No.21. PLOTS OF ΔE AND $\log \rho$ AS A FUNCTION OF COMPOSITION FOR $\text{CuCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$



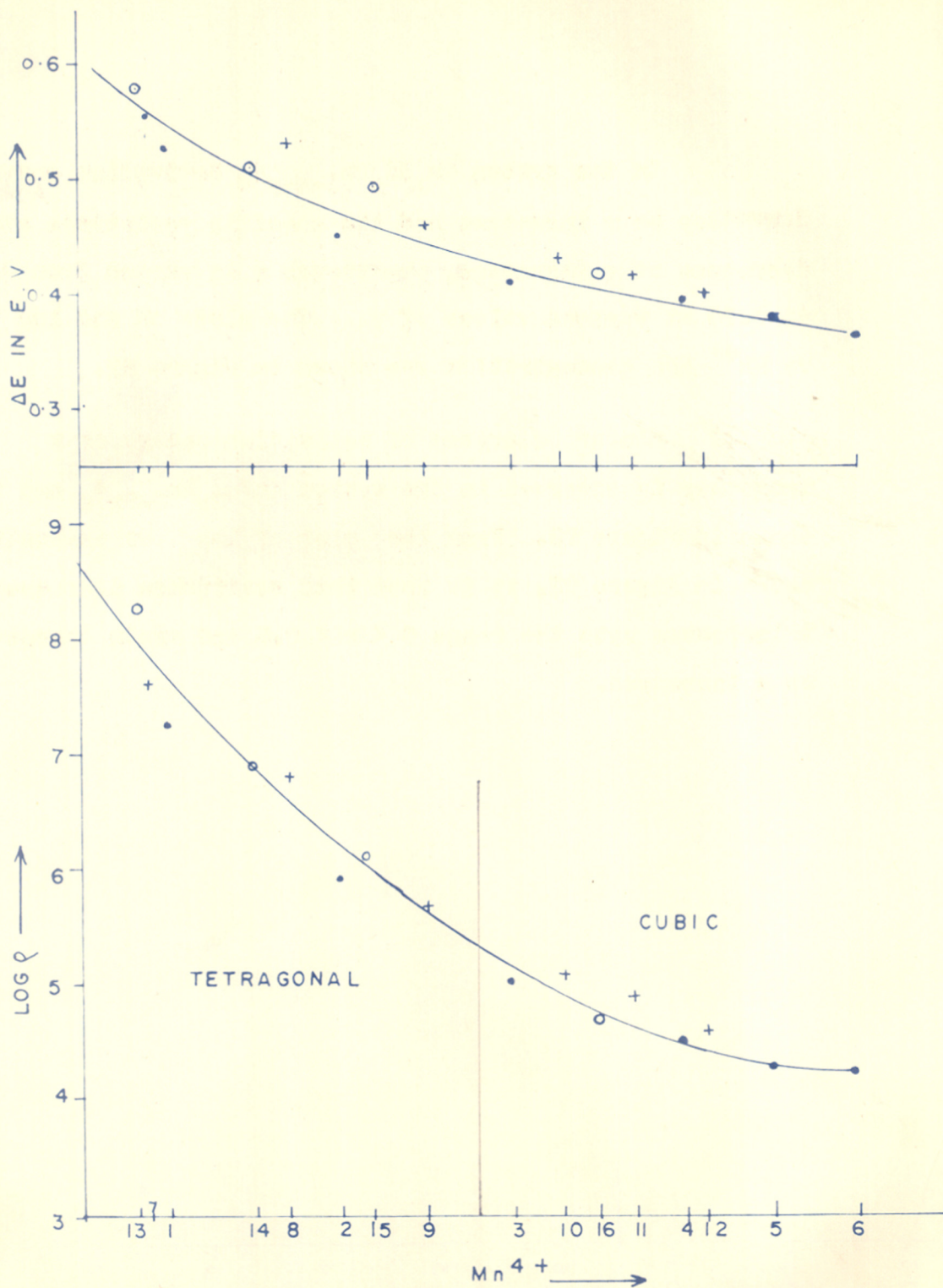


FIG No 22 PLOTS OF ΔE AND $LOG \rho$ AS A FUNCTION OF COMPOSITION

FOR $Zn_xNi_yMn_{3-x-y}O_4$

(Numbers according to the serial number in table No 25)

In the system $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$ activation energy decreases as y increases and the specific resistance also decreases as y increases, even though x is varied from 0.5 to 0.75 at various values of y . The plots ΔE and $\log \rho$ vs Mn^{4+} ion concentration are shown in Figure 22.

Linear decrease of activation energy as x increases is observed in the system $\text{ZnFe}_{2x}\text{Mn}_{2-2x}\text{O}_4$ and is shown in Figure 23. From the plot of $\log \rho$ vs composition shown in Figure 23, it is seen that resistance decreases as x increases upto the range $0 < x < 0.5$ and again increases as x increases.

3.3.

MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Paramagnetic susceptibilities of all the present compounds have been measured by the Gouy method described earlier. The measurements have been carried out at various temperatures from 90°K to 600°K. From the experimental results the values of molar susceptibility (χ_m) have been calculated and $1/\chi_m$ plotted as a function of temperature. The plots are either linear obeying the Curie-Weiss law

$$\frac{1}{\chi} = T/C + \theta/C$$

or are hyperbolic obeying the Neel's equation

$$\frac{1}{\chi_m} = \frac{T}{C} - \frac{\theta}{C} + \frac{\theta^2}{T^2}$$

At high temperatures, the hyperbolic approximates to a straight line following the Curie-Weiss equation given above. The Curie-Weiss constants θ and θ_m can, therefore, be determined from the slope and the intercept of the linear $1/\chi$ vs T plot. This has been done for all the compounds of the present series. Furthermore, as is well known, value of θ depends on the number of free electrons in an atom (assuming angular momentum to be quenched) and the relationship between the number of free spins in the ion and its θ value is given by the equation

$$\theta = \frac{8\pi N \mu_B^2}{3k_B} S(S+1)$$

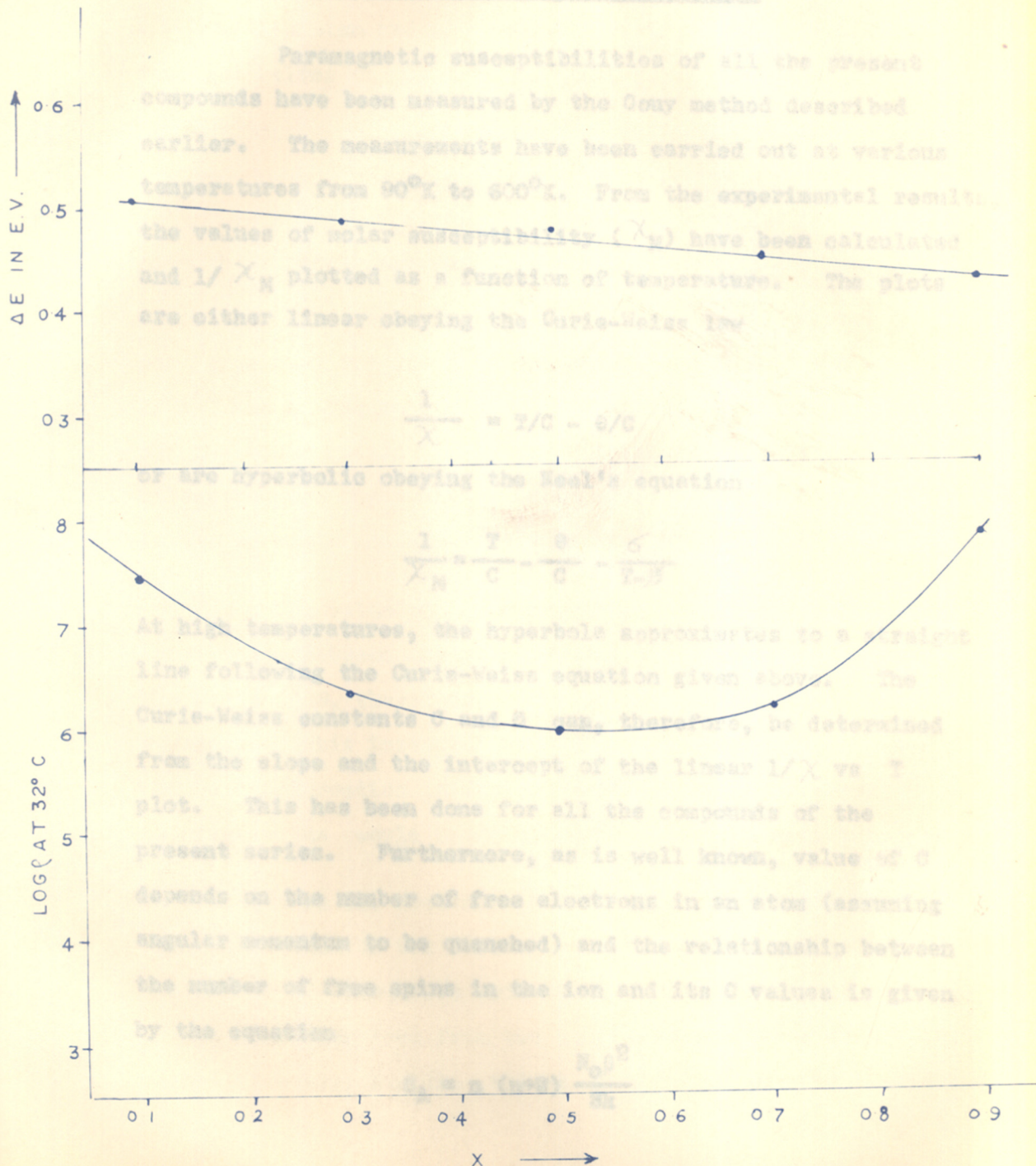


FIG No 23 PLOTS OF ΔE AND $\log Q$ AS A FUNCTION OF COMPOSITION FOR
 $\text{Zn Fe}_{2x} \text{Mn}_{2-2x} \text{O}_4$

3.3. MAGNETIC SUSCEPTIBILITY MEASUREMENTS

Paramagnetic susceptibilities of all the present compounds have been measured by the Gouy method described earlier. The measurements have been carried out at various temperatures from 90°K to 600°K. From the experimental results, the values of molar susceptibility (χ_M) have been calculated and $1/\chi_M$ plotted as a function of temperature. The plots are either linear obeying the Curie-Weiss law

$$\frac{1}{\chi} = T/C - \theta/C$$

or are hyperbolic obeying the Neel's equation

$$\frac{1}{\chi_M} = \frac{T}{C} - \frac{\theta}{C} - \frac{\sigma}{T-\theta}$$

At high temperatures, the hyperbola approximates to a straight line following the Curie-Weiss equation given above. The Curie-Weiss constants C and θ can, therefore, be determined from the slope and the intercept of the linear $1/\chi$ vs T plot. This has been done for all the compounds of the present series. Furthermore, as is well known, value of C depends on the number of free electrons in an atom (assuming angular momentum to be quenched) and the relationship between the number of free spins in the ion and its C values is given by the equation

$$C_A = n(n+2) \frac{N_0 \beta^2}{3k}$$

where K = Boltzmann constant, N_0 = Avogadro's number,
 B = Bohr magneton and n = number of free spins on an ion.
 Thus the values of C_A for different values of n are:

n	1	2	3	4	5
C_A	0.37	0.99	1.86	2.98	4.34

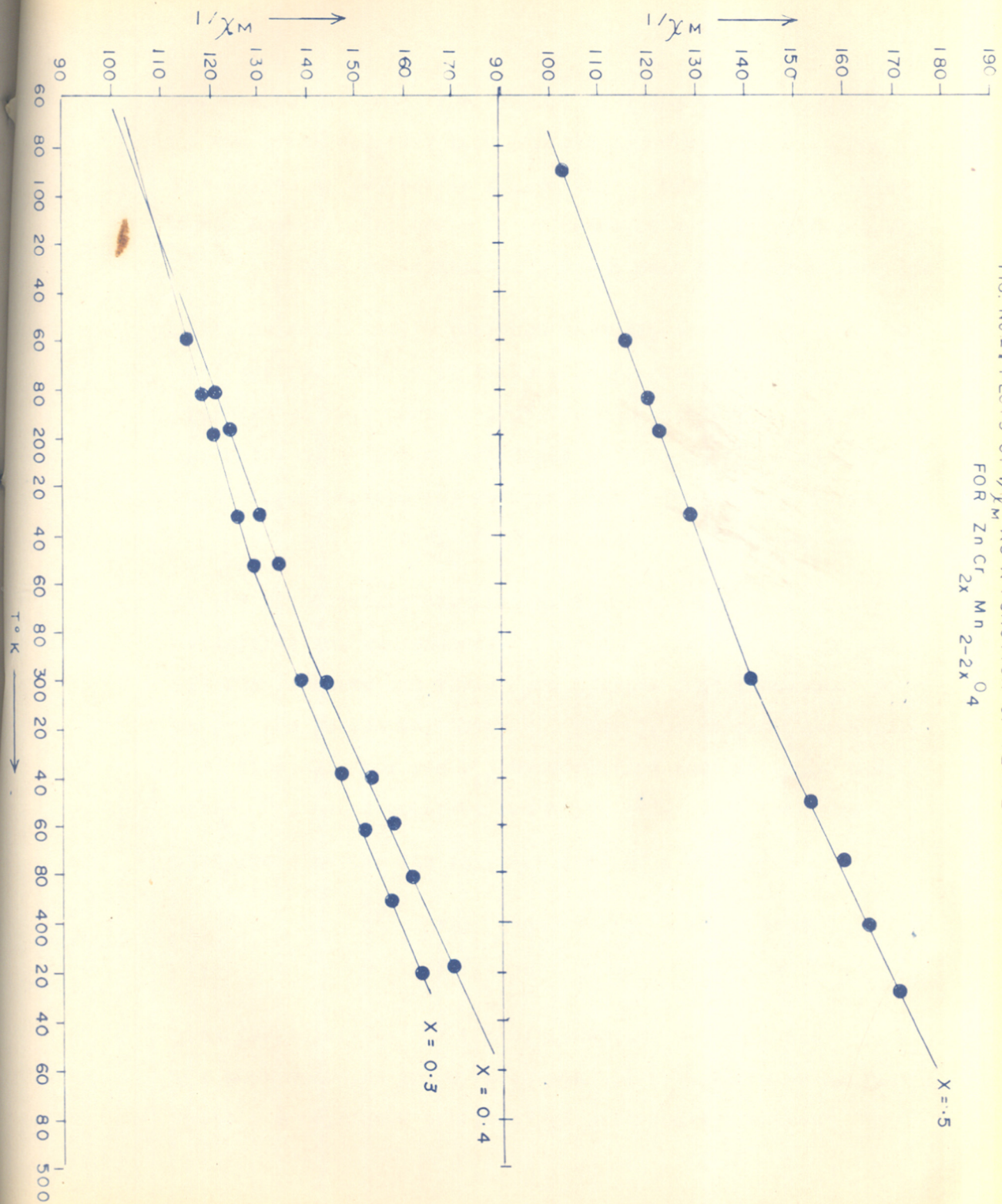
Also the C values are additive i.e. $C_M = \sum n_i C_i$

where C_M = Curie constant per mole, C_i = Curie constant per gram atom for the i^{th} paramagnetic ion, n_i = the number of i^{th} ion in the molecule. Summation is taken over for all the paramagnetic ions. The C value can, therefore, be calculated for the probable spin configuration of the ion in the molecule and compared with the experimental value.

The value of θ , on the other hand, depends on the interaction between the neighbouring spins in the solid. The value of θ , therefore, gives an idea of the nature and strength of this interaction. A positive value of θ means that the interaction is ferromagnetic in nature whereas negative value would indicate an antiferromagnetic interaction.

Once the constants C and θ have been determined the other constants of the Neel's equation can be evaluated by the method of successive refinement. An approximate value of σ and ϕ are obtained from two experimental points in the low temperature region. The values of σ and ϕ thus obtained are

FIG. No 24 PLOTS OF $1/\chi_M$ AS A FUNCTION OF TEMPERATURE
FOR $Zn^{+2}Cr^{+3}Mn^{+2}O_4$



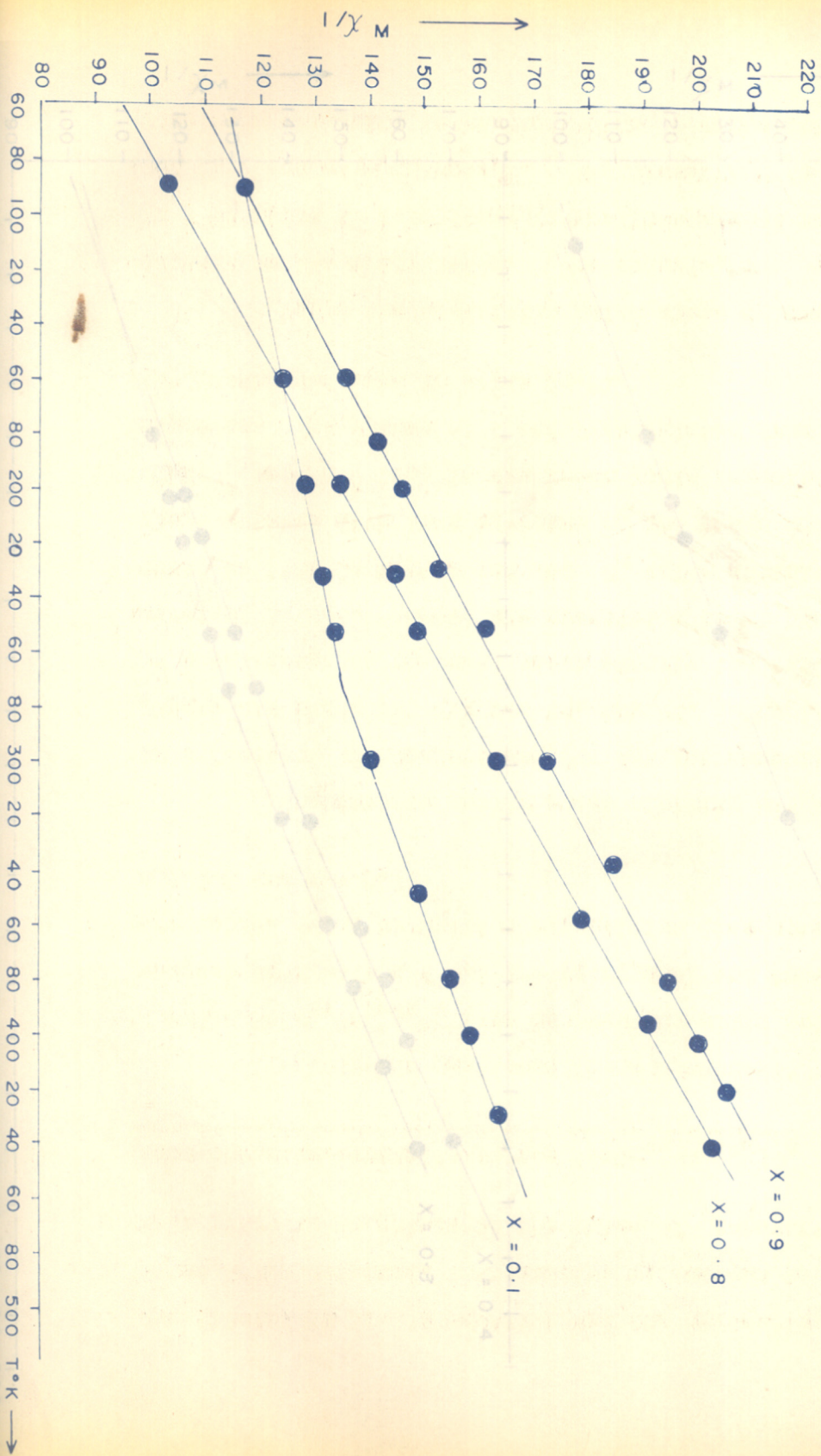


FIG No.25 PLOTS OF $1/X_M$ AS A FUNCTION OF TEMPERATURE FOR $ZnCl_2 \cdot x Mn^{2+} \cdot 2x O_4$

substituted in Neel's equation and the refined values of C and θ are obtained. Successive refinement is continued till there is no change in the value of constants.

Zinc chromite-manganite series ($\text{ZnCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$)

As already mentioned the compounds of the general formula $\text{ZnCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$ form homogeneous solid solutions. The compositions with $x < 0.5$ are tetragonal and those with $x > 0.6$ are cubic. The transition composition lies somewhere between $x = 0.5$ and $x = 0.6$.

The inverse molar susceptibility has been plotted as a function of temperature for all the compositions and the graphs are shown in Figures 24, 25, 26. The $1/\chi_M - T$ plots of the tetragonal compound shows clearly two intersecting straight lines. Above the transition point the slope of the straight line is higher and the C_M value calculated from this slope matches with that expected on the basis of the C values of Cr^{3+} and Mn^{3+} ions in the known ionic formula of the compound. The values of C and θ calculated from this part of the graph are given in Table No.21.

Below the transition point slope is smaller and also depends on the composition. For example, for pure ZnMn_2O_4 ($x = 0$) slope is zero (temperature independent susceptibility) and it rises as x increases. The transition temperature for pure zinc manganite is around 200°K . For the other compounds

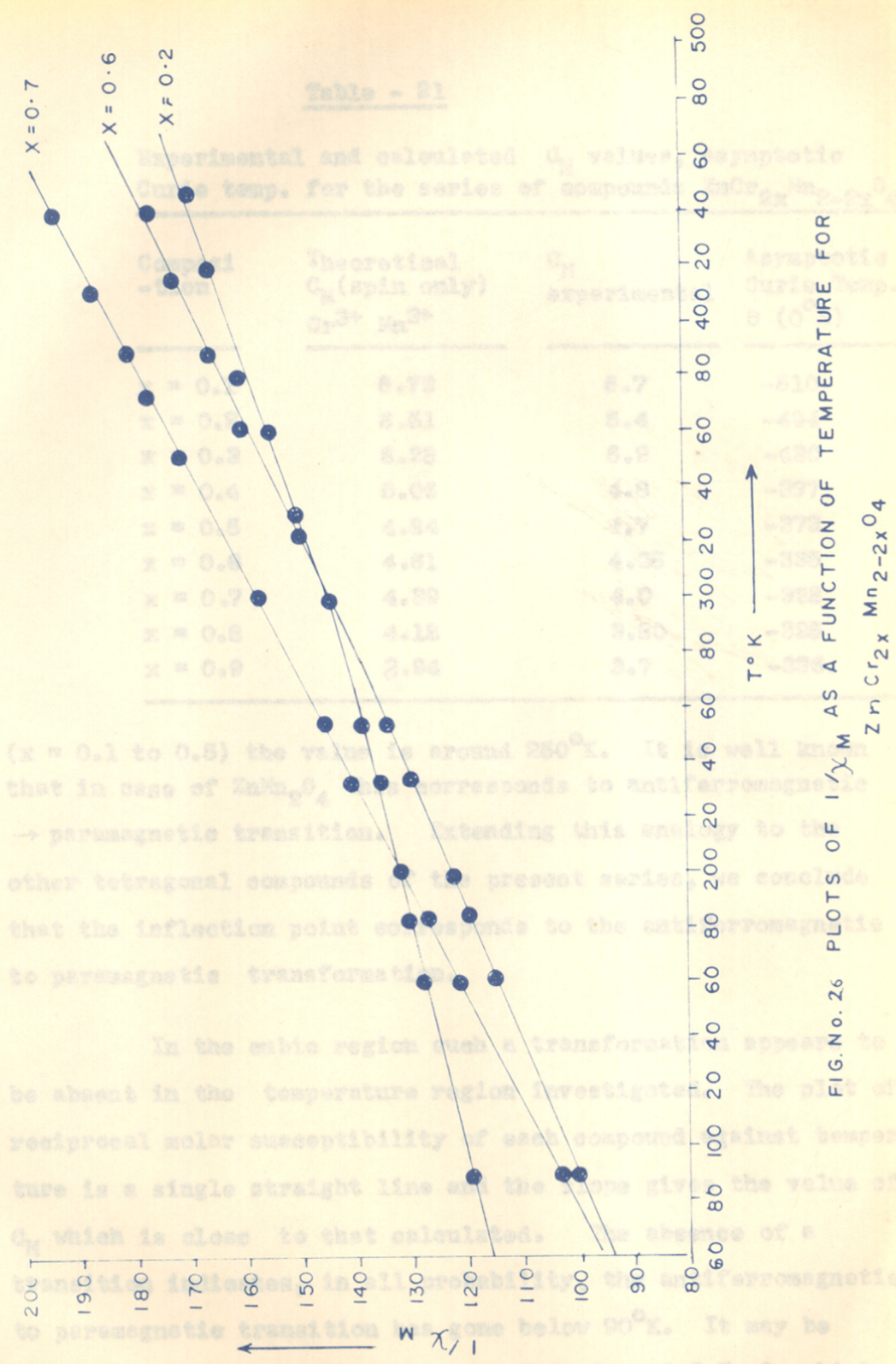


FIG. No. 26 PLOTS OF $1/\chi_M$ AS A FUNCTION OF TEMPERATURE FOR $ZnCr_{2x}Mn_{2-2x}O_4$

Table - 21

Experimental and calculated Q_M values for the series of compounds $ZnCr_{2x}Mn_{2-2x}O_4$			
Compound	Theoretical Q_M (spin only)	Q_M experimental	Asymptotic Curie temp.
	Zn^{2+}	Mn^{2+}	θ (°K)
$x = 0.1$	8.73	8.7	-31
$x = 0.2$	8.51	8.4	-42
$x = 0.3$	8.29	8.2	-52
$x = 0.4$	8.06	7.9	-62
$x = 0.5$	7.84	7.7	-72
$x = 0.6$	7.61	7.55	-82
$x = 0.7$	7.39	7.4	-92
$x = 0.8$	7.16	7.35	-102
$x = 0.9$	6.94	7.7	-112

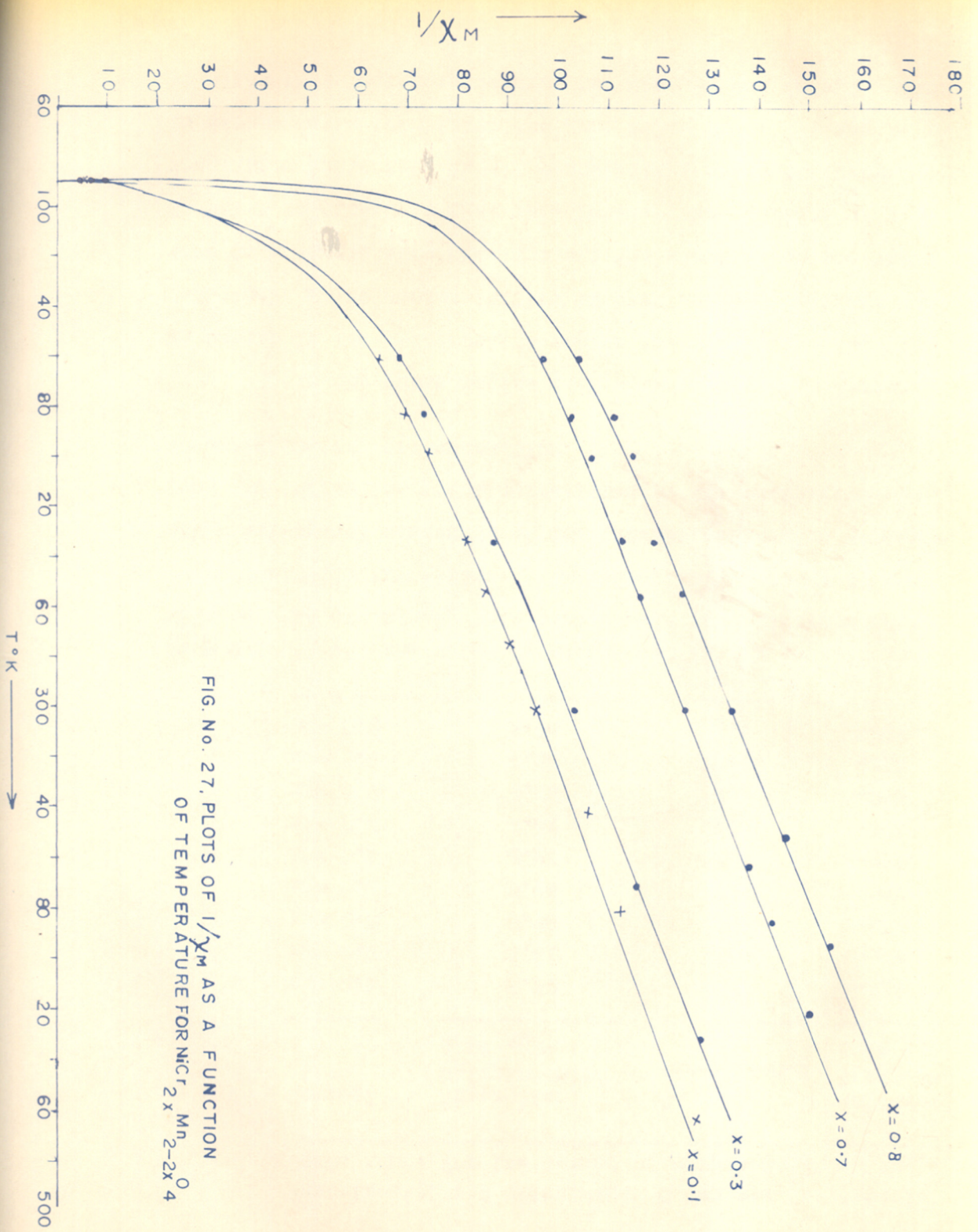
Table - 21

Experimental and calculated C_M values, asymptotic Curie temp. for the series of compounds $ZnCr_{2x}Mn_{2-2x}O_4$

Composi- -tion	Theoretical C_M (spin only) Cr^{3+} Mn^{3+}	C_M experimental	Asymptotic Curie Temp. θ ($^{\circ}K$)
$x = 0.1$	5.73	5.7	-510
$x = 0.2$	5.51	5.4	-494
$x = 0.3$	5.28	5.2	-430
$x = 0.4$	5.06	4.8	-397
$x = 0.5$	4.84	4.7	-373
$x = 0.6$	4.61	4.35	-335
$x = 0.7$	4.39	4.0	-328
$x = 0.8$	4.18	3.80	-325
$x = 0.9$	3.94	3.7	-336.

($x = 0.1$ to 0.5) the value is around $250^{\circ}K$. It is well known that in case of $ZnMn_2O_4$ this corresponds to antiferromagnetic $\rightarrow$ paramagnetic transition. Extending this analogy to the other tetragonal compounds of the present series, we conclude that the inflection point corresponds to the antiferromagnetic to paramagnetic transformation.

In the cubic region such a transformation appears to be absent in the temperature region investigated. The plot of reciprocal molar susceptibility of each compound against temperature is a single straight line and the slope gives the value of C_M which is close to that calculated. The absence of a transition indicates, in all probability, the antiferromagnetic to paramagnetic transition has gone below $90^{\circ}K$. It may be recalled that Neel temperatures for $ZnCr_2O_4$ and $ZnFe_2O_4$ which



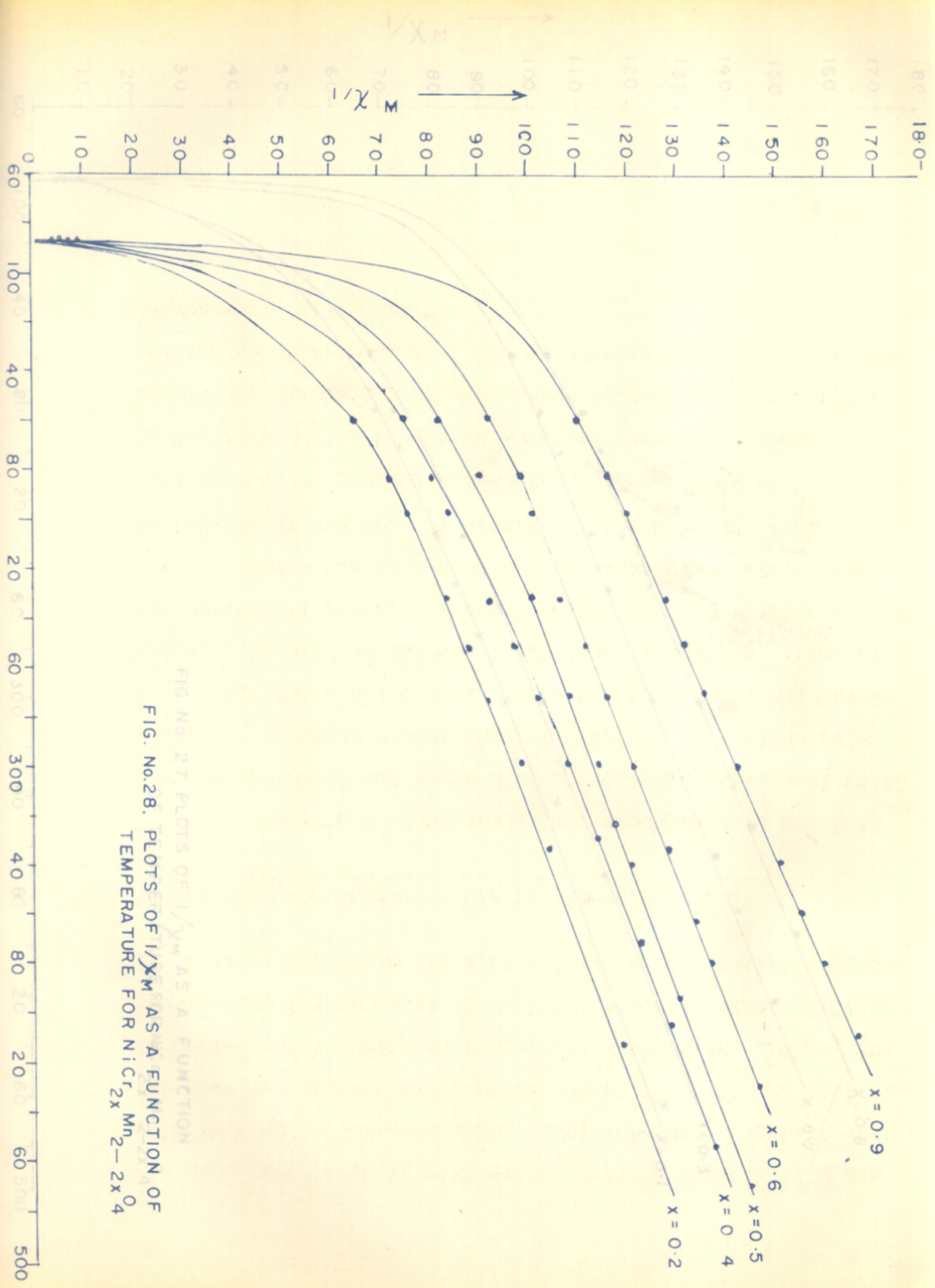


FIG. No. 28. PLOTS OF $1/\chi_M$ AS A FUNCTION OF TEMPERATURE FOR $\text{NiCr}_2\text{Mn}_{2-2x}\text{O}_4$

are also cubic spinels with normal cation distribution are only 15°K and 9°K respectively. It, therefore, appears that the Neel temperature for a cubic spinel is small and that it is raised considerably on tetragonal distortion. Also, the temperature independence of antiferromagnetic susceptibility is observed only when there is a large tetragonal distortion.

Nickel chromite-manganite system ($\text{NiCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$)

As already mentioned, the compounds with $x = 0$ to $x = 0.9$ are cubic and those with $x > 0.9$ are tetragonal with $c/a > 1$. In cubic region there is also an inflection point at $x = 0.5$ for $0 < x < 0.5$. There are no Ni^{2+} at the tetrahedral site and for $0.5 \leq x < 1.0$ there are no Mn^{3+} ions at the octahedral sites. The values of $1/\chi_M$ for compositions $x = 0.1$ to $x = 0.9$ as a function of temperature are plotted in Figures 27 and 28. It appears from the figure that $1/\chi_M$ follows Neel's hyperbolic equation. The values of constants in Neel's equation have been computed from experimental results by the method of successive approximation described earlier in this chapter. The calculated values of constants are given in Table No. 22.

Table - 22

Values of constants in Neel's equation for
 $\text{Ni}(\text{Cr}_{2x}\text{Mn}_{2-2x})\text{O}_4$

Composi- tion	C_M experi- mental	C_M theore- tical spin only $\text{Cr}^{3+}\text{Mn}^{3+}\text{Ni}^{2+}$	θ/C	σ	ϕ
$x = 0.1$	6.3	6.72	-53	1206	70
$x = 0.2$	6.2	6.5	-53	1226	71.2
$x = 0.3$	5.9	6.27	-57	1463	69.2
$x = 0.4$	5.8	6.05	-60	1065	75.3
$x = 0.5$	5.7	5.83	-62	646	80.5
$x = 0.6$	5.55	5.610	-68	400	84.7
$x = 0.7$	5.45	5.38	-72	353	85.2
$x = 0.8$	5.17	5.16	-77	274	86.8
$x = 0.9$	4.85	4.93	-81	311	86.8

Values of $1/\chi_M$ using these constants are calculated at different temperatures using the Neel's equation. The full line shown in Figures 27 and 28 gives the calculated values of $1/\chi_M$ at various temperatures. The full circles in the graph corresponds to $1/\chi_M$ experimentally observed at various temperatures. It is clear from the graph that experimental values are in good agreement with the theoretical curve representing the Neel's equation. It is also seen that the calculated value of C_M (see Table No.22) matches fairly well with the experimental value taking into consideration that chromium and manganese are in Cr^{3+} , Mn^{3+} states. The slight difference between the calculated and the observed C_M values

appears to be within the limits of our experimental error. The Curie temperature is $\sim 90^\circ\text{K}$ for all compositions.

It is interesting to compare the magnetic properties of some related spinels containing Ni^{2+} ions given in Table No.23.

Table - 23

Formula	Magnetic order below transition temperature	Transition temperature	Reference
$\text{Fe}[\text{NiFe}]_4\text{O}_4$	Neel	858	75
$\text{Fe}[\text{NiMn}]_4\text{O}_4$	Neel	600	61
$\text{Fe}[\text{NiCr}]_4\text{O}_4$	Neel	570	76
$\text{Mn}[\text{NiCr}]_4\text{O}_4$	?	$\sim 90^\circ\text{K}$	
$\text{Mn}[\text{NiMn}]_4\text{O}_4$	Star to Neel	$\sim 100^\circ\text{K}$	74

Copper chromite-manganite systems $\text{CuCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$

The X-ray diffraction studies on these compounds have revealed that for $0 \leq x \leq 0.5$ the compounds have the cubic spinel structure and for $0.8 \leq x \leq 1.0$ the structure is tetragonal with $c/a < 1$. However, for $x = 0.6$ and 0.7 , a homogeneous solid solution is not formed and one merely gets a mixture of cubic and tetragonal phases.

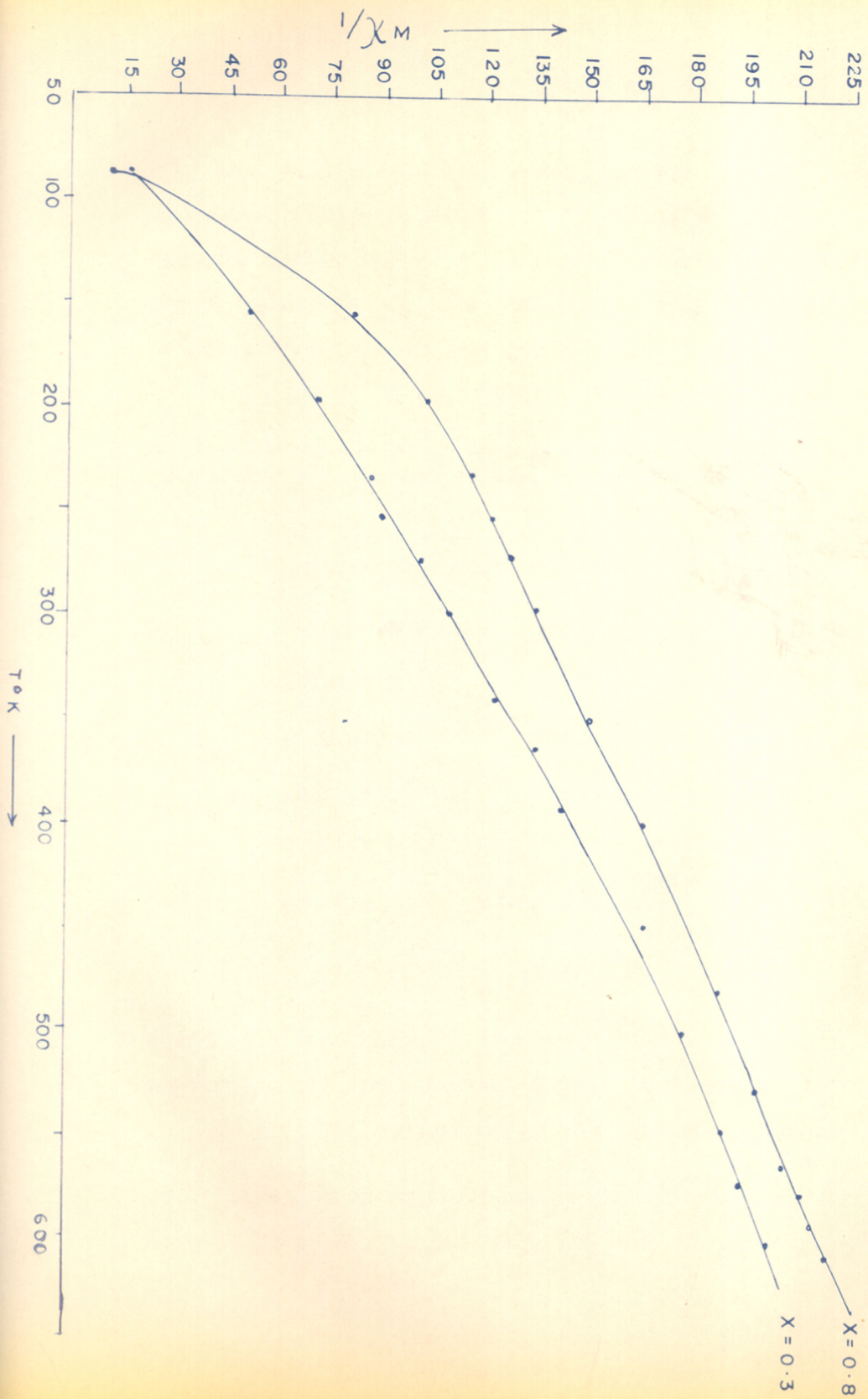


FIG. No. 29. PLOTS OF $1/\chi_M$ AS A FUNCTION OF TEMPERATURE FOR $\text{CuCl}_2 \cdot x\text{H}_2\text{O}$ $M_2 = 2 \times 10^4$

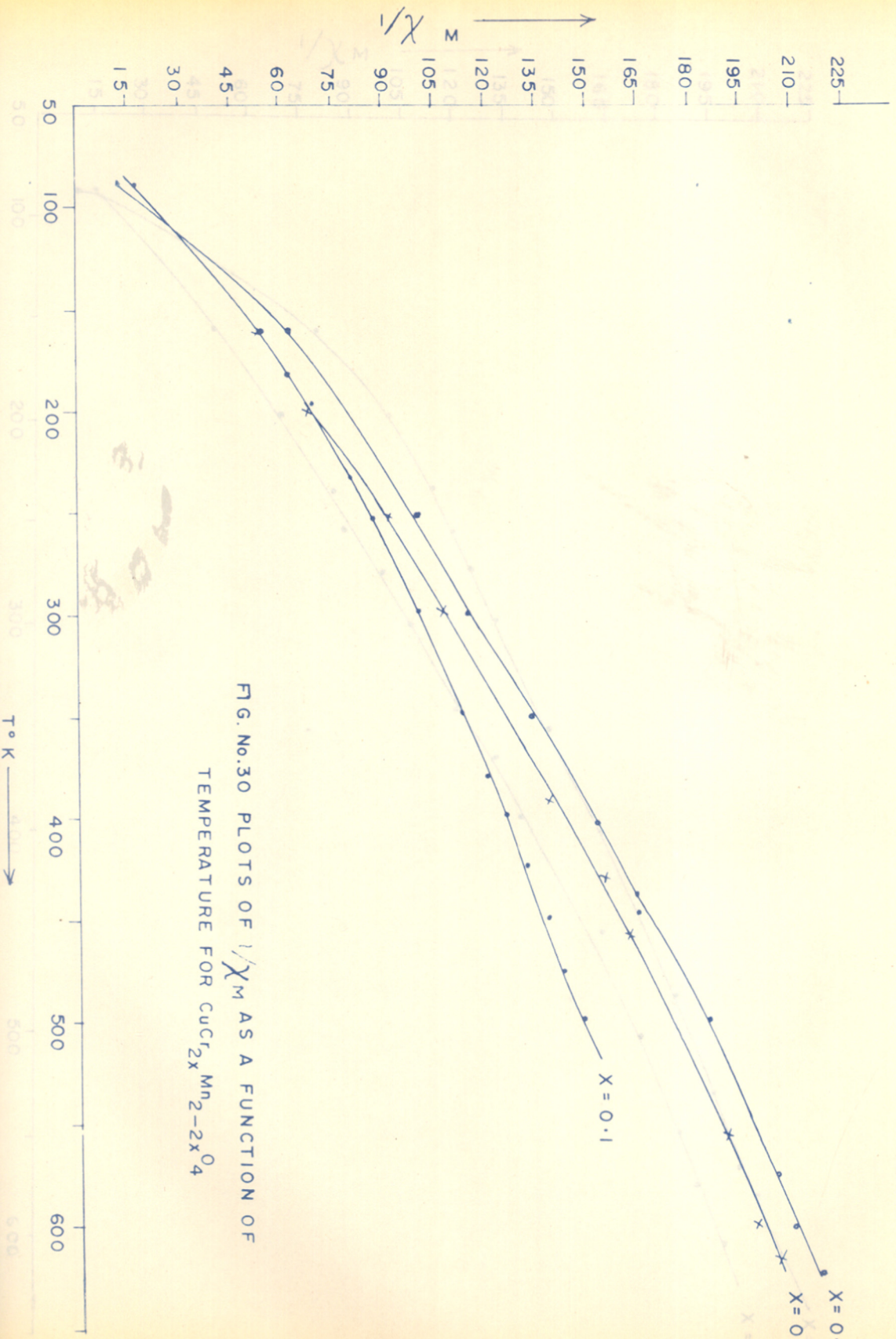


FIG. No. 30 PLOTS OF $\frac{1}{\chi_M}$ AS A FUNCTION OF
TEMPERATURE FOR $CuCr_{2x}Mn_{2-2x}O_4$

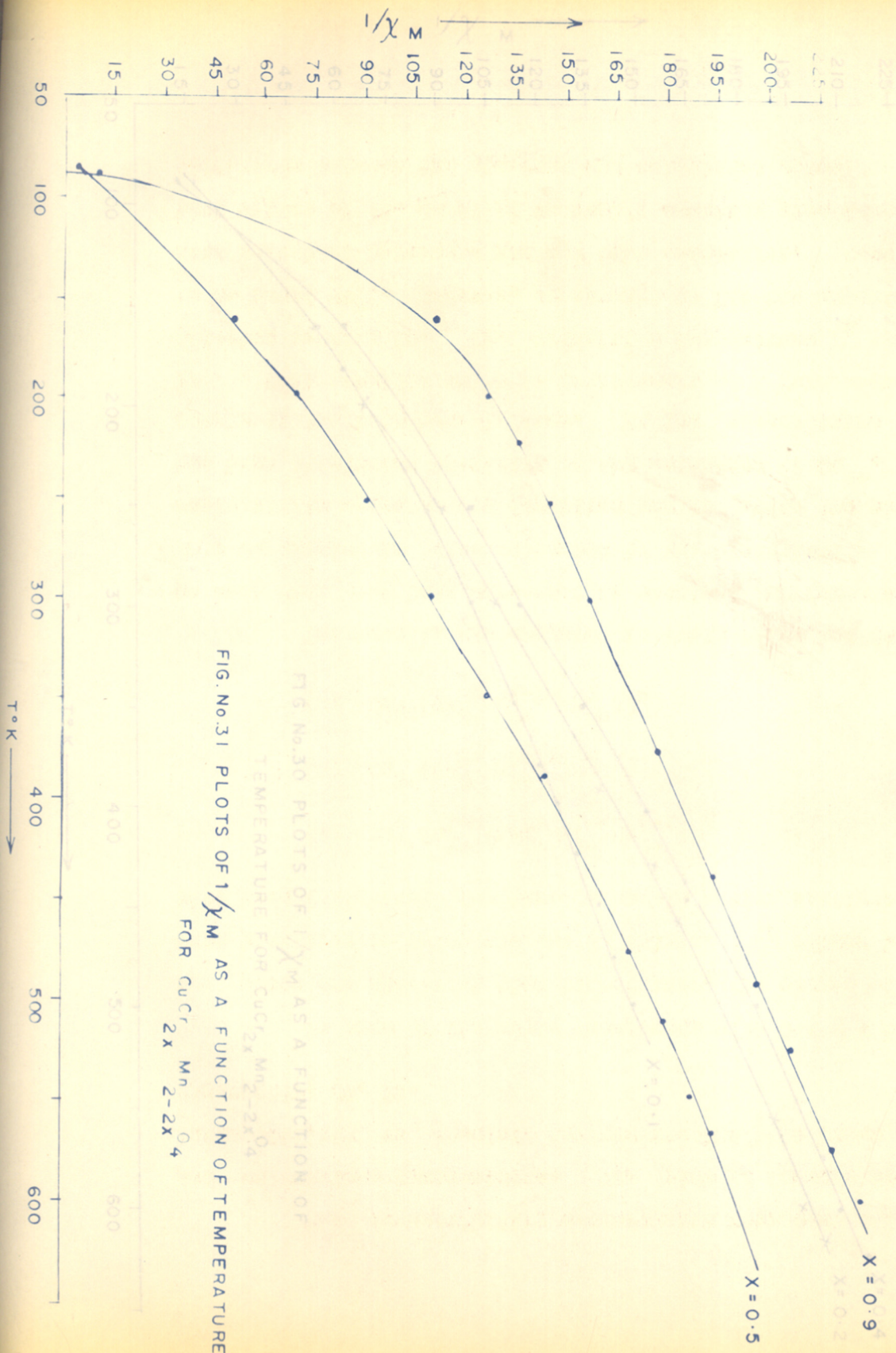
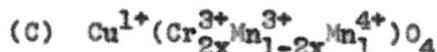
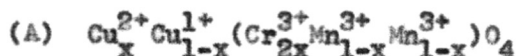


FIG. NO. 31 PLOTS OF $1/\chi_M$ AS A FUNCTION OF TEMPERATURE FOR $CuCr_{2x}Mn_{2-2x}O_4$

The susceptibility measurements have been carried out at various temperatures. The plot of inverse molar susceptibility vs absolute temperature has been shown in Figures 29, 30, 31.

In case of the cubic compounds with $0 < x \leq 0.5$ the plots are linear at high temperature, the slopes of which have been used to calculate the C_M values. C_M values have also been calculated for three probable cation configurations.



The results are compared in Table No.24 and it can be seen that the best agreement is obtained for formula (A). This conclusion is also supported by the electrical conductivity measurements described earlier where the conduction has been attributed partially to the existence of Cu^{2+} , Cu^{1+} couple at the tetrahedral sites. At low temperatures the $1/\chi_M$ falls rapidly which is reminiscent of a ferrimagnetic ordering setting in. The transition temperature T_c appears to be around 90°K . However, an attempt to fit the experimental data on a Neel hyperbola has not been successful. Even the best values of the constant in Neel's equation give a considerable difference between the observed and calculated value.

Table - 24

Experimental and calculated C_M values for
the series of compounds $\text{CuCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$

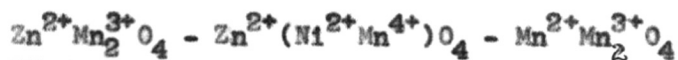
Composi- -tion	Theoretical C_M (spin only) $\text{Cu}^{1+}, \text{Cu}^{2+}, \text{Mn}^{3+},$ $\text{Mn}^{4+}, \text{Cr}^{3+}$ (A)	Theoretical C_M (spin only) $\text{Cu}^{2+}, \text{Cr}^{3+},$ Mn^{3+} (B)	Theoretical C_M (spin only) $\text{Cu}^{1+}, \text{Mn}^{3+},$ $\text{Mn}^{4+}, \text{Cr}^{3+}$ (C)	C_M Experi- mental
$x = 0.1$	4.765	6.136	4.61	4.65
$x = 0.2$	4.69	5.912	4.39	4.61
$x = 0.3$	4.615	5.68	4.17	4.5
$x = 0.4$	4.54	5.464	3.94	4.32
$x = 0.5$	4.465	5.24	3.72	4.20
$x = 0.8$	4.24	4.57	3.57	4.1
$x = 0.9$	4.165	4.314	3.50	4.05

No attempt is made to deduce any conclusions from the magnetic data on compounds with $x = 0.6$ and $x = 0.7$ as they are heterogeneous mixtures of more than one phase.

The tetragonal compounds (i.e. $x = 0.8$ and 0.9) also give a linear $1/\chi_M - T$ plot at high temperatures and the C_M values deduced from these graphs are given in Table No. 24.

C_M values have been computed for three possible cation configurations viz. (A) and (B) as above, and
(C) $\text{Cu}_{2x-1}^{2+}\text{Cu}_{2-2x}^{1+}(\text{Cr}_{2x}^{3+}\text{Mn}_{2-2x}^{4+})\text{O}_4$.

The change in formula (C) on going from the region $0 \leq x \leq 0.5$ to the region $0.5 < x \leq 1$ arises from the fact that at $x > 0.5$ there are not enough Mn^{4+} ions to keep all the Cu_{tet} as $\text{Cu}_{\text{tet}}^{1+}$. Once again the agreement is the best for the formula (A). These compounds also appear to become ferrimagnetic below the transition temperature which appears to be around 90°K .



Magnetic susceptibility of sixteen compounds of this series has been measured as a function of temperature. The compositions of the various compounds can be represented by the general formula $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$ where x and y have the values given in Table No.25. The structure of the various compounds are also given in the same table.

Table - 25

Structure of the series of compounds $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$

S. No.	x	y	Structure
1	0.75	0.075	T
2	0.75	0.225	T
3	0.75	0.375	T
4	0.75	0.525	C
5	0.75	0.600	C
6	0.75	0.675	C
7	0.60	0.060	T
8	0.60	0.180	T

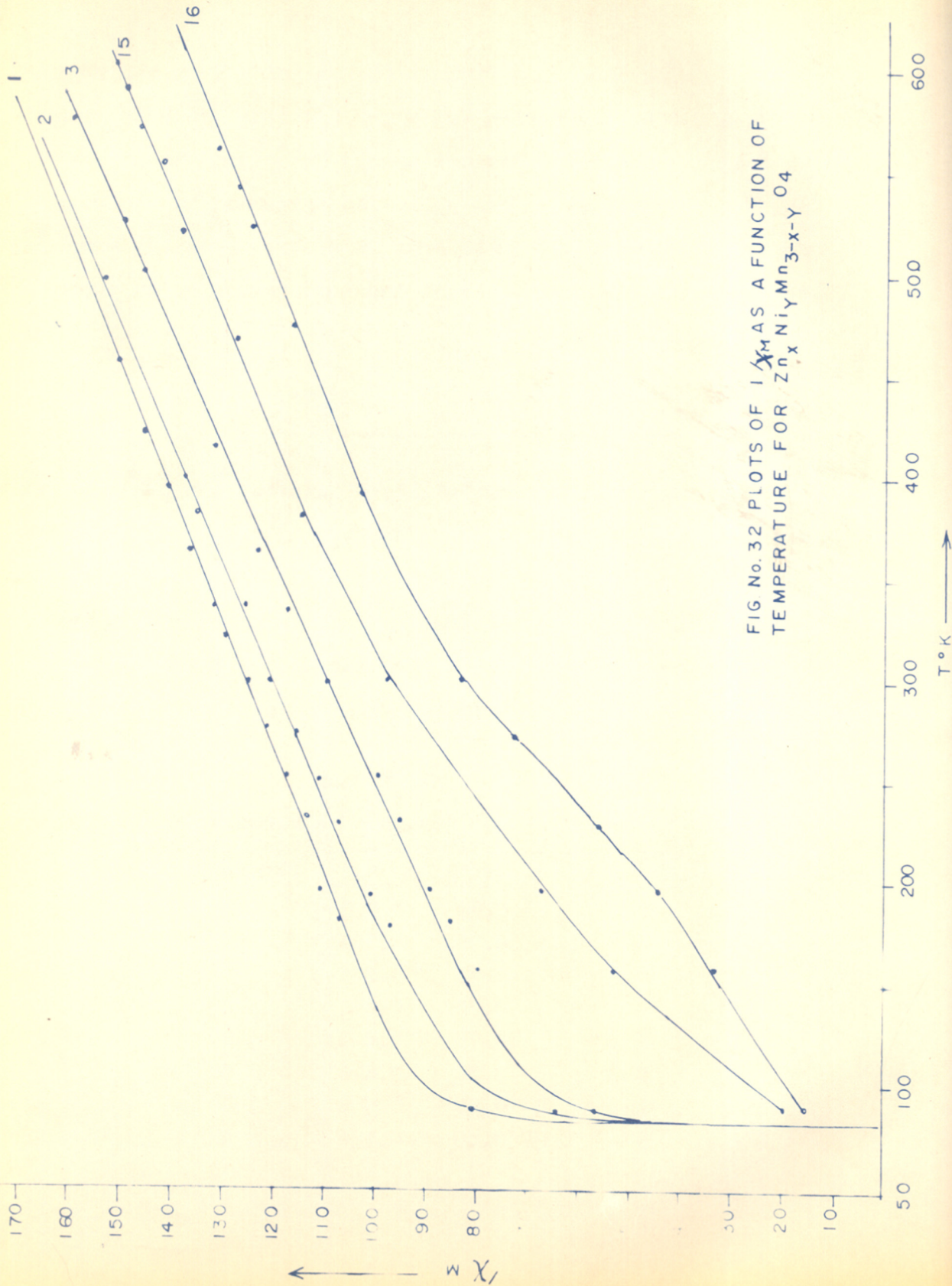


FIG No.32 PLOTS OF $1/\chi_M$ AS A FUNCTION OF TEMPERATURE FOR $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$

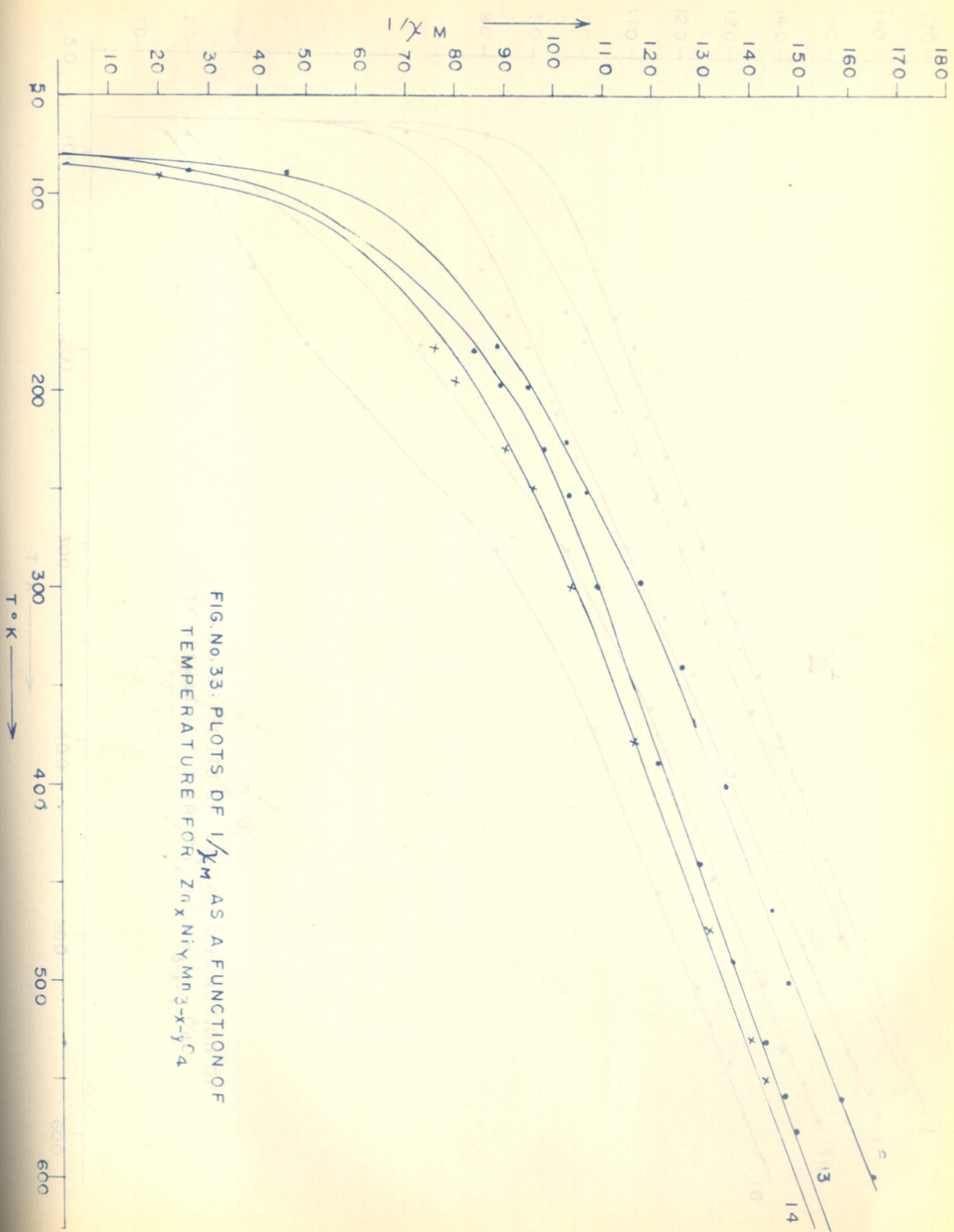


FIG. No. 33. PLOTS OF $1/\chi_M$ AS A FUNCTION OF TEMPERATURE FOR $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$

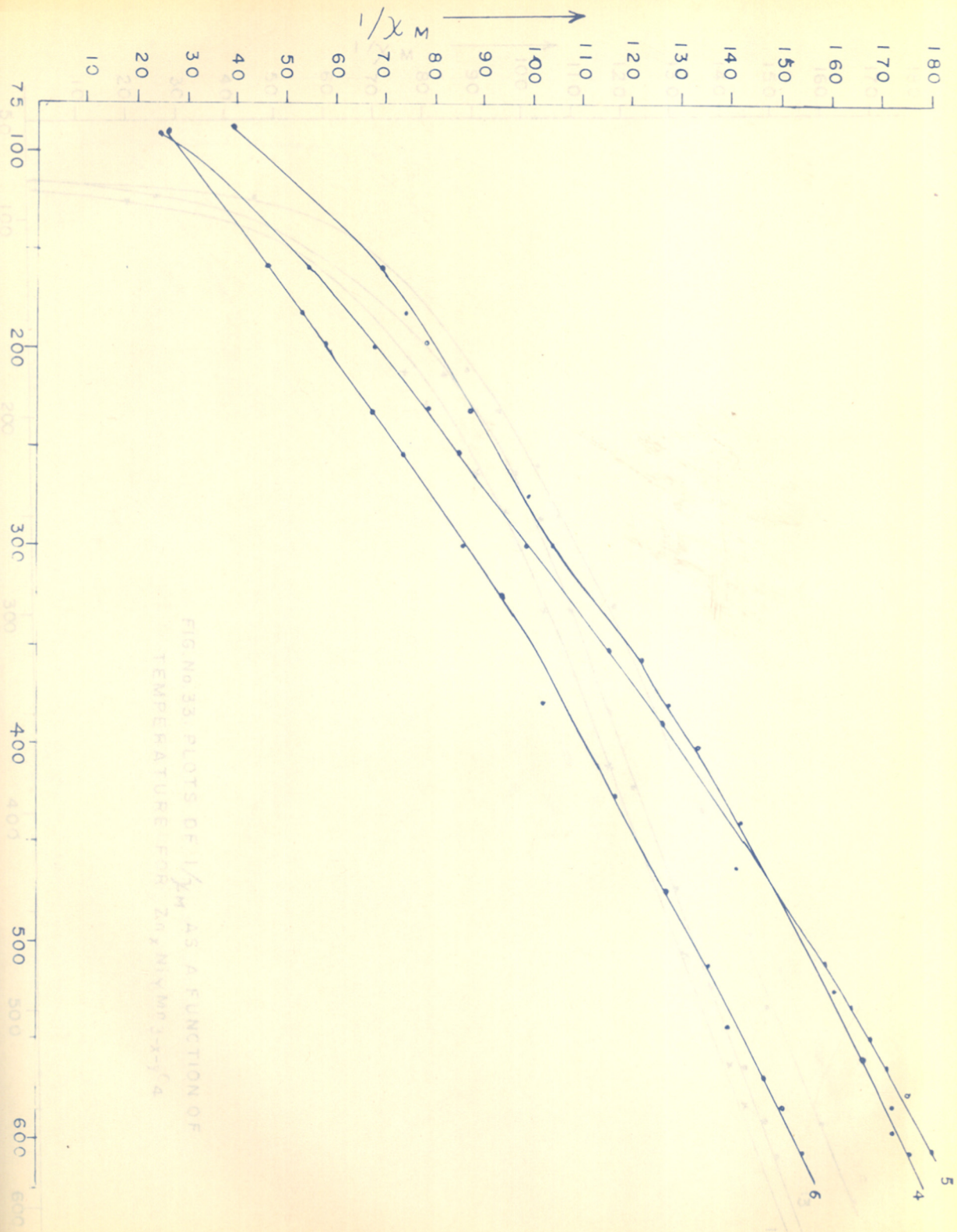


FIG. No 34. PLOTS OF $1/\chi_M$ AS A FUNCTION OF TEMPERATURE FOR $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$

FIG. No 34. PLOTS OF $1/\chi_M$ AS A FUNCTION OF TEMPERATURE FOR $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$

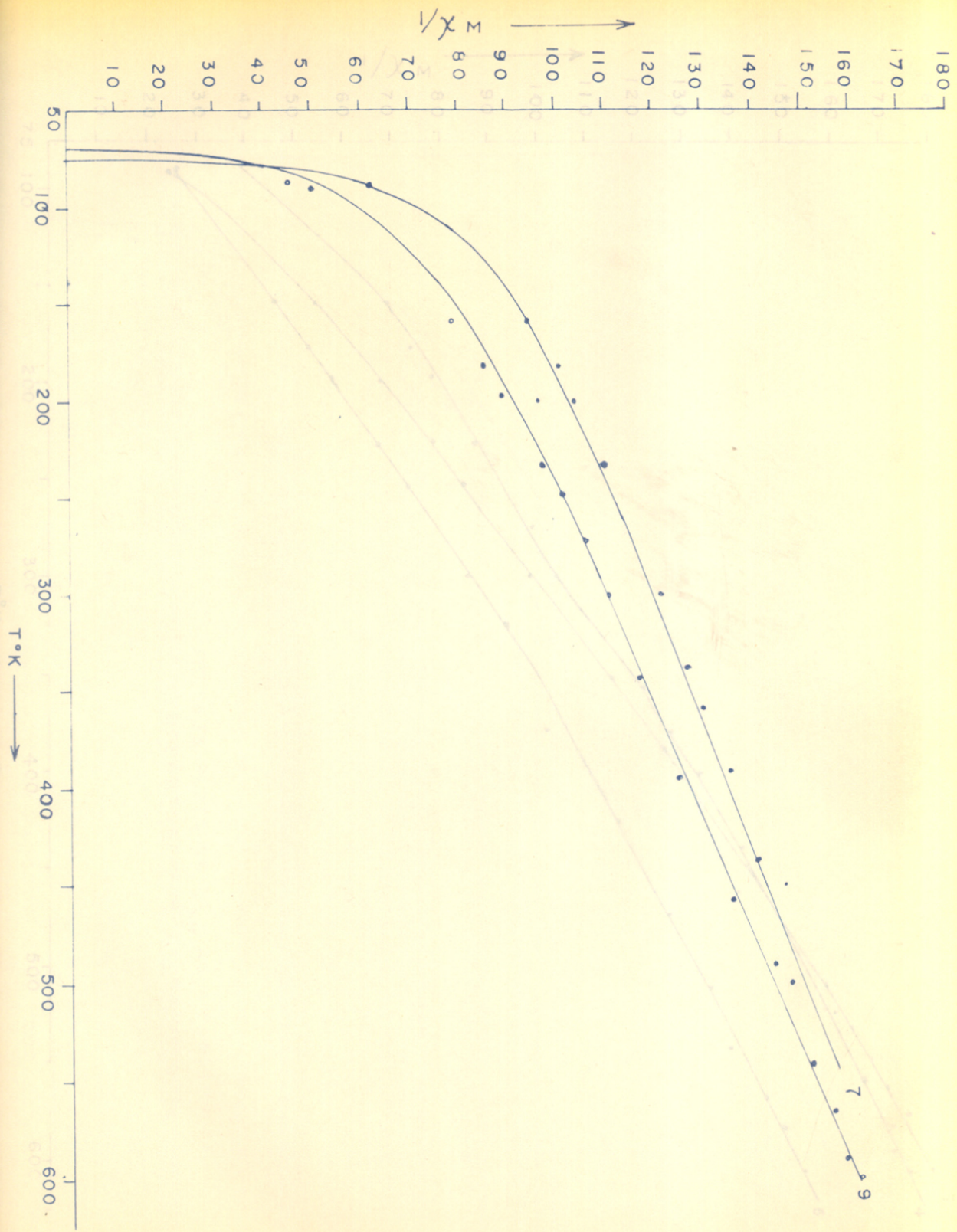


FIG. No. 35 PLOTS OF $1/\chi_M$ AS A FUNCTION OF TEMPERATURE FOR $Zn_xNi_yMn_{3-x-y}O_4$

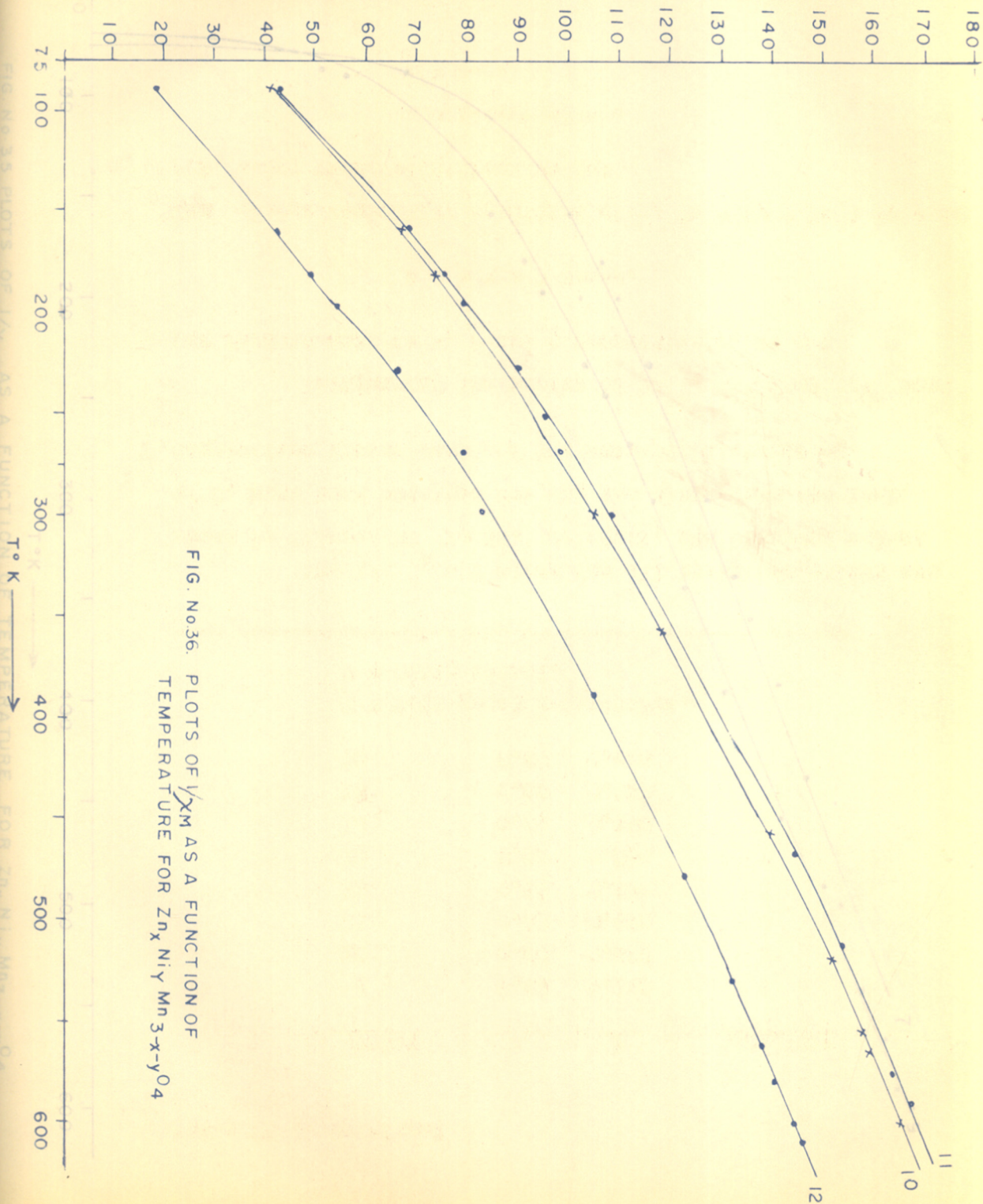


FIG. No.36. PLOTS OF $1/X_M$ AS A FUNCTION OF TEMPERATURE FOR $Zn_xNi_yMn_{3-x-y}O_4$

Table 25 .. continued

<u>S. Number</u>	<u>x</u>	<u>y</u>	<u>Structure</u>
9	0.60	0.300	T
10	0.60	0.420	C
11	0.60	0.480	C
12	0.60	0.540	C
13	0.50	0.660	T
14	0.50	0.150	T
15	0.50	0.250	T
16	0.50	0.450	C

T = Tetragonal hausmannite.

C = Cubic spinel.

The $1/\chi_M$ - T plots for all these compounds are shown in Figures 32 to 36. As usual, the observed values of C_M have been obtained for all the cases from the high temperature linear part of the susceptibility graph.

Designating the number of Mn^{2+} , Mn^{3+} and Mn^{4+} ions per formula unit as a, b and c respectively, we get

$$a + b + c = 3 - x - y.$$

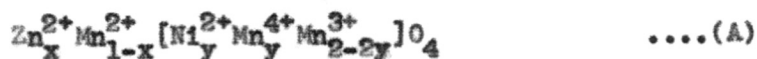
The charge neutrality condition gives $2x + 2y + 2a + 3b + 4c = 8$, using these conditions we get

$$a = 1 - (x + y) + c$$

$$b = 2 - 2c.$$

The calculated values of C_M then turns out to be $C_M = 10.30 + 0.24c - 3.35y - 4.34x$. As the values of x and y are known for each composition, at least in principle, one can get the value of c from the measured value of C_M . Knowing c , one can find out the number of Mn^{2+} , Mn^{3+} and Mn^{4+} ions in the formula unit. However, as the coefficient of c in the above equation is small, any error in the experimental determination of C_M is going to introduce a large uncertainty in the determined value of c i.e. in the value of Mn^{2+} , Mn^{3+} and Mn^{4+} ions in the formula. This arises from the fact that Curie constant for two Mn^{3+} ions (5.96) and that for one Mn^{2+} and one Mn^{4+} ion (6.20) is only slightly different and it is not possible, from magnetic susceptibility data alone to tell whether we have Mn^{3+} or $Mn^{2+} + Mn^{4+}$ ions in the solid. We, therefore, approach the problem from a slightly different angle and make use of the structural and conductivity data as well to arrive at the valence states of the manganese ions in the formula.

These compounds may be treated as homogeneous solid solutions of $ZnMn_2O_4$, $ZnNiMnO_4$ and Mn_3O_4 in appropriate proportions. Assuming that the ions maintain the same ionisation state and the same site which they had in the parent compounds, then we arrive at the general formula:



This is the special case of the general formula described earlier with

$$a = 1-x$$

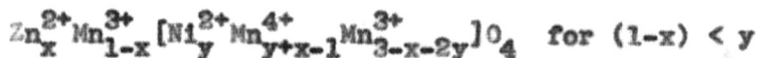
$$b = 2-2y$$

$$c = y$$

In this formula, it is accepted that the Mn^{2+} and Mn^{4+} coexist in the compound. In case this is not possible, then we get the other possible formulae viz.



or



..(B)

The actual number of Mn^{2+} , Mn^{3+} and Mn^{4+} ions per formula unit for the two formula are worked out for the various compounds and are listed in Table No. 26.

One can see that in the cases marked (*) in the Table No. 26 the number of Mn^{3+} ions at the octahedral sites is much larger than the critical composition for cubic to tetragonal transformation generally observed. It is, therefore, concluded that the observed cubic symmetry in these cases goes strongly against the formula B and would support formula A. Formula A is also supported by the conductivity results. For example, in compound Nos. 7-12, the number of Mn^{4+} ions at the octahedral sites is too small to account for the observed conductivity.

Table - 26

Ionic configuration in two probable formulae (A) and (B)

S. No.	Struc- -ture	Formula A			Formula B			
		Mn ²⁺ _{tet}	Mn ³⁺ _{oct}	Mn ⁴⁺ _{oct}	Mn ²⁺ _{tet}	Mn ³⁺ _{tet}	Mn ³⁺ _{oct}	Mn ⁴⁺ _{oct}
1.	T	0.25	1.85	0.075	0.175	0.075	1.925	0
2.	T	0.25	1.55	0.225	0.025	0.225	1.775	0
3.	T	0.25	1.25	0.375	0	0.25	1.50	0.125
4.	C	0.25	0.95	0.525	0	0.25	1.20	0.275
5.	C	0.25	0.80	0.600	0	0.25	1.05	0.350
6.	C	0.25	0.65	0.675	0	0.25	0.90	0.425
7.	T	0.40	1.88	0.060	0.34	0.06	1.94	0
8.	T	0.40	1.64	0.180	0.22	0.18	1.82	0
9.	T	0.40	1.40	0.300	0.10	0.30	1.70	0
10.	C	0.40	1.16	0.420	0	0.40	1.56*	0.02
11.	C	0.40	1.04	0.480	0	0.40	1.44*	0.08
12.	C	0.40	0.92	0.540	0	0.40	1.32*	0.14
13.	T	0.50	1.90	0.050	0.45	0.05	1.95	0
14.	T	0.50	1.70	0.150	0.35	0.15	1.85	0
15.	T	0.50	1.50	0.250	0.25	0.25	1.75	0
16.	C	0.50	1.10	0.450	0.05	0.05	1.55*	0

The C_M values calculated for the various compounds using the formula A are presented in Table No.27, along with the experimentally observed values. The agreement is good.

Table - 27

Experimental and calculated C_M values

S.No.	Structure	C_M experimental	C_M theoretical
1	T	6.4	6.81
2	T	6.0	6.34
3	T	5.6	5.88
4	C	5.26	5.41
5	C	5.1	5.18
6	C	5.0	4.95
7	T	7.32	7.50
8	T	6.75	7.13
9	T	6.4	6.76
10	C	6.3	6.38
11	C	6.17	6.20
12	C	5.90	6.01
13	T	7.5	7.97
14	T	7.2	7.66
15	T	7.05	7.36
16	C	6.45	6.73

At low temperatures all these $1/\chi_M - T$ graphs show a departure from linearity, curves for compounds 1, 2, 3, 7, 8, 9, 13, 14, could be fitted on to the Neel hyperbola with appropriate values of the constants. The values of the constants which give the best fit with Neel's hyperbola in these compounds are listed in Table No. 28.

Table - 28

Value of constants in Neel's equation for $Zn_xNi_yMn_{3-x-y}O_4$

Compound S. No.	C_M experimental	$1/\chi_0$	σ	ϕ
1	6.4	78	59.3	85
2	6.0	71	220	80.1
3	5.6	56	125	81.9
7	7.32	82	835	64
8	6.75	75	1042	65.4
9	6.4	68	1209	51.8
13	7.5	74	1397	66.74
14	7.2	68	1654	62.44

The other graphs do not fit with Neel's hyperbola, although in these cases $1/\chi_M$ approaches to 0 at temperature around 90°K. It therefore appears reasonable to conclude that all these compounds would become ferrimagnetic at low temperatures, but there could be a complicated type of ordering.

Zinc-ferrite-manganite system ($\text{ZnFe}_{2x}\text{Mn}_{2-2x}\text{O}_4$)

All these compounds are paramagnetic in the temperature range investigated and obey the Curie-Weiss law. The magnetic susceptibility of this series of compounds has been measured and reported by Blasse⁷⁹ (1965) and O'Keeffe⁵³ (1961). Our results match generally with their results and hence we do not present them here.

One interesting result is that the observed value of the Curie constant, C_M is very much lower than what is expected on the basis of the chemical formula $\text{Zn}^{2+}\text{Fe}_{2x}^{3+}\text{Mn}_{2-2x}^{3+}\text{O}_4$ if the ions are assumed to be in the high spin state as can be seen from the Table No. 29. This observation would be taken for discussion in the next section.

Table - 29

Blasse ⁷⁹			Present work		
Composition	Curie constant per mole spinel		Composition	Observed C_M value	C_M values calcd. on the basis of the formula
	Experimental	Spin only (Fe^{3+} , Mn^{3+})			
$\text{ZnFe}_{1.5}\text{Mn}_{0.5}\text{O}_4$	6.54	8.07	$x = 0.1$	5.52	6.2
$\text{ZnFe}_{1.25}\text{Mn}_{0.75}\text{O}_4$	6.39	7.72	$x = 0.2$	5.63	6.5
ZnFeMnO_4	6.54	7.38	$x = 0.3$	5.91	6.7
$\text{ZnFe}_{0.5}\text{Mn}_{1.5}\text{O}_4$	6.27	6.69	$x = 0.4$	6.05	7.0
			$x = 0.5$	6.4	7.3
			$x = 0.6$	6.7	7.6
			$x = 0.7$	6.91	7.8
			$x = 0.8$	7.25	8.1
			$x = 0.9$	7.53	8.4

CHAPTER - IV

DISCUSSION

B-B interactions in manganites

As already mentioned, the A-B interaction in spinels containing paramagnetic ions at A sites is generally stronger than the B-B interaction and, therefore, the magnetic behaviour of such compounds is dominated by the former. These compounds are, therefore, unable to give much information about the B-B interactions. However, the A-B interaction is absent in the compounds in which the A ion is diamagnetic and so we can study the nature of the B-B interactions from the magnetic properties of these spinels.

In Table No. 30 we list out the magnetic properties of some selected compounds of this class from which we can deduce the nature of the B-B interaction. The interaction between $\text{Mn}^{3+}(\text{d}^4) - \text{Mn}^{3+}(\text{d}^4)$ must obviously be negative in oxidic spinels because ZnMn_2O_4 and CdMn_2O_4 are known to be antiferromagnetic. $\text{Mn}^{4+}(\text{d}^3) - \text{Mn}^{3+}(\text{d}^4)$ interaction must also be negative because a number of compounds containing Mn^{4+} and Mn^{3+} at B sites are known to be ferrimagnetic (see the Table No.30). Cr^{3+} is isoelectronic with $\text{Mn}^{4+}(\text{d}^3)$ and $\text{Zn}(\text{CrMn}^{3+})\text{O}_4$ affords another compound from which the nature of d^3-d^4 interactions can be deduced. This compound is antiferromagnetic indicating once again that the $\text{d}^4 - \text{d}^3(\text{B-B})$ interaction is negative. It is interesting to note that the negative interaction between the $\text{Mn}^{4+}(\text{d}^3) - \text{Mn}^{3+}(\text{d}^4)$ ions give rise to ferrimagnetism, whereas

Table - 30

B-B interactions

Electronic configuration	Ion pair	compound	Type of magnetic order	Sign of inter-action	Ref.
$d^4 - d^4$	$Mn^{3+} - Mn^{3+}$	$Zn^{2+}[Mn_2^{3+}]O_4$	A	Negative	52
		$Ca^{2+}[Mn^{3+}]O_4$	A	Negative	52
$d^4 - d^3$	$Mn^{4+} - Mn^{3+}$	$Cu^{1+}[Mn^{3+}Mn^{4+}]O_4$	Ferrimagnetic	Negative	52
		$Zn^{2+}[Li^{1+}Mn^{3+}Mn^{4+}]O_4$	Ferrimagnetic	Negative	56
		$Zn^{2+}Cu^{1+}[Mn^{3+}Mn^{4+}]O_4$	Ferrimagnetic	Negative	56
	$Cr^{3+} - Mn^{3+}$	$Zn[Cr^{3+}Mn^{3+}]O_4$	A	Negative	Present work
$d^3 - d^3$	$Mn^{4+} - Mn^{4+}$	$Li_{0.5}Zn_{0.5}[Li^{1+}Mn^{4+}]O_4$	F	Positive	58
		$Cu^{1+}[Mg^{2+}Mn^{4+}]O_4$	F	Positive	58
		$Cu^{1+}[Rh^{3+}Mn^{4+}]O_4$	F	Positive	58
	$Cr^{3+} - Cr^{3+}$	$Cr^{3+}Zn[Cr^{3+}]O_4$	A	Negative	80
$d^5 - d^5$	$Fe^{3+} - Fe^{3+}$	$Zn[Fe_2^{3+}]O_4$	A	Negative (weak)	68
$d^5 - d^4$	$Fe^{3+} - Mn^{3+}$	$Zn[Fe^{3+}Mn^{3+}]O_4$	A	Negative (weak)	Present work

A = Antiferromagnetic

F = Ferromagnetic

Ferrimagnetic

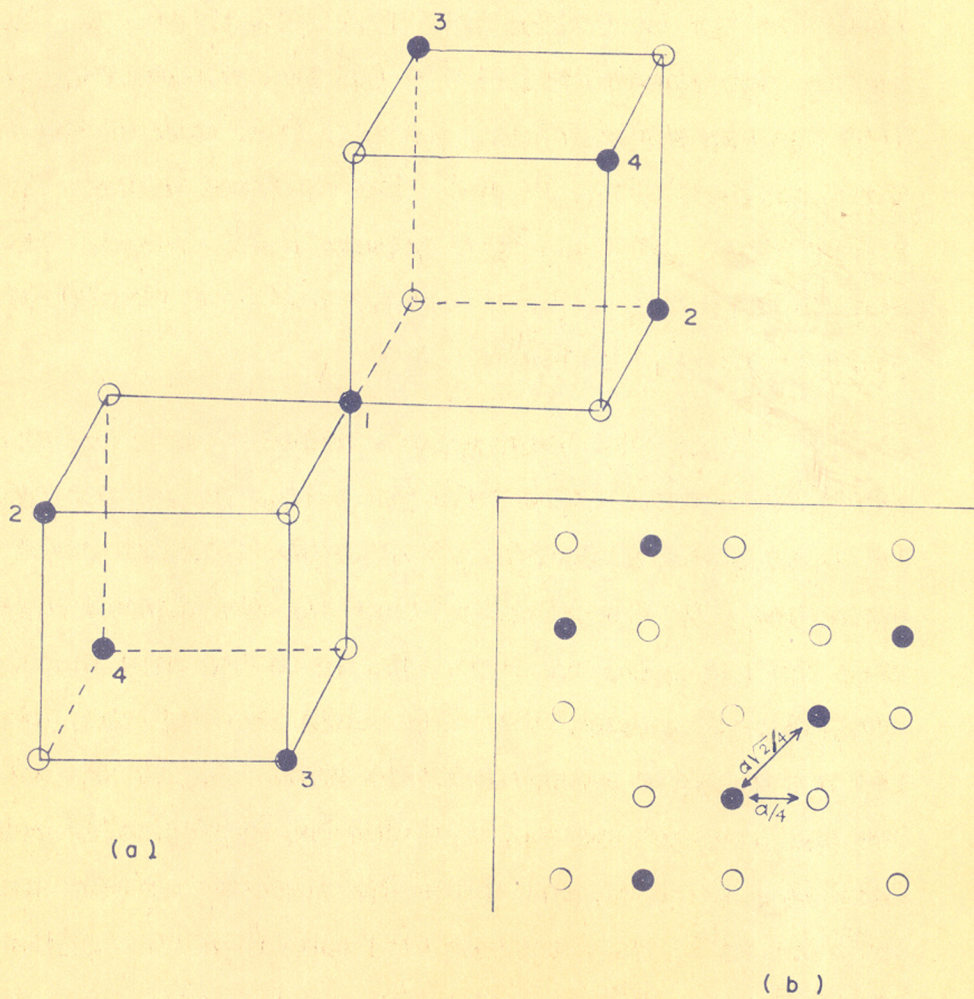


FIG. No. 37 SIX NEAREST METAL ION NEIGHBOURS OF AN OCTAHEDRAL METAL ION

● — METAL ION
○ — OXYGEN ION

the same type of interaction in an isoelectronic pair $\text{Cr}^{3+}(d^3) - \text{Mn}^{3+}(d^4)$ leads to antiferromagnetism.

As is well known, the B lattice of the spinel structure can be divided into four sublattices, B_1 , B_2 , B_3 and B_4 (see Figure 37). A 'B' ion is surrounded by six O^{2-} ions and six other B ions, two each from each of the remaining three lattices (Fig. 37 a). The distance between two adjacent B ions is $a\sqrt{2}/4$ and that between B- O^{2-} is $a/4$. The surroundings of a B ion in one of the three biaxial planes is as shown in Fig. 37(b).

When antiferromagnetic ordering sets in, the four sublattices would align into two pairs, in one the spins would be aligned in one direction and in the other it would be the opposite. If the d^3 and d^4 ions are distributed randomly over the two sets, which appears to be the case in $\text{Zn}[\text{Cr}^{3+}\text{Mn}^{3+}]\text{O}_4$ the magnetic moment over them would be equal and opposite, hence the net magnetic moment would be zero. If, on the other hand, the two ions get ordered over the two magnetically ordered lattices, which appears to be the case for spinels containing Mn^{3+} and Mn^{4+} , then the magnetic moment on the lattice containing the Mn^{3+} ions (d^4) would be four units whereas that on the lattice containing the Mn^{4+} ions (d^3) would be only three units. Thus the antiferromagnetically ordered solid would have a net resultant magnetic moment (ferrimagnetism). It is possible to imagine the reason why the spinel containing Mn^{3+} , Mn^{4+} can get ordered whereas not the ones containing Mn^{3+} and Cr^{3+} ions.

Firstly, the ordering of Mn^{3+} and Mn^{4+} ions involve only electronic exchange which can take place even at low temperatures (below Neel temperature), whereas the ordering of Cr^{3+} and Mn^{4+} ions would involve ionic motion which would be more or less hindered at such low temperatures.

Secondly, in a compound of mixed valencies the electrostatic energy is lowered on ordering because, in a disordered structure, one gets clusters of Mn^{3+} or Mn^{4+} ions which increase the energy. In $Zn[Cr^{3+}Mn^{3+}]O_4$ where both the ions are trivalent such a driving force is absent. The ferrimagnetic nature of the compounds of the general formula $Zn^{2+}[Ni_x^{2+}Mn_x^{4+}Mn_{2-2x}^{3+}]O_4$ studied by Ghare²⁷ (1968) of this laboratory appear to be due to this very reason.

It, therefore, appears reasonable to conclude that d^4-d^3 interaction is negative and that a substance is ferrimagnetic or antiferromagnetic depending on whether there is an ionic ordering present along with magnetic ordering or not.

As regards the d^3-d^3 interaction, we choose three isoelectronic pairs viz. $Mn^{4+}-Mn^{4+}$, $Cr^{3+}-Mn^{4+}$ and $Cr^{3+}-Cr^{3+}$. It is really interesting to find that in this series the first pair gives ferromagnetic compounds suggesting a positive d^3-d^3 interaction, whereas the other two give antiferromagnetic compounds suggesting a negative d^3-d^3 interaction. McGuire et.al.⁸⁰ (1952) have also concluded that the magnetic interaction

in $\text{Cr}^{3+} - \text{O}^{2-} - \text{Cr}^{3+}$ (90°) is very strongly negative in case of spinels MgCr_2O_4 and ZnCr_2O_4 . The asymptotic Curie temperature θ_A is -370°K and -350°K respectively.

This difference in the behaviour of Cr^{3+} and Mn^{4+} is of a type different than that discussed earlier (i.e. $\text{Mn}^{3+} - \text{Mn}^{4+}$ and $\text{Mn}^{3+} - \text{Cr}^{3+}$). Here the sign of interaction itself is changed as we go from Mn^{4+} to Cr^{3+} , whereas in the earlier case the interaction remained negative in both cases and the difference arose due to the presence or absence of the ionic ordering. The B-B interaction in these compounds can arise (i) due to direct interaction of the t_{2g} electrons of the neighbouring B ions, and (ii) due to indirect interaction between the two d^3 ions via the intervening oxygen ion. The B-O-B angle is 90° .

The variation of the strength of interaction in several isoelectronic configurations has been considered by several workers. Blasse⁵⁸ (1966) has concluded that the difference in ionic radii and several other factors determine the nature of interaction in such systems. He considered that the cation-cation direct interaction as well as cation-anion-cation superexchange interaction are important for the d^3-d^3 pair. The cation-cation direct interaction is expected to be negative, whereas the cation-anion-cation interaction positive. The relative magnitude of the two would then determine the sign of the resultant interaction. In case of cations which are not too small relative

to the anions and are bonded ionically, the cation-cation interaction predominates. In case of systems where the cation is small in size, its charge is not too high and the electronegativity of anion is small, the cation-anion-cation interaction is positive and dominant over the direct interaction. In such cases the resultant is, therefore, weakly positive.

Wickham and Goodenough⁶⁹ (1959) have also attributed the negative $\text{Cr}^{3+} - \text{Cr}^{3+}$ interaction in ZnCr_2O_4 as due to direct cation-cation interaction. Lotgering⁴⁶ (1956) has predicted a weakly positive interaction in ZnCr_2S_4 in view of the fact that the charge of the cation is high and the electronegativity of the anion is small which increases the Me-O-Me superexchange interaction.

Goodenough⁷⁷ (1960) has also attributed the variation of the exchange interaction to the variation in interionic distance. Increasing distance means decreasing direct overlap and consequently a stronger positive exchange. The effect may even be strengthened by large size of the A ions. A large cation at the A site implies a large u parameter so that the Me-O-Me angle becomes larger than 90° . This decreases the direct overlap, but increases the superexchange interaction.

The variation in the relative strengths of the various mechanisms contributing to the 90° superexchange itself can also account for the change in the sign of the interaction. These factors have been discussed by Goodenough⁶⁸ (1963). For the

d^3-d^3 pair the results are as follows:

Outer electron configuration	Delocalization superexchange			Correlation superexchange		
	$t_{2g}-t_{2g}$	e_g-t_{2g}	e_g-e_g	Via S	Via $p\sigma, p\pi$	Via $p\sigma, p\sigma'$
d^3-d^3	$\uparrow\downarrow$	$\boxed{\uparrow\uparrow}$	-	$\uparrow\downarrow$	$\boxed{\uparrow\uparrow}$	$\boxed{\boxed{\uparrow\uparrow}}$

It can be seen that $t_{2g}-t_{2g}$ delocalization superexchange and the correlation superexchange via the 'S' orbitals lead to negative exchange whereas the $t_{2g}-e_g$ delocalization superexchange and the correlation superexchange via $p\sigma, p\pi$ and via $p\sigma, p\sigma'$ lead to positive exchange interaction. Thus, it is possible to get negative or positive interaction depending on the relative strengths of these factors. This offers another possible explanation as to why the nature of interaction changes as one goes from Mn^{4+} to Cr^{3+} . In fact, it is known that the alignment changes from antiparallel to parallel when one goes from oxide to chloride of these ions [Goodenough⁶⁸(1963)].

The other series of compounds containing diamagnetic A ion has the general formula $Zn[Fe_{2x}^{3+}Mn_{2-2x}^{3+}]O_4$. All these compounds have been found to be antiferromagnetic. This leads us to conclude that the $Fe^{3+}(d^5) - Mn^{3+}(d^4)$ interaction is negative and that there is no ordering of the ions over the two magnetic sublattices. However, the Neel temperature for these compounds appears to be low - about $90^\circ K$ or lower. It is interesting to

find that even a small amount of replacement of Mn^{3+} ion by Fe^{3+} [10%] decreases the Curie temperature from 200°K for pure ZnMn_2O_4 to less than 90°K for $\text{Zn}[\text{Fe}_{0.2}\text{Mn}_{1.8}^{3+}]_4\text{O}_4$. This shows that the negative Fe^{3+} - Mn^{3+} interaction is very much weaker than the negative Mn^{3+} - Mn^{3+} interaction.

In the system ZnMn_2O_4 - $\text{Zn}(\text{MnNi})_4\text{O}_4$ - Mn_3O_4 , the compounds have the general formula $(\text{Zn}_x^{2+}\text{Mn}_{1-x}^{2+})(\text{Ni}_y^{2+}\text{Mn}_y^{4+}\text{Mn}_{2-2y}^{3+})_4\text{O}_4$ and they are expected to have the canted or spiral spin arrangement because in these cases the A-B interaction is weak because (i) Mn^{2+} ion at the A site gives rise to weak A-B interaction as can be seen from the fact that Mn_3O_4 has the canted spin structure and (ii) the presence of the diamagnetic Zn ions at A site further weakens the A-B interaction.

It may also be noted that the compositions 4, 5, 6, 10, 11, 12 and 16, appear to have very low Curie temperature. This indicates that in these compounds the negative A-B interaction is of comparable magnitude to the negative B-B interaction. The value of Curie temperature decreases as the Mn^{3+} ions are progressively replaced by Mn^{4+} and Ni^{2+} ions. In other words, the Mn^{3+} - Mn^{4+} and Mn^{3+} - Ni^{2+} interactions are negative and stronger than Mn^{3+} - Mn^{3+} interaction. We can see that Fe^{3+} - $\text{Cr}^{3+}(\text{d}^5-\text{d}^3)$ B-B interaction is also negative because $\text{Zn}(\text{FeCr})_4\text{O}_4$ is antiferromagnetic. These experimental

results clearly prove that the d^3-d^3 , d^4-d^4 and d^5-d^5 interaction are all negative and their strength is in the following order $d^3-d^3 > d^3-d^4 > d^4-d^4 > d^4-d^5 > d^5-d^5$. The strength of the d^3-d^5 interaction lies in between these two extremes. This conclusion is also supported by the fact that ferrites usually show Neel type collinear arrangement (weak B-B as compared to A-B) whereas manganites and chromites have canted spin arrangement (B-B and A-B comparable).

The other interesting observation is the low Curie constant C_M for $Zn[Fe_{2x}^{3+}Mn_{2-2x}^{3+}]O_4$ systems. A possible explanation for this could be that some of the ions are present in the low spin state. At least for the tetragonal compounds it is unlikely that Mn^{3+} is in low spin state because in that case no Jahn-Teller distortion would be possible. The only other possibility is that Fe^{3+} ions are present in the low spin state i.e. $(t_{2g})^4(e_g)^1$. In this low spin configuration the Fe^{3+} ion also becomes a distorting cation or alternatively it may be argued that the tetragonal distortion of neighbouring octahedra forces the Fe^{3+} ion to acquire an electronic configuration which itself would give the same distortion. However, in absence of any additional proof for this, it is not possible to say anything more in this matter. It must be admitted that such low spin Fe^{3+} ions are not common in ferrites. The saturation magnetization results generally agree with a value of five free spins for Fe^{3+} .

Blasse⁷⁹(1965) has considered the possibility of cluster formation but in view of so many uncertainties definite conclusion could not be drawn.

Temperature independent antiferromagnetism

As has already been mentioned, zinc manganite shows temperature independent antiferromagnetism which has been attributed by Sinha and Sinha³⁵(1962) to the anisotropy in exchange interactions. It has been assumed that the interactions in the a-b planes are much stronger than those in the a-c or b-c planes. Under these conditions, the stable ordering corresponds to a linear antiferromagnetic chain along the $[110]$ and $[\bar{1}\bar{1}0]$ directions. This type of arrangement has been shown to lead to temperature independent susceptibility. Dey and Anderson⁵⁷(1965), and Rosenberg and Nicolau⁵⁵(1964) also have observed this type of behaviour in CdMn_2O_4 . Blasse⁷⁹(1965) while accepting the above linear antiferromagnetic chain model, prefers to calculate the magnetic susceptibility using the Ising model. The calculated and observed values of magnetic susceptibility show a good agreement if corrections are allowed for non-infinite chains.

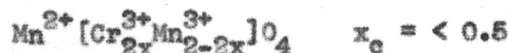
We have investigated the systems ZnMn_2O_4 - ZnCr_2O_4 and ZnMn_2O_4 - ZnFe_2O_4 systems with a view to see the effect of (a) substitution of distorting d^4 by non-distorting d^3 and d^5 ions, and (b) changing the symmetry from tetragonal to cubic on this phenomenon of temperature independent antiferromagnetism. All these spinels are normal, so that the Zn^{2+} ions always occupy the tetrahedral sites. Unfortunately, however, in case of

ZnMn_2O_4 - ZnFe_2O_4 , the addition of even ten per cent Fe^{3+} ion lowers the Neel temperature from 200°K for pure ZnMn_2O_4 to less than 90°K for $\text{ZnMn}_{1.8}\text{Fe}_{0.2}\text{O}_4$ leaving the compounds paramagnetic in the temperature region in which we have worked. However, in case of ZnMn_2O_4 - ZnCr_2O_4 the Neel temperature is not affected so much by the replacement of Mn^{3+} by Cr^{3+} . Here one finds that the $1/\chi_M - T$ slope becomes non-zero for even a ten per cent substitution of Cr^{3+} for Mn^{3+} and it keeps on increasing as the Mn^{3+} ion concentration decreases. Thus the temperature independence disappears much before the tetragonal to cubic transition composition is reached. In other words, we have a number of compounds whose crystal structure is tetragonal, but they do not show the temperature independent antiferromagnetism. This leads us to believe that it is not crystal anisotropy alone which is responsible for this behaviour.

Critical concentration for tetragonal distortion

Earlier studies^{16,13} on solid solutions of manganites have revealed that for tetragonal bulk distortion a certain minimum number of Mn^{3+} ion is required at the octahedral sites. For most manganites a value of $x_c \simeq 0.6$ has generally been obtained. In other words, if the number of octahedral sites occupied by the distorting Mn^{3+} ions per unit cell becomes less than 9.6 (16×0.6) then the structure at room temperature changes to cubic¹³. Later studies, however, have revealed a number of cases where x_c values less than 0.6 have been reported. The

following list gives some of these cases:



Some cases of x_c higher than 0.6 have also been reported but they can be attributed to our insufficient knowledge about the cation distribution and the valence state. If some Mn^{3+} ions migrate to the tetrahedral sites or change to Mn^{2+} or Mn^{4+} then the actual number of Mn^{3+} could be lower. However, the lower value of x_c is more difficult to explain because there is no way which one can suggest for increasing the number of distorting cations at the octahedral sites.

Goodenough⁶⁸ (1963) has considered some factors which effect the value of x_c . For example Fe^{2+} and Co^{2+} ions might modify the x_c due to spin-orbitcoupling. Cation size is also thought to play a small but measurable role. Also the nature of bonding and Jahn-Teller distortion at A sites may play a role in determining the critical concentration. However, it does not seem possible to systematise all the observations on the basis any of these mechanisms.

Blasse⁷⁹ (1965) has considered two possible explanations for this behaviour:

(A) If there are ions with different charges, the energy is lower, if there is an ordering of the ions at the octahedral sites, whereas if all the octahedral cations have the same charge then there is no gain in electrostatic energy on ordering. He further suggests that the ordering of cation would reduce the interaction between the distorted octahedral so it would be easier to destroy the long range distortion in case ionically ordered solids. In other words, the tetragonal cubic transformation can take place at higher x_c when cations of different charges are present.

(B) If there are ions with different charges and if they are randomly distributed they would polarise the different oxygen ions differently and the cubic symmetry around the central ion would be lost. If the symmetry lowering takes place in all directions at random then no cooperative Jahn-Teller distortion would be expected.

We consider the first explanation as less likely because the ionic ordering is known to take place only at fairly low temperatures. For example, in case of Fe_3O_4 such an ordering takes place only at 119°K . On the other hand, the second explanation looks more attractive. In addition to the indirect influence through oxygen polarisation, the cations may play a more direct role. If the charges on these cation which from the second nearest neighbour to the distorting cation differ then

the non-homogeneous charge distribution can remove the degeneracy of the e_g orbital. This splitting though small may be enough to fix the direction of the local distortion. In view of the random distribution of charges, the distortion would tend to be randomly oriented. In other words, this effect would, to some extent, oppose the ordering of distorted octahedra. This would mean that the critical concentration for transformation would go up. Thus the value of $x_c = 0.6$ would represent values for such systems where the ordering is opposed by the assymetric charge distribution and the lower value ($x = 0.3$) would correspond to the symmetric charge distribution. It would not be surprising if the true value is even lower and that all observed higher values may be due to the variable amount of assymetry introduced due to the assymetric charge distribution.

The critical concentration required for distortion by cations at tetrahedral site apparently shows a considerable variation from system to system. Some examples collected from literature are given below:

$(Cu_x Me_{1-x})[Cr_2]O_4$ for Me = Mg, Zn, Cd, Co.	$x_c = 0.5$	Ref. 71.
$Cu_x^{2+} Mn_{1-x}^{3+} [Cr_{1+x}^{3+} Cu_{1-x}^{2+}]O_4$	$x_c = 0.8$	Ref. 71.
$Cu_x^{2+} Ga_{1-x}^{3+} [Cr_{1+x}^{3+} Cu_{1-x}^{2+}]O_4$	$x_c = 0.7 - 0.75$	Ref. 17
$Cu_x^{2+} Fe_{1-x}^{3+} [Cr_{1+x}^{3+} Cu_{1-x}^{2+}]O_4$	$x_c = 0.5$	Ref. 17
$Cu_x^{2+} Al_{1-x}^{3+} [Cr_{1+x}^{3+} Cu_{1-x}^{2+}]O_4$	$x_c = 0.2$	Ref. 71

The compounds in the last four series also contain distorting Cu^{2+} ions at the octahedral sites, so the x_c values of these compounds cannot be taken as representative. Even if these values are left out of consideration, the remaining ones show a variation amongst themselves. This variation cannot be attributed to the asymmetry in charge distribution around the distorting cations because the four series are completely similar in that respect. This anomaly appears to be mainly due to the uncertainties in the above-mentioned distribution and the valence state of the cations.

As far as copper-chromite-manganite is concerned our present work has clearly established that the cubic structure is maintained up to the formula $\text{CuMn}_{1.0}\text{Cr}_{1.0}\text{O}_4$ which corresponds to $\text{Cu}_{0.5}^{1+}\text{Cu}_{0.5}^{2+}[\text{Mn}_{0.5}^{3+}\text{Mn}_{0.5}^{4+}\text{Cr}_{1.0}^{3+}]_4$ giving value of x_c as 0.5.

Furthermore the low value of x_c observed for copper chromite aluminate appears to be due to erroneous cation distribution. It is very reasonable to expect that some Al^{3+} ions are at octahedral sites. This would raise the value of Cu^{2+} ions at the tetrahedral sites and the value of x_c . It appears that when correct cation distribution is arrived at the value of x_c would turn out to be between 0.5 - 0.7 in all cases.

Valence states of ions in copper-manganite

The valence state of cations in copper manganite has been a subject of considerable controversy. The compound was found to have normal cubic spinel structure by Sinha, Sanjana

and Biswas⁶⁴(1957). They explained the cubic structure as due to the compound having the formula

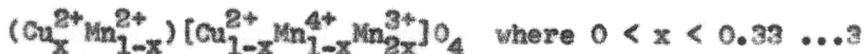


Miyahara²¹(1962), Baltzer and Lopatin²²(1964), Miller⁷⁰(1968) and O'Keeffe⁵³(1961), consider this as unreasonable and have preferred the formula



They have argued that Cu^{2+} ions at the tetrahedral sites tend to distort the structure with $c/a < 1$ whereas the Mn^{3+} ions tend to distort the structure with $c/a > 1$. The two effects mutually balance and hence the cubic structure is maintained.

Sheftel, Zaslavskii and Kurvlina⁸¹(1961,1962) have found that depending on the preparation condition, the copper manganite can show a slight departure from the normal spinel structure. They have ascribed the following formula to the compound:



In what follows, we examine the above three formulae with a view to see that one is able to explain the properties of pure copper manganite and its solid solutions.

The calculated Curie constant C_M for the three formulae are:

(1) 4.84.

(2) 6.95.

(3) $7.2 - 0.24x$ $x = 7.2 - 7.11$ for
 $x = 0 - 0.33$.

Buhl²³(1969) has recently measured the magnetic susceptibility of copper manganite as a function of temperature and got the value of C_M as 4.75. This strongly supports formula (1) as against (2) as well as (3).

Copper manganite is known to have much higher electronic conductivity than what is normally obtained for oxidic spinels. This observation cannot be explained by formula (2). However, both the formula (1) and (3) can explain this behaviour. The present results on the electrical conductivity of copper chromite-manganite can, however, be better explained by formula 1 than by formula 3. We have found that the conductivity of the system $\text{CuCr}_{2-2x}\text{Mn}_{2-2x}\text{O}_4$ increases with x upto $x = 0.5$ where it is maximum. After $x = 0.5$ the value starts decreasing again. This can be explained only if we assume:

(A) that formula (1) is correct, and

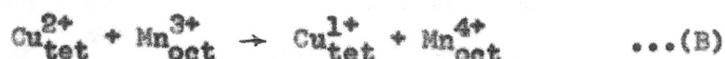
(B) that electron exchange between Cu^{1+} and Cu^{2+} at tetrahedral site also contributes to conductivity.

As formula (3) cannot explain either this result on the electrical conductivity or the C_M value obtained from the magnetic

data, there does not seem to be any justification for accepting (3) in preference to (1). Even if some manganese ions are present at the tetrahedral sites in a particular preparation that can be present as Mn^{3+} and there is no reason to choose the conversion



in preference to



The high conductivity of CuMnCrO_4 i.e.

$\text{Cu}_{0.5}^{1+}\text{Cu}_{0.5}^{2+}[\text{Mn}_{0.5}^{3+}\text{Mn}_{0.5}^{4+}\text{Cr}^{3+}]_4$ is attributed to conduction taking place both at the octahedral and tetrahedral sites.

It has generally been assumed that in the spinel structure the large distance between the tetrahedral-tetrahedral cations precludes any electron exchange between them. This is likely to be true for cases where electrons are localised and conduction takes place by hopping of the charge carriers.

It is known that in oxides containing full d shell e.g. Cu_2O , ZnO , etc. the band picture gives a more appropriate description of the transport properties of electrons whereas in oxides containing partially full d shell such as Fe_2O_3 , NiO , etc. the Heitler London or hopping model is applicable. In the present case the d electrons on the Cu^{1+} are expected to form a narrow d band. A mixture of Cu^{2+} and Cu^{1+} would then correspond to a partially filled band which would give rise to enhanced conductivity. The band width, of course, is expected to be small,

hence the mobility would also be small. Further work would, however, be required to confirm this interesting possibility.

The electrical conductivity of the other compounds studied in this thesis can be explained by the hopping mechanism. Compounds 1-16 of the series ZnMn_2O_4 - $\text{Zn}(\text{NiMn})\text{O}_4$ - Mn_3O_4 have a mixture of Mn^{3+} and Mn^{4+} ions at the octahedral site. The conductivity would, therefore, arise from the electron exchange between these ions. As the number of Mn^{4+} ions is less than that of Mn^{3+} ions (except No. 6) Mn^{3+} levels can be treated as more than half full. In other words, the conduction can be described as hole jumping and hence the materials are expected to be p-type, which is indeed borne out by the preliminary measurements of the sign of the thermoelectric coefficient.

It is interesting to find that the activation energy and the resistivity measured on a large number of samples give a smooth variation with the Mn^{4+} ion concentration (Fig. 22). This supports the conclusion that in these samples conduction takes place by the electron exchange between the Mn^{3+} and Mn^{4+} ions. No break is however observed on going from the tetragonal to cubic composition.

Cubic structure of $\text{Mn}^{3+}[\text{Ni}^{2+}\text{Cr}^{3+}]\text{O}_4$

According to Dunitz and Orgel⁸ (1957) $\text{Cr}^{3+}(\text{d}^3)$, $\text{Ni}^{2+}(\text{d}^8)$, $\text{Mn}^{3+}(\text{d}^4)$ and $\text{Cu}^{2+}(\text{d}^9)$ ions when located at tetrahedral sites should produce a tetragonal distortion (with $c/a > 1$ for the first two and with $c/a < 1$ for the latter two). Whereas, a

number of examples of Jahn-Teller distortion in spinels containing Ni^{2+} or Cu^{2+} ions at the tetrahedral sites are known, no case of such a distortion with $\text{Cr}_{\text{tet}}^{3+}$ or $\text{Mn}_{\text{tet}}^{3+}$ has so far been found. Of course, there is no spinel known with Cr^{3+} ion at the tetrahedral site. But there are some such compounds e.g. Mn_2O_3 , NiMn_2O_4 , etc. known with Mn^{3+} ions at the tetrahedral sites. These compounds unfortunately do not give any idea about the nature of distortion caused by the tetrahedral Mn^{3+} ions because the octahedral site also contains the distorting Mn^{3+} ion. However, the compound $\text{Mn}^{3+}[\text{Ni}^{2+}\text{Cr}^{3+}]\text{O}_4$ studied in the present work has the advantage that there are no distorting ions at the octahedral sites. The cubic symmetry of this compound clearly proves that Mn^{3+} ion at the tetrahedral site is non-distorting. This, in our view, is due to the effect of spin-orbit interaction. As Goodenough⁶⁸ (1963) has already pointed out that if $\Delta_{\text{LS}} > \Delta_{\text{t}}$ (where Δ_{LS} is the splitting due to spin-orbit interaction and Δ_{t} the splitting due to distortion from cubic symmetry), the spin-orbit interaction quenches out the Jahn-Teller mechanism. As the angular momentum for the tetrahedral d^3 , d^4 , d^8 and d^9 ions is known to be large, the relationship $\Delta_{\text{LS}} > \Delta_{\text{e}}$ is indeed very likely to be fulfilled in these cases. Mn^{3+} ion at the tetrahedral site is, therefore, non-distorting. This explains the cubic symmetry of $\text{Mn}^{3+}[\text{Ni}^{2+}\text{Cr}^{3+}]\text{O}_4$ and also the fact that c/a for $\gamma\text{-Mn}_2\text{O}_3$ is as high as some other manganites such as Mn_3O_4 , ZnMn_2O_4 , etc. which contain the non-distorting cations at the tetrahedral site. This also explains the cubic nature of $\text{Mn}^{3+}[\text{Ni}^{2+}\text{Mn}^{3+}]\text{O}_4$.

S U M M A R Y

Manganites of the general formula:

- 1) $\text{ZnCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$,
- 2) $\text{NiCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$,
- 3) $\text{CuCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$,
- 4) $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$ and
- 5) $\text{ZnFe}_{2x}\text{Mn}_{2-2x}\text{O}_4$,

have been synthesised and their structural, electrical and magnetic properties have been studied.

Appropriate compounds have been taken in proper ratios and mixed well by grinding under alcohol for about three hours to form a homogeneous mixture. The mixture is then fired in oxygen atmosphere at 1000°C for about 5 hours. The resultant product is once again finely ground in alcohol and again reacted at $1150-1300^\circ\text{C}$ in oxygen atmosphere for several hours. The reacted mass thus obtained has been analysed by X-ray diffraction to ensure complete reaction.

Crystal structure of these compounds has been determined by X-ray powder diffraction patterns and the unit cell parameters have been determined by the method of successive refinement. From the well known site preference energies, we came to the conclusion that Zn^{2+} , Mn^{2+} and also Cu^{1+} , Cu^{2+} occupy tetrahedral sites and Cr^{3+} occupies the octahedral sites. In case of compounds of the general formula $\text{NiCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$, the results of X-ray intensity analysis reveal

that the Mn^{3+} ions occupy tetrahedral site completely in the range $0 < x \leq 0.5$. For higher values of x , Mn^{3+} ions at tetrahedral sites are replaced gradually by Ni^{2+} ions. The compound $\text{Mn}^{3+}[\text{Ni}^{2+}\text{Cr}^{3+}]_0.4$ is found to be cubic which clearly proves that Mn^{3+} ion at the tetrahedral site is non-distorting. This, in our view, is due to the effect of spin-orbit interaction. It is concluded that Δ_{LS} is greater than Δ_{t} so the spin-orbit interaction quenches out the Jahn-Teller mechanism.

The study of distortion as a function of Mn^{3+} ions at octahedral sites reveals that the critical concentration required to bring about the tetragonal is generally 0.6. However, in some systems the critical concentration is much lower. In case of copper ions at tetrahedral site, we observed the critical concentration of these ions required for distortion $x_c = 0.5$.

The compounds prepared as described above have been ground and pressed into pellets with an appropriate binder. The pellets have then been sintered at about 1250-1300°C in oxygen atmosphere and cooled slowly in the same atmosphere. The conductivity of these pellets have been measured at various temperatures from room temperature to about 300°C. The change of electrical conductivity with temperature follows the well known relationship:

$$\sigma = \sigma_0 \exp -\Delta E/kT$$

ΔE is the energy of activation dependent on the composition. The results have been interpreted on the basis of Verwey's theory of electron-hopping at octahedral sites.

The high conductivity of CuCrMnO_4 i.e. $\text{Cu}_{0.5}^{1+}\text{Cu}_{0.5}^{2+}(\text{Mn}_{0.5}^{3+}\text{Mn}_{0.5}^{4+}\text{Cr}^{3+})\text{O}_4$ is attributed to conduction taking place both at the octahedral and tetrahedral sites.

Thermoelectric coefficient measurements indicate that all compounds in the system $\text{CuCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$ are p-type and the value of ST is small indicating that the Fermi level is close to the conduction level.

Paramagnetic susceptibility of all the compounds has been measured by the Gouy method in the temperature range 90°K to 600°K . The compounds in the system $\text{NiCr}_{2x}\text{Mn}_{2-2x}\text{O}_4$ and $\text{Zn}_x\text{Ni}_y\text{Mn}_{3-x-y}\text{O}_4$ are ferrimagnetic at low temperatures. It is expected that in these compounds the A-B interaction is of comparable magnitude, to the negative B-B interaction giving rise to a non-linear spin arrangement.

We have also studied a number of manganites containing paramagnetic ions only at B sites. From an analysis of these results it is concluded that d^4-d^3 interaction is negative and that a substance is ferrimagnetic or antiferromagnetic depending on whether there is an ionic ordering present along with magnetic ordering or not. As regards the d^3-d^3 interaction, we choose three isoelectronic pairs viz. $\text{Mn}^{4+}-\text{Mn}^{4+}$, $\text{Cr}^{3+}-\text{Mn}^{4+}$ and $\text{Cr}^{3+}-\text{Cr}^{3+}$. The origin of the change in the nature of magnetic interaction as one goes from Cr^{3+} to Mn^{4+} has been analysed. It is concluded that the superexchange mechanism dominates over the direct cation-cation exchange interaction.

A study of $\text{Zn}(\text{Fe}_{2x}^{3+}\text{Mn}_{2-2x}^{3+})_4$ has revealed that $\text{Fe}^{3+} - \text{Mn}^{3+}$ interaction is negative and is very much weaker than the $\text{Mn}^{3+} - \text{Mn}^{3+}$ interaction.

The experimental results clearly prove that the $d^3 - d^3$, $d^4 - d^4$, $d^5 - d^5$, $d^3 - d^4$ and $d^4 - d^5$ interactions are all negative and their strength is in the following order $d^3 - d^3 > d^3 - d^4 > d^4 - d^4 > d^4 - d^5 > d^5 - d^5$.

The effect of replacing Mn^{3+} ion in ZnMn_2O_4 by Cr^{3+} or Fe^{3+} on the temperature independent antiferromagnetism has also been studied.

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