High-pressure phase of the cubic spinel NiMn2O4

Åsbrink, S.; Waskowska, A.; Olsen, J. Staun; Gerward, Leif

Published in:
Physical Review B

Link to article, DOI:
10.1103/PhysRevB.57.4972

Publication date:
1998

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
High-pressure phase of the cubic spinel NiMn$_2$O$_4$

S. Åsbrink  
Department of Inorganic Chemistry, Arrhenius Laboratory, Stockholm University, 106 91 Stockholm, Sweden

A. Waśkowska  
Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50 950 Wrocław, Poland

J. Staun Olsen  
Niels Bohr Institute, Oersted Laboratory, University of Copenhagen, 2100 Copenhagen, Denmark

L. Gerward  
Department of Physics, Technical University of Denmark, 2800 Lyngby, Denmark

(Received 21 April 1997; revised manuscript received 15 October 1997)

It has been observed that the fcc spinel NiMn$_2$O$_4$ transforms to a tetragonal structure at about 12 GPa. The tetragonal phase does not revert to the cubic phase upon decompression and its unit-cell constants at ambient pressure are $a_0 = 8.65(8)$ and $c_0 = 7.88(15)$ Å (distorted fcc). Within the experimental uncertainty, there is no volume change at the transition. The $c/a$ ratio of the tetragonal spinel is almost independent of pressure and equal to 0.91. The phase transition is attributed to the Jahn-Teller-type distortion and the ionic configuration can be assumed as $(\text{Mn}^{2+})_{1-x}[\text{Ni}^{2+}\text{Mn}^{3+}]_x$. The bulk modulus of the cubic phase is 206(4) GPa.

INTRODUCTION

A considerable effort has been devoted to understanding the physical properties of the $3d$ transition-metal oxides, in particular those of the spinel type. The distribution and valencies of the metal ions in the spinels are of great importance for the interpretation of the magnetic, electric, and crystallographic properties of these materials.

NiMn$_2$O$_4$ is ferrimagnetic at low temperatures. Its negative temperature coefficient of resistivity has been found useful in electronic applications. The conditions determining the valency and the lattice site preferences of these materials have been broadly discussed in the literature (see Åsbrink et al. and Refs. 1–7 therein), but still they remain uncertain. Experiments have shown that the stoichiometry may strongly depend on the methods of preparation, i.e., on the temperature of synthesis and the annealing rate. These factors also determine the lattice constants and even the crystal system. Thus NiMn$_2$O$_4$ is cubic when prepared above about 1000 K and tetragonal$^2$ with $c/a > 1$ when the synthesis takes place at the lower temperature 473 K. In certain cases the crystal symmetry of spinels can give information about the valency states present. The distortion of the cubic symmetry can be detected for ions with octahedral coordination and electron configuration $d^x$ or $d^9$. Thus a possible tetragonal distortion can be used to identify these ions.$^3$

Recently, temperature-dependent magnetic, calorimetric, and single-crystal x-ray-diffraction investigations of stoichiometric NiMn$_2$O$_4$ were reported by Åsbrink et al.$^1$ A phase transition of purely magnetic nature was established at $T_c = 145$ K with the cubic crystal structure persisting below $T_c$.

Although both nickel and manganese ions can adopt more than one valence state, a detailed structure analysis suggested a cation configuration where all the nickel ions are in the Ni$^{2+}$ state and the manganese ions in the Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ states. Thus the formula is $(\text{Ni}^{2+}_{x-Mn}^{2+})[\text{Ni}^{2+}_x\text{Mn}^{3+}_{2(1-x)}\text{Mn}^{4+})_x]_y$. The observed magnetic moment per formula unit is $\mu_{\text{eff}} = 6.9\mu_B$. This value indicates that the magnetic interaction between the tetrahedral $A$ and the octahedral $B$ sites dominates over the $A-A$ and $B-B$ interactions. The manganese cations take part in this antiferromagnetic coupling which involves an electron exchange $\text{Mn}^{3+}_A\text{O}^2-\text{Mn}^{3+}_B \rightarrow \text{Mn}^{3+}_A\text{O}^2-\text{Mn}^{4+}_B$. Besides, the existence of Mn in two different valence states at the octahedral sites explains the electrical conductivity$^3$ as well as the absence of the Jahn-Teller tetragonal distortion, which only can take place if the Mn$^{3+}$ ($d^5$) part of the octahedral cations exceeds the critical value 0.52.$^3$

The present experiment is an extension of our previous work$^1$ into the high-pressure regime. The aim has been to study the structural stability of NiMn$_2$O$_4$ under high pressure. The tetragonal phase obtained by de Vidal$^6 et al.$ by way of synthesis at 473 K in the system Ni$_x\text{Mn}_{3-x}\text{O}_4$ does not seem to be a direct transformation from the prototype cubic phase by just lowering the temperature. This tetragonal phase has a density of mass 6.6% lower than the density of the cubic phase, and therefore it cannot be supposed to form at high pressure. However, the low-temperature study of Åsbrink et al.$^3$ shows that the inversion parameter increases from 0.80 at room temperature to 0.87 at 115 K. The parallelity between the effects of lowering the temperature and increasing the pressure suggests the possibility of further increasing the Mn occupation at the tetragonal sites by using high pressure, thereby inducing a transition to another tetrag-
onal phase. The results of the present work will be discussed in view of the presence of the Jahn-Teller active Mn$^{3+}$ cations.

**EXPERIMENTAL PROCEDURE**

The NiMn$_2$O$_4$ sample used in this work was obtained from powdered single crystals. The latter were prepared by prolonged heating of equimolar mixtures of NiO and Mn$_2$O$_3$ in a sealed and evacuated silica tube, kept at the temperature 1323 K for 45 days and subsequently quenched in water. This method provides the high-temperature modification of NiMn$_2$O$_4$ with stoichiometric composition.

X-ray powder-diffraction spectra were recorded using synchrotron radiation and the white-beam energy-dispersive method. The experiments were performed at the Hamburg Synchrotron Radiation Laboratory (HASYLAB) using radiation in the 15–70 keV photon energy range from a bending magnet. The diffractometer, working in the energy-dispersive mode, has been described elsewhere. High pressures in the range 0–60 GPa were obtained in a Syassen et al. unit cell; cf. Gerward.

The cubic spinel NiMn$_2$O$_4$ belongs to the space group Fd$3m$. Previous determinations of the lattice constant include Larson et al. 8.396(2) Å, Boucher 8.4028(3), and Renault et al. 8.400 Å. More references can be found in Asbrink et al., who have obtained $a_0 = 8.379(1)$ Å and $V_0 = 588.27(2)$ Å$^3$ in their single-crystal study at 115 K. We have used $a_0 = 8.390(15)$ Å as determined from an in situ zero-pressure diffraction spectrum. New diffraction lines appear at pressures about 12 GPa indicating a structural phase transformation. There is a considerable hysteresis in the transformation, and upon decompression the sample does not revert to the cubic phase. Thus it has been possible to determine the lattice constants of the high-pressure phase at ambient conditions, as will be discussed below.

The diffraction spectra of the high-pressure phase have been indexed according to a tetragonal distortion of the fcc unit cell; cf. Gerward et al. Inspection of the 311/113 doublet indicates a $c/a$ ratio less than one. In the tetragonal system the 311 line is about twice as strong as the 113 line, mainly because of the multiplicity factor. For $c/a < 1$ the 311 line occurs at a lower energy than the 113 line, i.e., $d_{311} > d_{113}$, in accordance with the observed diffraction spectrum (Fig. 1). The lattice constant $a_c$ of the cubic phase as well as $a$ and $c$ of the tetragonal phase are shown as functions of pressure in Fig. 2.

The experimental pressure-volume data for the cubic spinel NiMn$_2$O$_4$ are given in Table I. The data have been described by the Birch equation of state in the pressure range $P < 11$ GPa, thus avoiding possible problems with nonhydrostatic pressures for $P > 12$ GPa. The equation of state can be written

$$P = \frac{3}{2} \left( x^7 - x^5 \right) \frac{1}{4} (B'_0 - 4) (x^2 - 1),$$

where $x = a_0/a$, $a$ being the lattice constant at pressure $P$ and $a_0$ the zero-pressure lattice constant. The parameter $B'_0$ is the bulk modulus and $B'_0'$ its pressure derivative, both parameters being evaluated at zero pressure. The scatter of the data points did not allow the use of $B'_0$ as a fitting parameter. Instead, it was assumed that the pressure derivative is 4.00, which is a typical value for most solids. We obtain $B'_0 = 206(4)$ GPa, where the estimated error within parenthesis

![Fig. 1. Indexed energy-dispersive diffraction spectrum of tetragonal NiMn$_2$O$_4$ at 38.1 GPa; lattice constants $a = 8.35(10)$ and $c = 7.49(15)$ Å; Bragg angle $\theta = 6.045^\circ$. The peak on the left-hand side of the 311 reflection is due to fluorescence in the detector contact material (Ag).](image)

![Fig. 2. Lattice constants for the cubic phase ($a_c$) and the tetragonal phase ($a$ and $c$) as functions of pressure.](image)
is the standard error of the fit. To the best knowledge of the authors there are no data in the literature to compare the present value with. It may be mentioned that the bulk modulus of the mineral spinel (MgAl2O4) is 196 GPa, i.e., about the same value as the one found here for NiMn2O4.

The tetragonal high-pressure phase does not revert to the cubic phase upon decompression. The lattice constants at ambient pressure are \(a_0 = 8.65(8) \text{ Å}\) and \(c_0 = 7.88(15) \text{ Å}\), giving the unit-cell volume \(V_0 = 589.6(20) \text{ Å}^3\). The latter value agrees with the corresponding value for the volume of the fcc unit cell to within 0.2%. Given the experimental uncertainty, it has not been possible, in the present work, to determine any volume difference between the cubic and the tetragonal phases. The \(c/a\) ratio for the tetragonal phase is 0.91(2) at zero pressure, and the ratio is found to be practically independent of pressure. It may be noted that the high-pressure phase of NiMn2O4 is isostructural with the tetragonal Cr2CuO4 spinel,13 which has a \(c/a\) ratio of 0.92.

The existence of two different tetragonal phases of NiMn2O4, one with \(c/a>1\) (de Vidales et al.2) and another with \(c/a<1\) (present work) is interesting. In the former phase the inversion parameter is assumed to be approximately zero, and the tetragonal structure with \(c/a>1\) is a result partly of the octahedral distortion (elongation) caused by Mn3+ acting as an octahedral Jahn-Teller ion, and partly of the tetrahedral elongation caused by Ni2+ acting as a tetrahedral Jahn-Teller ion. In the present work we have not been able to determine positional parameters and we have no direct evidence of the cation distribution. However, some qualitative estimates can be derived from the results of Åsbrink et al.,1 where the inversion parameter was found to increase with decreasing temperature. Thus we assume that, at sufficiently high pressure, the inversion parameter is approximately equal to one, and that the tetragonality (\(c/a < 1\)) is a result of the distortion (flattening) caused by Mn3+, now acting as a tetrahedral Jahn-Teller ion. The Mn3+ ions are assumed to be formed by the superexchange interaction

\[
\text{Mn}_{A}^{2+} + \text{Mn}_{B}^{4+} \rightarrow \text{Mn}_{A}^{3+} + \text{Mn}_{B}^{4+}.
\]

The proposed cation distribution is therefore given by the formula (Mn3+)\([\text{Mn}^{3+}\text{Ni}^{2+}]\text{O}_4\). The observed hysteresis of the cubic to tetragonal transition can be explained by the existence of a potential energy barrier, hampering the electron exchange between the Mn cations in the tetrahedral and octahedral sites. Thus the tetragonal phase can be quenched to atmospheric pressure.

ACKNOWLEDGMENTS

We thank HASYLAB-DESY for permission to use the synchrotron-radiation facility. Financial support from the Danish Natural Science Research Council (L.G. and J.S.O.) and from the Nordic Academy for Advanced Study (S.A.) is gratefully acknowledged. The work of S.A. and A.W. was performed within the Cooperation Program between the Royal Swedish Academy of Sciences and the Polish Academy of Sciences.

TABLE I. Compressibility data for cubic NiMn2O4 for \(P < 11\) GPa. A fit of the Birch equation of state to the experimental data gives \(B_0 = 206(4)\) GPa and \(B_0' = 4.00\) (see text).

<table>
<thead>
<tr>
<th>(P) (GPa)</th>
<th>(a_c) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00(10)</td>
<td>8.390(15)</td>
</tr>
<tr>
<td>2.21(10)</td>
<td>8.362(15)</td>
</tr>
<tr>
<td>2.91(10)</td>
<td>8.349(11)</td>
</tr>
<tr>
<td>3.41(10)</td>
<td>8.346(12)</td>
</tr>
<tr>
<td>4.72(10)</td>
<td>8.326(15)</td>
</tr>
<tr>
<td>6.04(10)</td>
<td>8.315(15)</td>
</tr>
<tr>
<td>6.95(10)</td>
<td>8.310(15)</td>
</tr>
<tr>
<td>8.68(10)</td>
<td>8.283(20)</td>
</tr>
<tr>
<td>10.92(10)</td>
<td>8.252(20)</td>
</tr>
</tbody>
</table>

12 F. Birch, J. Appl. Phys. 9, 279 (1938).