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STRUCTURAL AND ELECTRONIC PROPERTIES OF $NiMn_2O_4$

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Abstract—A theoretical study, based on computer simulation techniques, of the spinel-structured oxide, $NiMn_2O_4$, is presented. The precise nature of the cation distribution and valencies in $NiMn_2O_4$ is uncertain and is of importance in interpreting the electrical properties of this material. An examination of the relative energetics of the normal and inverse structures of $NiMn_2O_4$ and other manganese and nickel spinels is carried out. The simulations are successful in predicting the observed structures, when our potential model is modified to include the effects of change in cation coordination. We proceed with an investigation of the possible valence states in $NiMn_2O_4$ by examining several important electronic processes. Our results suggest that the observed semiconducting behaviour is due to hopping of charge-carriers between Mn^{2+} and Mn^{3+} ions at octahedral sites.

Keywords: $NiMn_2O_4$, computer simulation, spinel, cation distribution, hopping conduction.

1. INTRODUCTION

A large group of mixed 3*d*-transition metal oxides crystallize in the spinel structure, based upon the cubic-close packing of oxygen ions in which the cations are situated on both tetrahedral and octahedral interstices (Fig. 1). In many cases, a major problem is the determination of the valencies and cation distribution among the two sublattices. The inverse spinel nickel manganite, $NiMn_2O_4$, is a typical example of this problem, as both manganese and nickel can adopt more than one valence state. The precise nature of the valencies and distribution of cations has proved to be controversial.

This material is also of considerable technological importance owing to its use in thermally-sensitive resistors (thermistors), a fact that arouses interest in the conductivity mechanism. It is well established that the semiconducting properties of $NiMn_2O_4$ is satisfactorilv described by a "hopping" mechanism of charge carriers via localized states [1], rather than by the band conduction model through delocalized states. Such hopping is most favourably encountered in compounds having the same cation in two or more different valence states on equivalent lattice sites, such as on the octahedral sublattice in the spinel structure [2]. Thus, a knowledge of the cation valencies is of great importance in the interpretation of the electrical properties of this material.

$NiMn_2O_4$ has been the subject of numerous investigations [3–11]. Azaroff [4] and Boucher *et al.* [7] have established, from neutron diffraction studies, that it is an inverse spinel, i.e., it contains octahedral nickel. The controversy is essentially whether the cations Mn^{2+} and Mn^{4+} are present on tetrahedral and octahedral sites respectively. Hopping conductivity between Mn^{3+} and Mn^{4+} ions has been proposed to explain the electrical properties [5, 10, 11]. However, O'Keeffe [6] and Boucher *et al.* [7, 8] suggest that only trivalent manganese is present on both sites. Considerable confusion therefore remains, with conclusions reached from the different experimental studies often being contradictory. In part this arises from difficulties in performing accurate experimental work on samples differing in methods of preparation and in the calcination temperatures employed. But there has also been no guidance in the construction of models from theoretical studies. In this paper the first theoretical survey of $NiMn_2O_4$ is presented, including the examination of the energetics of several important electronic processes. The study is based upon computer simulation techniques, which are now well established and have been successfully applied to studies of transition metal oxides [12, 13].

As a preliminary to our main study the relative energetics of the normal and inverse structures of $NiMn_2O_4$ were investigated. The calculations were used to examine the comparative importance of the factors that determine the distribution that is adopted and to show that our potential models can predict the observed structure. We then proceeded with an investigation of the possible valence states in $NiMn_2O_4$ using defect energy calculations.

2. TECHNIQUES

2.1. *Simulation methods*

Detailed discussions of the techniques employed are given by Catlow and Mackrodt [13]. Essentially

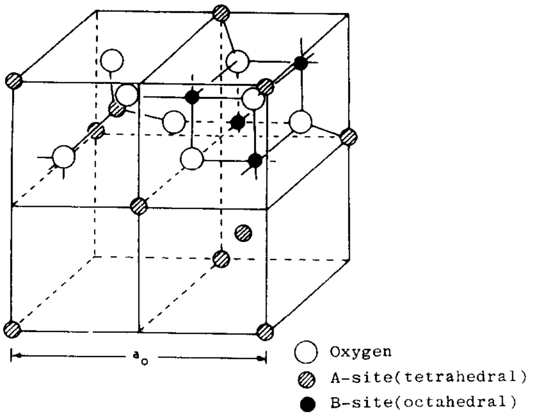

Fig. 1. Two quadrants of the cubic $A[B_2]O_4$ spinel structure.

the calculations divide the lattice into a spherical inner region surrounding the defect where there is explicit relaxation with specified lattice ion and defect pair-potentials; the surrounding region is treated by a continuum model based on the method of Mott and Littleton [14]. The effect of ionic polarizability is generally included and represented by the shell model of Dick and Overhauser [15]. The computer code CASCADE [16] was used for all the defect calculations, with an inner region containing approx. 200 ions.

2.2. *Potentials*

The calculations are based on the use of the Born model and require the specification of potential parameters representing the interactions between the lattice ions and between lattice and defect species. The short-range interionic forces are represented by a function of the Buckingham form:

$$V_{ij(r)} = A_{ij}\exp(-r/\rho_{ij}) - C_{ij}r^{-6}.$$

It is known that the bond lengths for cations in tetrahedral and octahedral coordination are different. This dependence on coordination number is included in our model by a modification of the pre-exponential factor through a Huggins–Mayer formulation,

$$A'_{ij} = A_{ij}\exp(-\Delta r/\rho)$$

where Δr is the change in bond length obtained using the Goldschmidt correction factor [17]. The potentials used were derived empirically by fitting to observed crystal data of the binary oxides [18]. In using these potentials transferability has been assumed; this assumption is valid considering the success of previous studies on ternary oxides [18, 19]. The only feasible method of obtaining potential parameters for the substitutional ions Mn^{3+} and Ni^{3+} is the electron-gas method [20] because there are no bulk crystal data for the appropriate oxides. Also, work of Butler *et al.* [21] has shown the importance of using consistently derived potentials. For such ions the semi-empirical correction [22] is employed. This essentially assumes that the required correction to the empirical potential is given by the difference between the electron-gas calculations, over a fixed range of interionic distances. The difference is then added to the empirical potentials calculated over the same range of interionic separations. The method described above for obtaining short-range potentials for Mn^{3+} and Ni^{3+} interactions is clearly approximate. It should, however, give a reasonable effect of the change in the charge state on the short-range repulsive term. The potential parameters used in this study are reported in Table 1.

We now test the reliability of the potentials by examining the structures and energies of the normal and inverse configurations of selected nickel and manganese spinels.

3. RESULTS AND DISCUSSION

3.1. *Cation distribution*

The question of the relative energies of normal and inverse spinel structures has attracted attention for many years and several factors are known to be important. One of the approaches to the problem has been the application of crystal field theory [23] which allows calculation of an octahedral site preference energy (OSPE) for each ion. Other important factors are Coulomb energies, ionic radius and covalency effects. Our investigation proceeded by calculating the lattice energy for both normal and inverse structures; in each case the minimum energy configuration was calculated using observed cell dimensions [24].

Table 1. Short-range potential and shell-model parameters. A^o and A^t are values appropriate for cations in an octahedral and tetrahedral anion environment respectively. Y is the shell charge and k the harmonic spring constant. Potential cut-off = 1.00 lattice unit

Interaction	A^o(eV)	A^t(eV)	ρ(Å)	C(eVÅ^{-6})	Ion	Y(e)	k(eVÅ^{-2})
$Mn^{2+} - O^{2-}$	715.8	611.3	0.3464	0.0	Mn^{2+}	3.42	95.0
$Ni^{2+} - O^{2-}$	683.5	593.9	0.3332	0.0	Ni^{2+}	3.34	93.7
$Al^{3+} - O^{2-}$	1114.9	1012.6	0.3118	0.0	Al^{3+}	3.00	99999
$Cr^{3+} - O^{2-}$	1734.1	1526.4	0.3010	0.0	Cr^{3+}	0.97	67.0
$Mn^{3+} - O^{2-}$	1001.7	881.6	0.3289	4.2	Mn^{3+}	3.00	99999
$Fe^{3+} - O^{2-}$	1102.4	876.6	0.3299	0.0	Fe^{3+}	4.97	304.7
$Ni^{3+} - O^{2-}$	930.5	831.0	0.3183	4.2	Ni^{3+}	3.00	99999
$Mn^{4+} - O^{2-}$	1180.6	1071.5	0.3217	6.3	Mn^{4+}	4.00	99999
$O^{2-} - O^{2-}$	22764.3	—	0.1490	27.88	O^{2-}	−2.39	18.41

Table 2.† Energies of inversion. ΔE is the calculated energy difference between normal and inverse structures with cation coordination not taken into account. A positive value indicates that the normal distribution is the most stable; $\Delta E'$ is the OSPE term added to ΔE; ΔE^c is $\Delta E'$ with the dependence on coordination included. λ is the fraction of B cations on tetrahedral sites [25]

Compound	a_o(Å)	λ_{obs}	ΔE (eV)	OSPE (eV)	$\Delta E'$ (eV)	ΔE^c (eV)
$MnCr_2O_4$	8.436	0	1.23	1.639	2.87	2.27
$MnAl_2O_4$	8.258	0	1.98	0.0	1.98	1.81
$NiCr_2O_4$	8.320	0	0.62	0.747	1.37	0.58
$MnFe_2O_4$	8.511	0.1	0.82	0.0	0.82	0.20
$NiAl_2O_4$	8.048	0.38	1.15	−0.892	0.26	−0.15
$NiFe_2O_4$	8.3532	0.5	0.10	−0.892	−0.79	−1.66
$NiMn_2O_4$	8.4028	0.5	0.39	0.093	0.48	−0.71

† In a companion paper (Cormack *et al.*) published in *J. Phys. Chem. Solids*, a different definition of $\Delta E'$ is used from that employed in the present work.

The difference in energies, ΔE, between normal and inverse structures were first calculated with the cation coordination not taken into account (Table 2). The positive values indicate that all the spinels are predicted to have a normal distribution. This suggests that the electrostatic term, although important, is not the sole factor determining which structure is adopted. Simple radius ratio arguments predict that smaller cations would prefer to occupy tetrahedral sites. In fact, from the observed structures the opposite trend is found. It is well known that due to ligand-field effects certain *d* electron configurations are stabilized in an octahedral field relative to a tetrahedral field. The energies $\Delta E'$ include the effect of the octahedral site preference energy term which must be added to the values of ΔE. Both $NiMn_2O_4$ and $NiAl_2O_4$ are still predicted to have a normal structure. Finally, an important feature is the dependence of short-range potentials on coordination number which may be considered a method of introducing a degree of covalency into the calculation. Inclusion of this latter "coordination-model" effect (calculated as described in Section 2.2) produces the energies ΔE^c and allows us to make correct predictions of the observed distribution in all the spinels considered. Of course, the various terms we have included to obtain ΔE^c may not be strictly additive. It is, however, difficult at present to devise any other procedure, and the terms are sufficiently independent for additivity to be a reasonable approximation. Clearly our results for $NiMn_2O_4$ are qualitatively in agreement with experiment which finds the inverse structure to predominate. It is not possible to make detailed comparison of our calculated energy of inversion with that obtained from thermopower measurements [10] as we favour a different model for the electronic structure of the material. The magnitude of this calculated value suggests that $NiMn_2O_4$ is not totally inverse but has a fraction of nickel on tetrahedral sites. This is also borne out in the calculations in the next section. Another interesting observation concerns $MnFe_2O_4$ which is calculated to show a small preference for the normal structure ($\Delta E^c = 0.20$eV). This is consistent with the observed λ value of 0.10, indicating a predominantly normal distribution where the energy of inversion is, however, low.

Finally in this section, on comparing our calculated anion *u* parameters, using the coordination model, with the values quoted in experimental studies we find good agreement (Table 3). This is the best agreement possible given that these are static simulations which omit any explicit representation of atomic thermal motions.

3.2. *Valence states*

Several configurations have been suggested by different investigators. On account of the cubic crystal structure Sinha *et al.* [3] proposed the valence distribution, $Mn^{2+}[Ni^{2+}Mn^{4+}]O_4$. Larson *et al.* [5] concluded that Mn^{2+} and Mn^{4+} ions are present on tetrahedral and octahedral sites respectively. From the viewpoint of crystal field theory O'Keeffe [6] considered the formula to be $Mn^{3+}[Ni^{2+}Mn^{3+}]O_4$, i.e., that only trivalent manganese is present. From neutron diffraction and magnetic studies Boucher *et al.* [7, 8] arrived at the same conclusion and reported a temperature-dependent cation distribution parameter *v* and the corresponding formula $Ni^{2+}_{1-v}Mn^{3+}_{v}[Ni^{2+}_{v}Mn^{3+}_{2-v}]O_4$, where *v* is equal to 0.93 at room temperature. Bhandage and Keer [9] suggested a small deviation from stoichiometry to explain their ESR data, which indicated the presence of Mn^{2+} (and not Mn^{4+}); $Mn^{3+}[Ni^{2+}Mn^{2+}_{0.10}Mn^{3+}_{0.90}]O_{3.95}$. From electrical properties [10] and X-ray photoelectron spectroscopy [11] the following valence distribution was proposed, $Ni^{2+}_{1-v}\ Mn^{2+}_{v}\ [Ni^{2+}_{v}\ Mn^{3+}_{2-2v}\ Mn^{4+}_{v}]O_4$

Table 3. Observed and calculated anion *u* parameters. u_{obs} from Ref. [24]

Compound	u_{obs}	u_{calc}	Δu
$MnCr_2O_4$	—	0.3923	—
$MnAl_2O_4$	0.390	0.3940	0.004
$NiCr_2O_4$	0.385	0.3880	0.003
$MnFe_2O_4$	0.3846	0.3923	0.0077
$NiAl_2O_4$	0.390	0.3867	0.003
$NiFe_2O_4$	0.381	0.3812	0.000
$NiMn_2O_4$	0.386	0.3851	0.001

Table 4. Charge transfer reactions—disproportionation. *t* and *o* refer to tetrahedral and octahedral sites respectively

	E_f(eV)
$Mn_t^{3+} + Mn_t^{3t} \rightarrow Mn_t^{2+} + Mn_t^{4+}$	5.27
$Mn_o^{3+} + Mn_o^{3+} \rightarrow Mn_o^{2+} + Mn_o^{4+}$	5.39
$Mn_t^{3+} + Mn_o^{3+} \rightarrow Mn_t^{2t} + Mn_o^{4t}$	5.12
$Mn_t^{3+} + Mn_o^{3+} \rightarrow Mn_o^{2+} + Mn_t^{4t}$	4.79

Table 5. Charge transfer reactions

	E_f(eV)
$Mn_t^{3+} + Ni_t^{2+} \rightarrow Mn_t^{2+} + Ni_t^{3+}$	0.63
$Mn_o^{3+} + Ni_o^{2+} \rightarrow Mn_o^{2+} + Ni_o^{3+}$	0.45
$Mn_t^{3+} + Ni_o^{2+} \rightarrow Mn_t{}^{2+} + Ni_o^{3+}$	0.41
$Mn_o^{3+} + Ni_t^{2+} \rightarrow Mn_o^{2+} + Ni_t^{3+}$	0.36

($v \approx 0.9$). This was proposed as there appears to be appreciable hopping conduction due to mixed cation valency on the octahedral sites.

Our approach to this problem is based on calculation of the energetics of electronic processes in the oxide. The electronic defects are treated as small polarons, localized at cation sites, giving ionic species which correspond closely to Mn^{2+}, Mn^{4+} and Ni^{3+} ions, etc. We assume that charge states may be determined by comparing the energies of various defects; that is, we neglect entropy terms. Given this assumption, the energies of formation of these charge transfer reactions are obtained by combining appropriate ionization potentials (of free ions) with the lattice energy term accompanying the formation of the electronic species.

First, let us consider the disproportionation process which creates an electron-hole pair on two manganese ions, on both octahedral and tetrahedral sites (Table 4). Relatively high and unfavourable energies of *ca.* 5eV are calculated indicating that tetravalent manganese is not present. It should be noted that about 17eV is required to produce $Mn^{2+} + Mn^{4+}$ from $2Mn^{3+}$ (the third and fourth ionization potentials of manganese are 33.667 and 51.2 eV respectively), with which the lattice energy term is unlikely to compete. From the magnitude of these charge transfer energies we conclude that only trivalent manganese is present. Is there any experimental support for our prediction of the dominance of Mn^{3+} in $NiMn_2O_4$? ESR data of Bhandage and Keer [9] indicated the presence of a small proportion of Mn^{2+} and found no evidence for Mn^{4+}. Analysis of the magnetic properties of the material [8] also found the presence of Mn^{3+} ions. In contrast, however, XPS studies [11] favour the presence of Mn^{4+}. In view of the contradictory information from experiment we return to the basic theoretical problem that would be posed by the coexistence of Mn^{2+} and Mn^{4+}. As noted above, and as commented previously by O'Keeffe [6], there is a very large ionization energy term associated with the disproportionation reaction required to create these species. It is therefore necessary to postulate that polarization energy must compensate the ionization term if the disproportionation is to occur. Although there are several approximations in our method, we consider that it is unlikely that we are underestimating this term by a large amount.

Processes involving exchange between Mn^{3+} and Ni^{2+} were also considered (Table 5). This shows that the following reaction

$$Mn_o^{3+} + Ni_t^{2+} \rightarrow Mn_o^{2+} + Ni_t^{3+}$$

although endothermic, is small (0.36 eV), sufficiently so to suggest that appreciable excitation could occur at higher temperatures. Therefore, it is proposed that Mn^{2+} ions are generated thermally. Once generated, motion of the charge-carriers occurs via a phonon-assisted hopping mechanism. Thus, the observed electrical properties and negative Seebeck coefficient [5, 9] can be explained by considering the hopping of electrons from Mn^{2+} to Mn^{3+} ions in the octahedral sublattice. The possible conduction at tetrahedral sites is neglected because the distance between them is too great to allow a comparable transfer of charge by this process. Furthermore, it is assumed that electron transport is controlled by the creation of electrons, for which a value of 0.36 eV is calculated. This is in good agreement with the observed activation energy of 0.37eV [5, 10]. These results demonstrate that there is a need in $NiMn_2O_4$ for a fraction of nickel on tetrahedral sites or a degree of "deinversion". Also from Section 3.1 the relative magnitude of ΔE^c suggests that this material is not totally inverse. Consequently, $NiMn_2O_4$ may be represented by the following formula with the distribution parameter $v \approx 0.9$ at room temperature [7],

$$Ni_{1-v}^{2+} Mn_v^{3+} [Ni_v^{2+} Mn_{2-v}^{3+}] O_4.$$

In proposing the creation of Ni^{3+} at high temperatures, we are aware that there is no evidence for the presence of this charge state of Ni in other spinels. But we stress that the Ni^{3+} is created by thermal excitations and is not present in the ground state of the material.

4. CONCLUSIONS

This paper has clearly shown that our potential models can predict the observed structure in all the spinel oxides considered, by incorporating the dependence on coordination of the short-range potential. From our study of electronic processes the disproportionation reaction to create $Mn^{2+} + Mn^{4+}$ is found to be unfavourable, and strongly suggests that the valence distribution in $NiMn_2O_4$ is:

$$Ni_{1-v}^{2+} \mathit{Mn}_v^{3+} [Ni_v^{2+} Mn_{2-v}^{3+}] O_4 \quad (v \approx 0.9).$$

In addition, the results suggest the importance of the charge-transfer reaction to create $Mn_o^{2+} + Ni_t^{3+}$, as excited states, the energy of which agrees very well with the observed activation energy of conduction. The subsequent Mn^{2+}/Mn^{3+} hopping process on the octahedral sublattice provides a mechanism for the semiconducting behaviour.

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