JOURNAL OF SOLID STATE CHEMISTRY **49**, 93–98 (1983)

X-Ray Photoelectron Spectroscopy Study of the Cation Valencies in Nickel Manganite

V. A. M. BRABERS, F. M. VAN SETTEN, AND P. S. A. KNAPEN

Department of Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received December 16, 1982; in revised form March 25, 1983

The X-ray photoelectron spectra of $NiMn_2O_4$, $NiMnZnO_4$, Mn_2TiO_4, $MnFe_2O_4$, and Mn_3O_4 are reported. The shift and broadening of the Mn-2*p*, Mn-3*s*, and Mn-3*p* lines in $NiMn_2O_4$, compared with those of the other compounds, are indicative of the charge distribution $Ni^{2+}_{1-\nu}Mn^{2+}_{\nu}[Ni^{2+}_{\nu}Mn^{3+}_{2(1-\nu)}Mn^{4+}_{\nu}]O_4$ ($\nu \simeq 0.9$). The values of multiplet splitting of the Mn-3*s* level also support this distribution.

Introduction

Some mixed crystals of 3*d*-transition metal oxides show characteristic properties which are determined by the occurrence of mixed valencies of the metal ions. For instance, if the metal ions are in crystallographically equivalent lattice sites, a noticeable conductivity can occur because of the fast exchange of valence electrons between the ions. A material that demonstrates this effect is magnetite (Fe_3O_4), which crystallizes in the spinel structure with Fe^{2+} and Fe^{3+} ions on octahedral sites, which in turn causes the high electrical conductivity ($\approx 10^2\ \Omega^{-1}\ cm^{-1}$).

A large group of mixed 3*d*-metal oxides crystallizes in the spinel structure. One of the major problems in the crystal chemistry of these mixed oxide spinels is the determination of the valencies and the distribution of the cations among the octahedral and tetrahedral sublattice sites of the spinel structure. In particular, if two different metals are present, each of which can adapt more than one valence state, the actual valencies of the cations in the material can be problematical.

The characteristic properties which are thought to be caused by the specific valencies of the ions in the compounds are often used to decide which of the valencies are present, although some doubt may remain because of the choice of models.

A typical example of this problem is the spinel nickel manganite ($NiMn_2O_4$). Boucher *et al.* (*1*) reported a temperature-dependent cation distribution parameter ν for this material, with a preference of nickel for octahedral sites at low temperature. On the basis of a particular model for the magnetic structure the same authors (*2*) proposed the valencies to be $Ni^{2+}_{1-\nu}Mn^{3+}_{\nu}[Ni^{2+}_{\nu}Mn^{3+}_{2-\nu}]O_4$, i.e. that only trivalent manganese is present on tetrahedral as well as on octahedral sites (ions between the brackets). Bhandage and Keer (*3*) arrived at the same conclusion, although they ignored the presence of nickel in the tetrahedral sites in the interpretation of their experimental data.

0022-4596/83 $3.00

Bongers (*4*) and Sinha *et al.* (*5*) proposed on the basis of the crystal structure the valence distribution $Mn^{2+}[Ni^{2+}Mn^{4+}]O_4$. Larson *et al.* (*6*) concluded from electrical conductivity and low temperature magnetization that Mn^{4+} ions are present on octahedral sites. Further, from infrared spectroscopy (*7, 8*) and electrical properties (*9*) strong evidence is found for an ionic structure that might be presented by

$$Ni^{2+}_{1-\nu}Mn^{2+}_{\nu}[Ni^{2+}_{\nu}Mn^{3+}_{2(1-\nu)}Mn^{4+}_{\nu}]O_4 \quad (1)$$

X-ray photoelectron spectroscopy can be used as a direct method to determine the valence distribution in nickel manganite. Since the core levels of atoms may shift because of valence changes and different crystallographic sites, the splitting of core levels is a direct proof of the presence of inequivalent atoms (*10*). Unfortunately, it is not always possible to find separate peaks if the shifts are too small, as was reported by Oku *et al.* (*11*) for the Mn^{2+} and Mn^{3+} states in Mn_3O_4, and the site differences for Mn^{3+} in γ-Mn_2O_3. However, broadening of the binding energy peaks of the core levels is still possible, which can be analyzed by a comparison with the spectra of compounds containing known species of ions.

To study the valencies in $NiMn_2O_4$, we have chosen the following reference materials, in which manganese is present as the species indicated in the following table:

$MnFe_2O_4$	$\rightarrow Mn^{2+}[Fe^{3+}_2]O_4$	Mn^{2+} in *A* sites
Mn_2TiO_4	$\rightarrow Mn^{2+}[Mn^{2+}Ti^{4+}]O_4$	Mn^{2+} in *A* and *B* sites
Mn_3O_4	$\rightarrow Mn^{2+}[Mn^{3+}_2]O_4$	Mn^{2+} in *A* sites, Mn^{3+} in *B* sites
$ZnNiMnO_4$	$\rightarrow Zn^{2+}[Ni^{2+}Mn^{4+}]O_4$	Mn^{4+} in *B* sites
$NiMn_2O_4$	$\rightarrow Ni^{2+}_{1-\nu}Mn_{\nu}[Ni^{2+}_{\nu}Mn_{2-\nu}]O_4$	Mn valencies uncertain.

As we will show, certain features in the XPS measurements on these materials prove the ionic structure of nickel manganite to be as indicated in formula (1).

II. Experimental

The XPS measurements were performed with a PHI Model 560 ESCA/SAM electron spectrometer using Mg$K\alpha$ radiation. The carbon 1*s* binding energy of contamination carbon, 284.6 eV, was used as calibration. The reproducibility of the binding energy values was within 0.2 eV.

X-ray photoelectron spectroscopy is a surface sensitive method which is performed under vacuum. The total pressure in the spectrometer ranges from 10^{-10} to 10^{-13} atm. For $NiMn_2O_4$ and $NiMnZnO_4$, which are very sensitive to loss of oxygen and to the formation of lower valencies in vacuum, some oxygen was flushed through the spectrometer; the oxygen pressure was estimated to be 10^{-10} atm. Using such an oxygen flow, no time-dependence of the peak structures was observed during the XPS measurements.

The specimens of $NiMn_2O_4$ and $NiMnZnO_4$ were ceramic samples, prepared by sintering spray-roasted mixtures of the nitrates in 1-atm oxygen at temperatures of 940 and 650°C, respectively. X-ray diffraction and microscopic investigation proved the specimens to be single phase spinels.

$MnFe_2O_4$, Mn_2TiO_4, and Mn_3O_4 were melt-grown samples, of which the ferrate

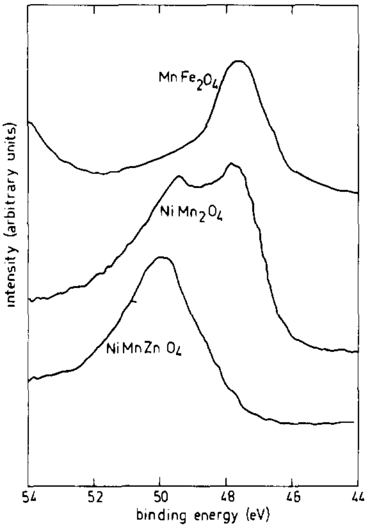

FIG. 1. Comparison of Mn-3p X-ray photoelectron spectrum of $NiMn_2O_4$ with that of $MnFe_2O_4$ and $NiMnZnO_4$.

and the titanate were single crystals and the hausmannite a microtwinned crystal (*12*).

III. Results and Discussion

In general, the binding energy of core levels shifts about 1 eV, through a change of the ionic charge of an atom by one unit, under the assumption that no other effects such as covalency are interfering. For nickel manganite with a distribution parameter $\nu \approx 0.9$ (*1*) (specimen annealed at 400°C in sealed silica tube under vacuum) the cation valencies may be represented by

$$Ni^{2+}_{0.1}Mn^{3+}_{0.9}[Ni^{2+}_{0.9}Mn^{3+}_{1.1}]O_4 \qquad \text{(a)}$$

or

$$Ni^{2+}_{0.1}Mn^{2+}_{0.9}[Ni^{2+}_{0.9}Mn^{3+}_{0.2}Mn^{4+}_{0.9}]O_4. \qquad \text{(b)}$$

In case (a), trivalent manganese is present on tetrahedral and octahedral sites and the only effect on the core levels may be caused by the site differences. As was already shown by Oku *et al.* (*11*) the effect of Mn^{3+} site difference upon the binding energies is small and may be of the order of a few tenths of an electron volt. In case (b), the main portion of the octahedral manganese ions is tetravalent and the tetrahedral is divalent, which may result in a shift of binding energies by about 2 eV. As the ligands are oxygen ions for both lattice sites, covalency effects are supposed to have only minor effect and the core levels of Mn^{2+} and Mn^{4+} ions must be distinguishable.

In Fig. 1 the 3p levels of manganese in $NiMn_2O_4$ are shown, together with those in $MnFe_2O_4$ and $NiMnZnO_4$. The separation into $3p_{1/2}$ and $3p_{3/2}$ is not seen either in the ferrate or in the Zn compound, although the energy differences for the $3p_{1/2}$ and $3p_{3/2}$ is ~1 eV (*13*). The Mn-3p lines have a FWHM of 1.8 and 2.8 eV for the ferrate and the zinc compound, respectively, which is large compared with the instrumental linewidth of about 0.7 eV. The absence of a clear separation into $3p_{1/2}$ and $3p_{3/2}$ for Mn Fe_2O_4 might be caused by a small broadening of the XPS lines due to shifting of manganese ions to octahedral sites (*14*). For the zinc compound the larger FWHM value of 2.8 eV may be caused by the reduction of some manganese ions to lower valencies under the experimental conditions in the spectrometer. Nevertheless, the majority of the Mn ions in $MnFe_2O_4$ and $NiMnZnO_4$ are supposed to be di- and tetravalent, respectively. Comparing the 3p spectra of manganese in $NiMn_2O_4$ with those in Mn Fe_2O_4 and $NiMnZnO_4$, we can see that the $NiMn_2O_4$ spectrum appears to be a superposition of the other two spectra. This is strong evidence for the simultaneous presence of tetrahedral Mn^{2+} ions (as in Mn Fe_2O_4) and octahedral Mn^{4+} ions (as in $NiMnZnO_4$). To be sure that the di- and tetravalencies are actual and that the site differences are not the main cause of the observed shift in $NiMn_2O_4$, the Mn-3p levels were also measured on $Mn^{2+}[Ti^{4+}Mn^{2+}]O_4$ and $Mn^{2+}[Mn^{3+}_2]O_4$, as is shown in Fig. 2. In both cases, the energy is 48.0 eV with a

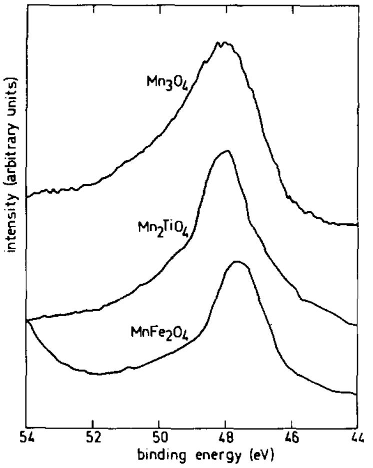

FIG. 2. Mn-3p X-ray photoelectron spectra of $Mn^{2+}[Ti^{4+}Mn^{2+}]O_4$, $Mn^{2+}[Mn_2^{3+}]O_4$, and $Mn^{2+}[Fe_2^{3+}]O_4$.

TABLE I

Mn-2p LEVELS AND FWHM FOR THE MANGANESE SPINELS

	$2p_{3/2}$	FWHM	$2p_{1/2}$	FWHM
$NiMn_2O_4$	641.1–642.6	4.5	652.8–654.3	4.5
$NiMnZnO_4$	642.5	2.8	654.4	3.0
$MnFe_2O_4$	640.8	2.8	—[a]	—
Mn_2TiO_4	640.6	3.0	652.6	3.0
Mn_3O_4	641.3	3.0	653.0	3.2

[a] The value of $2p_{1/2}$ for $MnFe_2O_4$ could not be determined because of interference with the Auger lines of iron.

FWHM of 2.4 and 3.0 eV, showing a much smaller effect in broadening and shifting due to site differences. The same effects were also observed for the $2p_{3/2}$ and $2p_{1/2}$ levels, as can be seen from the energy values in Table I. The values of the 2p levels for the Mn^{4+} ions in $NiMn_2O_4$ and $NiMnZnO_4$ were shifted by 1.5–1.9 eV to higher values with respect to the 2p levels of the Mn^{2+} ions in the other spinels. The $2p_{3/2}$ and $2p_{1/2}$ are separated by about 12 eV from each other; a complete splitting within these lines due to the presence of nonequivalent ions (such as Mn^{4+} and Mn^{2+}) was not observed. However, the presence of these ions in nickel manganite can be deduced from the FWHM value of 4.5 eV, as compared with ~3 eV for the other compounds, where no combinations of Mn^{4+}–Mn^{2+} ions are present.

Aside from the core levels of manganese in nickel manganite, the levels of nickel also point to the proposed model; i.e., only Ni^{2+} ions are found to be present. In Table II the 2p and 3p core level energies for Ni in $NiMn_2O_4$ and $NiMnZnO_4$ are given; a comparison of the $2p_{3/2}$ values with those for Ni^{2+} or Ni^{3+} in other oxides (*15*) provide an indication that in our materials nickel is present as divalent ion.

The use of the chemical shift of the core levels as a proof for differences in valencies can be erroneous in some cases because of the charging effect of the substrate during

TABLE II

CORE LEVEL ENERGIES OF NICKEL, MEASURED ON $NiMn_2O_4$ AND $NiMnZnO_4$

	$NiMn_2O_4$	FWHM	$NiMnZnO_4$	FWHM	Ni^{2+} (*15*)	Ni^{3+} (*15*)
$3p_{3/2}$	67.1	2.5	66.9	2.0		
$3p_{1/2}$	68.2		68.0			
$2p_{3/2}$	855.0	2.0	855.1	2.0	854.9	857.1
$2p_{3/2}$sat	861.3	2.5	861.5	2.5	862.1[a]	863.0
$2p_{1/2}$	872.1	2.0	872.3	2.2		
$2p_{1/2}$sat	888.1	2.5	888.0	2.5		

[a] The $2p_{3/2}$ level for Ni^{2+} and Ni^{3+} with oxygen as ligand is taken from the literature (*15*), and is referred to the $4f_{7/2}$ line of gold (83.8 eV).

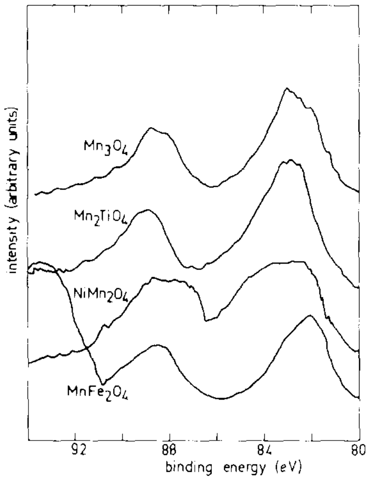

FIG. 3. Mn-3*s* XPS spectra of $NiMn_2O_4$, $MnFe_2O_4$, Mn_2TiO_4, and Mn_3O_4.

the measurements and the influence of covalency effects upon the shift of the levels. As was stated before, the last effect is supposed to be small because we deal with oxides. The charging effect can also be neglected because the two different "species" of manganese in nickel manganite are subject to the same influence of charging, and the same occurs in Mn_3O_4 and Mn_2TiO_4. Furthermore, corrections are made for charging effects, using the C-1*s* level as a standard.

Additional evidence for certain valencies can be obtained by checking for the presence of satellites or for multiplet splitting in the spectra. The satellite structure for the manganese 2*p* and 3*p* levels was not very pronounced in our spectra; the multiplet splitting of the 3*s* level of manganese, however, was very clear.

In Fig. 3 the 3*s* level for manganese is shown. Unfortunately, the Mn-3*s* spectrum of $NiMnZnO_4$ reveals no clear multiplet splitting, because the Zn-3*p* levels are interfering in the same energy range. The 3*s* multiplet splitting which can be deduced from the spectra ($\Delta E = E\,3s(1) - E\,3s(2)$) is now 6.8, 6.5, and 5.5 eV, for $MnFe_2O_4$, Mn_2TiO_4, and Mn_3O_4, respectively. The 3*s* spectrum of $NiMn_2O_4$ again shows broadening of lines (FWHM ~ 4 eV), which has been analyzed in first approximation as being the superposition of two spectra caused by two species of Mn ions; the multiplet splittings deduced from this range from 4.5 to 6.5 eV. Shirley (*16*) has shown that the experimental values for 3*s* multiplet splitting in 3*d*-transition metal compounds depends on the number of 3*d* electrons, being maximal, ~7 eV, for $3d^5$ ions and decreasing ~1 eV per electron if the number of electrons is changed. The multiplet splittings reported by Shirley for Mn^{2+} ($3d^5$), Mn^{3+} ($3d^4$), and Mn^{4+}($3d^3$) are in good agreement with the values we have found in the manganese spinels. The broad 3*s* lines in $NiMn_2O_4$ again point to two different valencies for manganese, the range of the deduced multiplet splitting (4.5–6.5 eV) providing strong evidence for the coexistence of di- and tetravalent manganese.

From the reported XPS spectra it might be concluded that the valency distribution, which was earlier proposed (*9*) to explain the electrical properties of $NiMn_2O_4$, is correct and may be represented by the formula

$$Ni^{2+}_{1-\nu}Mn^{2+}_{\nu}[Ni^{2+}_{\nu}Mn^{3+}_{2-2\nu}Mn^{4+}_{\nu}]O_4 \ (\nu \simeq 0.9).$$

References

1. B. Boucher, R. Buhl, and M. Perrin, *Acta Crystallogr. Sect. B* **25**, 2326 (1969).

2. B. Boucher, R. Buhl, and M. Perrin, *J. Phys. Chem. Solids* **31**, 363 (1970).

3. G. T. Bhandage and H. V. Keer, *J. Phys. C* **9**, 1325 (1976).

4. P. F. Bongers, Ph.D. thesis, University of Leiden (1957).

5. A. O. B. Sinha, N. R. Sanjana, and A. B. Biswas, *Acta Crystallogr.* **10**, 439 (1957).

6. E. G. Larson, R. J. Arnott, and D. G. Wickham, *J. Phys. Chem. Solids* **23**, 1771 (1962).

7. J. Preudhomme, *C.R. Acad. Sci. (Paris) Ser. A* **267**, 1632 (1968).

8. V. A. M. Brabers, *Phys. Status Solidi A* **12**, 629 (1972).

9. V. A. M. Brabers and J. C. J. M. Terhell, *Phys. Status Solidi A* **69,** 325 (1982).
10. M. Oku and K. Hirokawa, *J. Solid State Chem.* **30,** 45 (1979).
11. M. Oku, K. Hirokawa, and S. Ikeda, *J. Electron. Spectrosc.* **7,** 465 (1975).
12. V. A. M. Brabers, *J. Cryst. Growth* **8,** 26 (1971).
13. "Handbook of X-Ray Photoelectron Spectroscopy" (G. E. Muilenberg, Ed.), Perkin–Elmer Corp., Eden Prairie, Minn. (1979).
14. V. A. M. Brabers, *J. Phys. Chem. Solids* **32,** 2181 (1971).
15. K. T. Ng and D. M. Hercules, *J. Phys. Chem.* **80,** 2094 (1976).
16. D. A. Shirley, *Phys. Scr.* **11,** 117 (1975).