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Search for Small-Angle Neutron Scattering in MnO at 1700K\*

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
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In order to investigate possible clustering of cation vacancies in a MnO single crystal, a preliminary small-angle scattering (SANS) experiment has been performed at the Intense Pulsed Neutron Source at Argonne National Laboratory. The experiment was performed at 1700K at oxygen partial pressures,  $p_{O_2}$ , of  $2.2 \times 10^{-4}$ ,  $1 \times 10^2$ , and  $2 \times 10^2$  Pa, which resulted in deviations from stoichiometry,  $\delta$ , in  $Mn_{1-\delta}O$ , of approximately 0.0015, 0.082, and 0.127. No statistically significant change in SANS was observed at this temperature with the above changes in  $p_{O_2}$ . Neither was any significant change observed in the wavelength-dependent sample transmission, also measured in-situ as a function of  $p_{O_2}$ . Hence, there was no evidence from these experiments that may be ascribed to clustering of cation vacancies. Therefore, either clustering of cation vacancies is negligible in MnO for these conditions, or the clusters are smaller than about  $5 \text{ \AA}$ . Of proposed cluster configurations, only the existence of the smallest (4:1, 6:2, or possible 8:3) appears to be consistent with these results.

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## Introduction

Rock-salt-structured monoxides of the 3d transition metals Ni, Co, Mn, and Fe are all cation deficient. Maximum deviations from stoichiometry,  $\delta$ , at atmospheric pressure are about  $10^{-3}$  for NiO,  $10^{-2}$  for CoO, and  $1.5 \times 10^{-1}$  for MnO and FeO.<sup>1</sup> Clustering of cation defects in quenched FeO has been detected by X-ray<sup>2</sup> and neutron diffraction<sup>3,4</sup> and by transmission electron microscopy.<sup>5</sup> Theoretical models predict the occurrence of such clusters,<sup>6-10</sup> typically for  $\delta$  greater than about  $10^{-2}$ .<sup>10</sup> These clusters are generally envisioned as four vacancies in a tetrahedron surrounding a central cation interstitial. Higher-order clusters consist of 4:1 clusters stacked with edge or corner sharing of vacant sites.<sup>7</sup> It should be mentioned that thermodynamic calculations are at odds with these models. Tetot and Gerdanian<sup>11</sup> have concluded that in MnO for  $T \leq 1423\text{K}$  the partial Gibbs free energy can be described well by invoking isolated vacancies only. They further suggest that similar results are probable for NiO and CoO.

If the cluster models are correct, clustering is to be expected for CoO for large oxygen partial pressures,  $p_{\text{O}_2}$ , and for MnO over a wide range of  $p_{\text{O}_2}$ . No direct measurements indicating the existence of clustering in MnO and CoO have been reported. Several experiments, however, suggest that cation-defect clustering may occur in CoO and MnO when  $\delta$  is large. The discussion that follows will be confined to the object of this investigation, MnO, and to a comparison of MnO with FeO.

In simple point-defect models for MnO,  $\delta$  is composed primarily of cation vacancies having various charge states. The models, which assume isolated point defects, can be used to describe the temperature and  $p_{O_2}$  dependencies of  $\delta$ , the cation tracer diffusion coefficient,  $D^*$ , or electrical properties; conductivity and thermopower. Point-defect theory predicts that  $\delta$  or  $D^*$  should vary as  $p_{O_2}^{1/m}$ , where  $m$  depends on the vacancy charge state and ranges from 2 to 6. Since neutral vacancies do not contribute to electrical properties, the  $p_{O_2}$  exponents for them should range from 4 to 6.<sup>1</sup> Existence of isolated cation vacancies with various charge states is adequate to model  $\delta$ <sup>12-15</sup> and  $D^*$ <sup>16,17</sup> for MnO.

In contrast to MnO, cation-diffusion data for FeO cannot be modeled on the basis of simple noninteracting point defects. Whereas  $D^*$  in MnO increases with increasing  $\delta$  for all temperatures in accordance with point-defect theory,  $D^*$  in FeO decreases or increases with or is independent of  $\delta$ , depending on  $T$ .<sup>18</sup>

Measurements of the isotope effect for cation diffusion, however, suggest that defect-defect interactions such as clustering may occur in MnO when  $\delta$  is large. For MnO, the quantity  $f\Delta K$  (where  $f$  is the correlation factor and  $\Delta K$  is the fraction of total translational kinetic energy at the saddle point that belongs to the jumping atom) decreases from a value of about 0.7 from small  $\delta$  (a value typical of vacancy-diffusion mechanisms in a cubic structure) to about 0.35 as  $\delta$  approaches 0.06.<sup>16</sup> Chen and Peterson<sup>16</sup> ascribe this effect to defect-defect interactions which could

be clustering. In contrast,  $f\Delta K$  for FeO ranges from about 0.45 to 0.30 and decreases with increasing  $\delta$ .<sup>18</sup>

Electrical measurements in MnO for large  $\delta$  can also be interpreted as evidence of possible cluster formation.<sup>19</sup> It has been found that the  $p_{O_2}$  exponents of the electrical conductivity and the thermopower can be as low as 3. Values of  $m < 4$  are not concordant with simple point-defect theory, but could be explained on the basis of cluster formation.

Unlike FeO, which at atmospheric pressure exists far from stoichiometry only, MnO ranges from nearly stoichiometric to  $\delta$  values greater than  $10^{-1}$  for high T and large  $p_{O_2}$ . Observation of a transition from isolated point defects to defect clustering may thus be possible in MnO. Such a transition may have been observed in deformation experiments conducted at 1200 and 1400°C. Anomalous increases in flow stress occurred when  $\delta$  increased to values above about 0.01.<sup>20,21</sup> This effect occurred in CO<sub>2</sub>/CO atmospheres, but not in Ar/O<sub>2</sub> atmospheres. Although the etiology of this effect is not well understood, formation of cation-defect clusters when  $\delta$  is large is a possible cause.<sup>20</sup>

Circumstantial evidence from investigations of deformation, electrical properties, and  $D^*$  in MnO indicates that clustering may possibly occur when  $\delta$  is greater than about  $10^{-2}$ . Unlike in FeO, however, no direct observations of clusters have been made in MnO. The objective of this investigation was to attempt to observe defect clustering at temperature in situ because studies of quenched specimens may prove unsatisfactory owing to difficulty in suppressing precipitation of Mn<sub>3</sub>O<sub>4</sub>.<sup>22</sup> This paper shall

report results from small-angle neutron scattering (SANS) experiments conducted at 1700K with  $\delta$  ranging from about  $1.5 \times 10^{-3}$  to  $1.3 \times 10^{-1}$ . With adequate resolution, such experiments should be capable of detecting the presence and measuring the average size of lattice disruptions such as the larger cation-defect clusters.

### Experiment

Growth and preparation of the MnO single crystals used in this study have been adequately described.<sup>20</sup> A single specimen, 19x19x3.5 mm was prepared by slicing and grinding one crystal into 3- slabs having dimensions of 19x6.3x3.5 mm.

The sample holder consisted of two rings of alumina held together near the periphery by Pt wire. The holder contained a 15 mm diameter hole so that the entire neutron beam would see only the MnO sample. The holder was positioned in the middle of a tight-fitting  $Al_2O_3$  tube by a fixed Pt-Pt + 10% Rh thermocouple which therefore contacted the holder. The entire assembly was placed into a horizontally mounted furnace containing vertically mounted heating elements (Applied Test Systems, Butler, PA). The ends of the 38 cm long tube were water-cooled brass fittings. The furnace was then placed into the small-angle diffractometer (SAD) of the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory and centered on the neutron beam.

The furnace containing the sample assembly was heated to 1700K which was then held constant to better than  $\pm 3^\circ C$  throughout the course of the

3-day experiment. Premixed, certified atmospheres were used to obtain desired  $\delta$  values. They are given in Table I, along with the resulting  $p_{O_2}$ <sup>16</sup> and the calculated<sup>14</sup> value of  $\delta$ . The samples were equilibrated for three hours prior to each test to ensure chemical equilibrium.

Figure 1 is the transmission coefficient ( $e^{-\mu t}$ ) plotted as a function of time channel, which is proportional to the wavelength,  $\lambda$ . The scattering data were corrected for empty camera (furnace) background scattering, dark current, and for the wavelength dependent transmission. The observed time-of-flight small angle neutron scattering data were converted to cross sections by comparison with the scattering from a 1-mm thick water sample. The channels are equally spaced in wavelength and cover the range from 0.5 to 14.0 Å. The solid lines are third order polynomials least-squares fitted to the observed data. One curve was obtained at  $p_{O_2} = 1 \times 10^2$  Pa while the other corresponds to  $p_{O_2}$  of  $1 \times 10^{-4}$  Pa. The former corresponds to a large  $\delta$  of 0.082 while the latter corresponds to  $\delta = 0.0015$ , very close to a stoichiometric compound. The transmission data obtained at  $\delta = 0.127$  in a  $CO_2/CO$  atmosphere are identical to the data shown.

Figure 2 presents the results of a scattering experiment for  $\delta = 0.082$ . In this figure, the log of the intensity, suitably corrected for background, etc., is plotted as a function of  $Q^2$ , where  $Q = \frac{4\pi}{\lambda} \sin \theta$ . The scattering angle is denoted by  $2\theta$ , while the neutron wavelength is  $\lambda$ . No structure is evident in this figure, nor was any present for the other values of  $\delta$ . The resultant, apparent Guinier radius, which was calculated

from the slope of Fig. 2, is  $5.5 \text{ \AA}$ . The observed Guinier radii for the three experiments are given in Table II.

The results shown in Table II indicate that the Guinier radius is independent of deviation of stoichiometry in MnO at 1700K. Therefore, any lattice disruption resulting from the ordering of vacancies and their subsequent clustering must have a Guinier radius significantly less than  $5.5 \text{ \AA}$  or the number density of clusters so low as to preclude their detection with the SANS experiment.

### Discussion

Table III presents approximate calculations of the radii of the clusters that have been proposed by Catlow et al.<sup>7</sup> The values given were calculated by taking the distance from the center of the cluster to the closest and the furthest cation vacancy, with the minimum radius being that for the 4:1 cluster. Approximate concentrations of the clusters (assuming that all vacancies form clusters) are also given for  $p_{O_2} = 2 \times 10^2 \text{ Pa}$ .

While the origin of the SANS which yields a Guinier radius of  $5.5 \text{ \AA}$  (corresponding to a spherical radius of  $7.1 \text{ \AA}$ ) is not fully understood at present, its presence would not mask the existence of particles of larger size. The presence of larger particles would produce a steeper, negative slope on a Guinier plot (Fig. 2).

Equally important from the present experiment is the independent observation that the total cross section is unchanged in going from nearly stoichiometric to highly nonstoichiometric MnO at 1700K, as shown in Fig.



1. Measurements of the latter type have been used successfully to detect the presence of small defect clusters and to model the complex lattice relaxations about the defects.<sup>23</sup>

It must be concluded that, within the resolution of this experiment, no significant number of large clusters occur in MnO at 1700K, even for  $\delta$  as large as 0.127. However, the results of this experiment cannot settle the controversy on whether clusters exist in highly nonstoichiometric oxides. The resolution of this SANS experiment was insufficient to detect the two smallest proposed cluster configurations: 4:1 and 6:2. Furthermore, it is possible that at 1700K the atomic mobility is so large that clusters are unstable. Indeed the oxygen exponent for the thermopower of MnO at 1500°C can be explained on the basis of single vacancies while clusters must be invoked to explain the results at, for example, 1300°C.<sup>19</sup>

Very recently this experiment was repeated at a lower temperature of 1500K for partial pressures of  $1.1 \times 10^{-6}$  and 5.7 Pa which result in  $\delta$ -values of 0.00072 and 0.041, respectively. As was the case at 1700K, no change in Guinier radius (4.6 Å) or transmission coefficient was observed with  $p_{O_2}$ . Experiments at much lower temperatures would require prohibitively long equilibration times. It should also be mentioned that plans are underway to measure diffuse elastic neutron scattering in situ.<sup>24</sup> It is hoped that these measurements which have a better resolution will help to settle the issue of whether cation-defect clusters exist in oxides other than FeO.

### Conclusions

No difference in wavelength dependent neutron transmission coefficient or in Guinier radius was detected between nearly stoichiometric and highly nonstoichiometric MnO at 1500 and 1700K. Of the proposed cluster configurations, only the existence of the smallest (4:1, 6:2, or possibly 8:3) appears to be consistent with these results.

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FIGURE CAPTIONS

Fig. 1. Transmission coefficient is shown as a function of time channel  
(proportional to  $\lambda$ ).

Fig. 2. Logarithm of intensity is plotted as a function of  $Q^2$  for  
 $p_{O_2} = 1 \times 10^2$  Pa.

**Table I. Atmospheres and Deviations from Stoichiometry  
Used in SANS Experiments**

Atmosphere	$p_{O_2}$ [Pa] at 1700K	$\delta$
$CO_2/CO = 0.67$	$1 \times 10^{-4}$	0.0015
0.1% $O_2$ in He	$1 \times 10^2$	0.082
$CO_2/CO = 645$	$2 \times 10^2$	0.127

**Table II. Guinier Radius as a Function of  $\delta$  at 1700K**

$\delta$	Guinier radius [ $\text{\AA}$ ]
0.0015	5.5
0.082	5.5
0.127	5.4



Table III. Sizes and Concentrations of Various Vacancy Clusters  
in MnO for 1700K and  $P_{O_2} = 2 \times 10^2$  Pa

Cluster	Concentration [mole fraction]	Radius [ $\text{\AA}$ ]
4:1	0.042	3.8
6:2	0.032	3.8-5.4
8:3	0.025	3.8-7.4
13:4	0.014	6.3-7.7
16:5	0.011	~9.4

