

CONF-881155--61

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M. Radler and J. B. Cohen  
Department of Materials Science & Engineering  
The Technological Institute  
Northwestern University  
Evanston, IL 60208

Received

APR 14 1989

John Faber, Jr.  
Materials Science Division  
Argonne National Laboratory  
Argonne, IL 60439

CONF-881155--61

DE89 009846

February, 1989

Submitted to 1988 MRS Fall Meeting: Symposium Q  
Boston, MA  
December, 1988

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\*Work supported by U.S. DOE, BES-Materials Sciences Contract #W-31-109-ENG-38.

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# A NEUTRON DIFFRACTION STUDY OF NON-STOICHIOMETRIC $Mn_{1-x}O$

M. Radler\*, J. Faber Jr.\*\*, and J.B. Cohen\*

\* Dept. of Materials Science & Engineering, The Technological Institute, Northwestern University, Evanston, IL 60208

\*\* Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

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## ABSTRACT

Rietveld analysis of Bragg intensities from in-situ neutron powder diffraction of nearly stoichiometric  $Mn_{0.9990}O$  reveals the presence of several percent Mn interstitials. Similar to isostructural  $Fe_{1-x}O$ , the cation interstitials are tetrahedrally coordinated in the rocksalt structure (Fm3m).

## INTRODUCTION

Point defects in oxides have received a great deal of attention recently because of their marked effects in superconducting ceramic oxides. But for many years researchers studying the nonstoichiometric transition metal monoxides (CoO, NiO, MnO, FeO) have used point defect models to explain observed high temperature physical properties. Only for FeO has sufficient diffraction work [1-3] been done to confirm their presence. Calculations of defect formation energies from first principles [4-6] suggest that in addition to FeO, large defect aggregates should also be present in MnO. No structural studies on  $Mn_{1-x}O$  ( $0 < x < 0.15$ ) have been reported. Physical properties such as Mn diffusion [7-9], electrical conductivity [10-13], and thermogravimetry [14-19] indicate that defect aggregation most likely occurs at large deviations from stoichiometry. In two separate studies, one of diffusion [7], and one of thermogravimetry [18], interstitial Mn occupation at stoichiometry has been suggested, but the results of both are disputed in the literature [19].

Cation vacancy and interstitial site occupations in the rocksalt structure are studied with diffraction by measuring their effect on the Bragg peak intensities. Analysis of the neutron scattering structure factor for MnO reveals some surprising information. If interstitial Mn atoms at tetrahedral sites are included in the rocksalt structure, the intensity of odd hkl peaks increases only slightly, less than 1 percent for each percent of interstitial occupation, as these peaks are more sensitive to the octahedral Mn occupation. Conversely the intensity of the even hkl can change quite substantially. For reflections with  $h+k+l=4n$  the intensity falls more than 6 percent for each percent of interstitial occupation; for the  $h+k+l=4n+2$  reflections the opposite occurs.

From the ratio of cation vacancies to cation interstitials one can gain insight into the most probable defect aggregates present. Several studies of this ratio have been carried out in FeO [1, 3, 20-22]. These studies all lacked precision because only 9 or 10 Bragg reflections could be measured. With Rietveld analysis and a pulsed neutron source more than 30 peaks can be measured. Radler [23] has studied Fe interstitial occupation in  $Fe_{1-x}O$  with this technique. Here we report results from time-of-flight neutron powder diffraction of  $Mn_{1-x}O$  at high temperature (1673°K).

## EXPERIMENT

Time-of-flight neutron powder diffraction profiles of  $Mn_{1-x}O$  were obtained on the General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory (ANL). Pressed cylindrical pellets of 99.999% MnO powder were prepared by Mr. C.L. Wiley of ANL. Typical pellet dimensions were 1.0 cm diameter by 1.0 cm high. A stack of pellets 5 cm high was placed in the furnace inside GPPD and heated to 1673 K. Sample composition was

controlled in-situ by flowing CO/CO<sub>2</sub> gas mixtures over the sample. The thermogravimetric data of Dieckmann et al. [19] were used to determine the sample composition for the various gas mixtures employed. All tank gases were commercially available, non-certified grade. Seven different sample compositions in the range  $0 < x < 0.02$  were studied, but only that nearest stoichiometry ( $x=0.001$ ) will be reported here. To ensure sample equilibrium, powder profiles were taken in two hour increments and refined for the cubic lattice parameter. When the lattice parameter for successive data sets fluctuated by 0.0002 Å or less (equilibrium was reached) another series of runs totaling 8 to 10 hours was collected. Then the gas mixture was changed. Equilibrium was fast for sample compositions near stoichiometry; typically less than 2 hours. After summing together the equilibrium profiles for each composition, a profile of measured background scattering from the empty furnace was scaled and subtracted. The scale factor used was the ratio of total incident neutrons measured in the incident beam monitor for the raw and background data sets. First order thermal diffuse scattering was calculated based on the method of Cole and Windsor [24], scaled same as above, and subtracted.

Standard Rietveld [25] analysis techniques were used to refine the summed powder profiles. The measured profile, namely the background, lattice parameter and peak shape, were refined first. Then the structural model incorporating Debye-Waller factors, site occupations, extinction and absorption, was refined. At elevated temperature, diffuse scattering around Bragg reflections could not adequately be treated by the available background fitting function. To remove the diffuse background we used the Fourier filtering technique of Richardson [26]. (Refinements with and without filtering on profiles of Fe<sub>1-x</sub>O at 1323°K showed filtering had no effect on refined site occupations.) The primary effect of filtering the data is to improve both background and Bragg peak fitting with the available analytic functions, and thereby reduce the magnitude of profile fitting statistics.

Two different refinements were made, one for ideal MnO and one with interstitial Mn occupation at the 1/4,1/4,1/4 position. For the ideal MnO the site occupation for Mn on octahedral sites was constrained to the known composition and isotropic Debye-Waller factors were used for both Mn and O. After completing refinement for octahedral Mn occupation only, the tetrahedral site was added to the structural model and the sum of the occupations for octahedral and tetrahedral sites was constrained to the known composition. The Debye-Waller factor for the tetrahedral site was constrained to equal that of the octahedral site, and the profile refined again.

## RESULTS

The refined powder pattern of Mn<sub>0.999</sub>O is shown in Figure 1. Displayed are the measured (+) points, calculated profile (solid line), and difference pattern. Despite some minor peak fitting errors the overall fit is quite good. Refined structural parameters and their standard deviations are given in Table 1. Included are values and statistics for refinements with and without tetrahedral occupation. From the calculated statistics of each fit and the number of points that comprise Bragg peaks a significance test, as described by Hamilton [27], can be performed. The tested hypothesis is:

$$H_0 : \text{There is no interstitial occupation in MnO}$$

Using the weighted profile R values, the number of points in Bragg peaks, 486, and the number of variables, 14, the test statistic is:

$$R_{1,474,0.01} = 1.007$$

and the observed ratio is :

$$R = 1.0836$$

The hypothesis is easily rejected at the 1% level.

Just as easily one could perform a difference scattering density calculation by refining the measured profile for an ideal MnO rocksalt structure. Subtracting the calculated structure factors from the profile fit from the observed structure factors, Fourier inversion and mapping on a 0,0,1/4 plane, as shown in Figure 2, reveals the presence of interstitial atoms at the 1/4, 1/4, 1/4 and symmetry related positions. The negative sign of the peak confirms that the atom is Mn, which has a negative neutron scattering length.

## DISCUSSION

Given the structural similarities between  $\text{Mn}_{1-x}\text{O}$  ( $0 < x < 0.15$ ) and  $\text{Fe}_{1-x}\text{O}$  ( $0.05 < x < 0.15$ ) the observation of Mn interstitials would not be unexpected. Moreover calculations [5] of defect and defect aggregate formation energies from first principles suggest that defect aggregates of cation vacancies and cation interstitials will dominate the defect structure of  $\text{Mn}_{1-x}\text{O}$  for  $x > 0.01$ . The data presented here give no information in that regard. Unless extra peaks appear in the powder pattern indicating some long range order the only additional information known at this point is the vacancy-interstitial ratio. For  $\text{Mn}_{0.9990}\text{O}$  at 1673°K the ratio is 1. The most energetically favorable defect from calculation is a 4:1 ( 4 octahedral vacancies tetrahedrally coordinated about 1 interstitial ) defect having a ratio of 4. From the observed ratio we can conclude that at stoichiometry the most probable aggregate, if one exists, is an interstitial vacancy pair. From theory [4] it has been shown that the Mn interstitial will maintain it's +2 valence, unlike Fe in FeO which becomes +3. The interstitial vacancy pair would have no net charge if the vacancy were doubly ionized, as has been suggested from diffusion and conductivity data near stoichiometry. Sykora [15] has found that large quantities of neutral species must be present to simultaneously account for the electrical conductivity and thermopower at large deviations from stoichiometry. This could be that neutral species.

## CONCLUSIONS

1) Mn interstitials have been observed in  $\text{Mn}_{0.9990}\text{O}$ .

2) The ratio of cation vacancies to cation interstitials indicates no large defect aggregates such as a 4:1 cluster are present near stoichiometry in MnO. The only possible aggregate is a vacancy-interstitial pair, which would be neutrally charged.

## ACKNOWLEDGEMENTS

This research has been supported by the Department of Energy under contract DOE-FG02-84ER45097 at Northwestern University and contract BES-Materials Sciences W-31-109-ENG-38 at ANL.

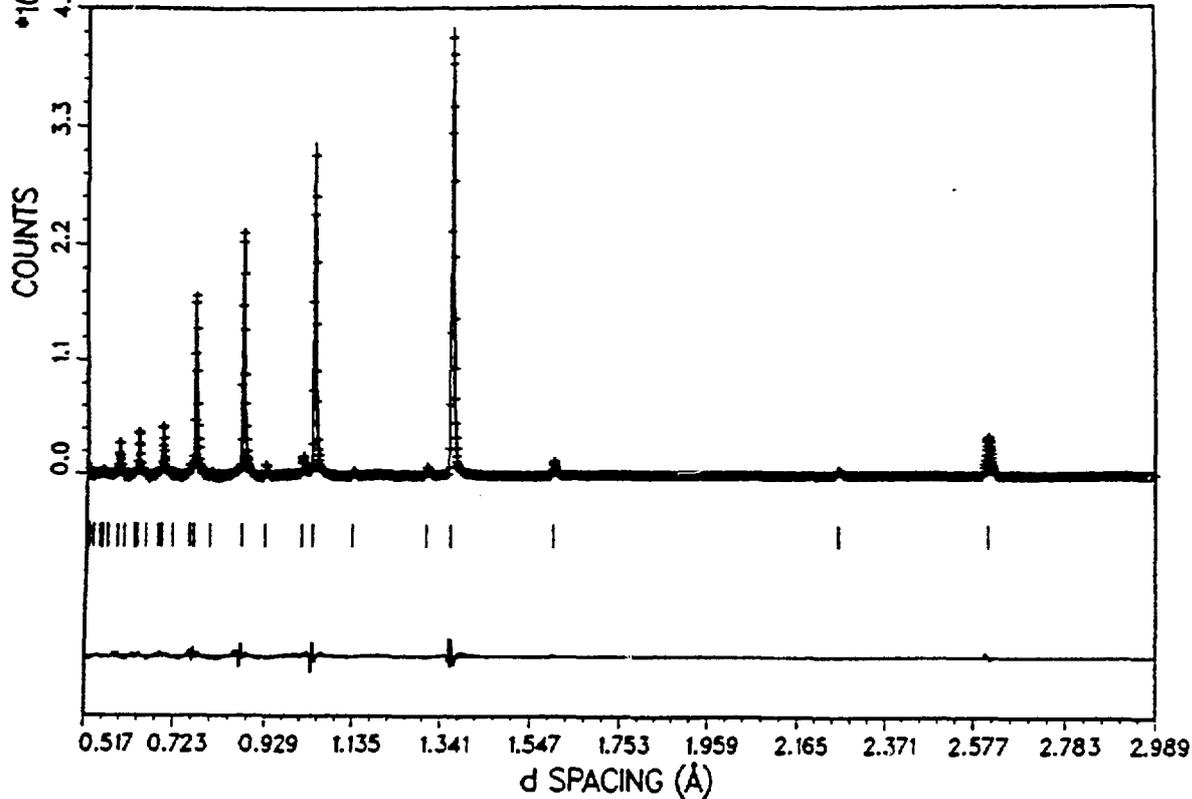
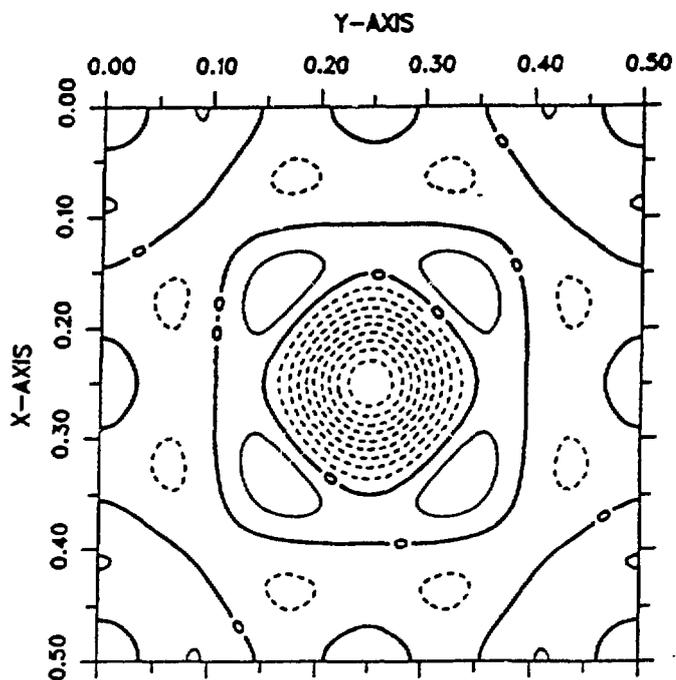


Figure 1 Rietveld refinement for MnO



Z SECTION = 0.2500

MINIMUM, MAXIMUM CONTOUR LEVELS = -900., 100.

—— LEVELS 0, 100, 200, 300 . . .  
 ..... LEVELS -100, -200, -300 . . .

SCALE: level 100 = density  $9.9975 \times 10^{-3}$

Figure 2 Difference Fourier Map of MnO

Table I. Results of Rietveld refinements on Mn<sub>0.9990</sub>O for a (A) model incorporating tetrahedral Mn interstitials, and (B) normal rocksalt structure.

|                       | A            | B            |
|-----------------------|--------------|--------------|
| Temp                  | 1400C        | 1400 C       |
| Runs                  | 2730-2734    | 2730-2734    |
| A                     | 4.53893(5)   | 4.53893(5)   |
| B                     | 4.53893(5)   | 4.53893(5)   |
| C                     | 4.53893(5)   | 4.53893(5)   |
| ALPHA                 | 90.00000     | 90.00000     |
| BETA                  | 90.00000     | 90.00000     |
| GAMMA                 | 90.00000     | 90.00000     |
| VOLUME                | 93.511(3)    | 93.511(3)    |
| X (MN )               | 0.00000      | 0.00000      |
| Y (MN )               | 0.00000      | 0.00000      |
| Z (MN )               | 0.00000      | 0.00000      |
| OCCUP (MN )           | 0.0946(5)    | 0.0999       |
| BISO (MN )            | 3.11(5)      | 3.35(5)      |
| X (MN1 )              | 0.25000      |              |
| Y (MN1 )              | 0.25000      |              |
| Z (MN1 )              | 0.25000      |              |
| OCCUP (MN1 )          | 0.0053(5)    |              |
| BISO (MN1 )           | 3.11(5)      |              |
| X (OX )               | 0.50000      | 0.50000      |
| Y (OX )               | 0.50000      | 0.50000      |
| Z (OX )               | 0.50000      | 0.50000      |
| OCCUP (OX )           | 0.10000      | 0.10000      |
| BISO (OX )            | 2.96(4)      | 2.87(3)      |
| SCALE                 | 0.705(9)     | 0.69(1)      |
| EXTINCT.              | 0.622(7)E-03 | 0.607(7)E-03 |
| ABSOR.                | 0.7000       | 0.7000       |
| OBSERVATIONS          | 486          | 486          |
| REFLECTIONS           | 34           | 34           |
| VARIABLES             | 14           | 13           |
| DEG. OF FREEDOM       | 472          | 473          |
| R(F <sup>2</sup> ; %) | 4.168        | 5.777        |
| R(P; %)               | 2.830        | 3.049        |
| R(WP; %)              | 3.852        | 4.174        |
| R(RIET; %)            | 8.893        | 9.577        |
| R(EXP; %)             | 1.326        | 1.327        |

$$R(F^2; \%) = 100 * \sum |I_{OBS} - I_{CALC}| / \sum I_{OBS}$$

$$R(P; \%) = 100 * \sum |Y_{OBS} - Y_{CALC}| / \sum Y_{OBS}$$

$$R(WP; \%) = 100 * (\sum [W * (Y_{OBS} - Y_{CALC})^2] / \sum [W * (Y_{OBS})^2])^{1/2}$$

$$R(RIET; \%) = 100 * \sum |Y_{OBS} - Y_{CALC}| / \sum |Y_{OBS} - BACK|$$

$$R(EXP; \%) = 100 * (\# \text{ DEGREES OF FREEDOM} / \sum [W * (Y_{OBS})^2])^{1/2}$$

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