Cationic Distribution in Defect Co-Mn Ferrites from Neutron Diffraction
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To cite this version:

HAL Id: jpa-00254866
https://hal.archives-ouvertes.fr/jpa-00254866
Submitted on 1 Jan 1997

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Abstract. Submicron stoichiometric cobalt manganese ferrites oxidized in air, at low temperature (<500°C) give defect spinel ferrites which exhibit a substantial increase in coercivity, reaching a maximum for ferrites oxidized near 350°C and slowly cooled (5°C/min) from the oxidation temperature. Two Co$_{0.936}$Mn$_{0.355}$Fe$_{1.665}$O$_{1.044}$O$_4$ samples oxidized at 350°C but exhibiting notably different coercivities because of different cooling rates (Hc=1750 Oe after quenching; Hc=2350 Oe after slow cooling) have been analyzed by neutron diffraction at T=6K. They exhibit almost exactly the same structural and magnetic parameters, indicating that the difference between the coercivities has a purely local origin. Similar cationic distributions have been inferred. Neutron diffraction reveals a classical collinear ferrimagnetism on the A and B sublattices of the spinel structure.

1. INTRODUCTION

We have used neutron diffraction at T=6K for analyzing two powdered samples obtained by oxidation in air at 350°C of the same stoichiometric phase Co$_{0.936}$Mn$_{0.355}$Fe$_{1.665}$O$_{1.044}$O$_4$ but submitted to very different cooling rates (quenching or slow cooling at 5°C/min ) from the oxidation temperature. Thermogravimetric analysis reveals that they have the same composition Co$_{0.936}$Mn$_{0.355}$Fe$_{1.665}$O$_{1.044}$O$_4$ with the same vacancy contents. However these two samples exhibit notably different coercivities because of their different cooling rates: Hc=1750 Oe for the quenched one; Hc=2350 Oe for the slowly cooled one.

2. NEUTRON DIFFRACTION RESULTS

Neutron diffraction spectra at low temperature (T=6K) appear almost identical, whatever the sample. Refinements reveal no structural nor magnetic significant differences, within some standard deviations. The reliability factors are R$_p$=3.92 , Rwp=5.19 (slowly cooled sample) and R$_p$=3.77 , Rwp=4.94 (quenched sample).

Table 1: Structural and magnetic parameters at T=6K of Co$_{0.936}$Mn$_{0.355}$Fe$_{1.665}$O$_{1.044}$O$_4$ (e.s.d.'s in parentheses)

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>u oxygen</th>
<th>Bcation (Å$^2$)</th>
<th>Banion (Å$^2$)</th>
<th>$&lt;b_{tetra}&gt;$ $10^{-12}$ cm</th>
<th>$&lt;b_{octa}&gt;$ $10^{-12}$ cm</th>
<th>MA(μB) tetra site</th>
<th>Mπ(μB) octa site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slowly cooled</td>
<td>8.3734(2)</td>
<td>0.3814(1)</td>
<td>0.15(2)</td>
<td>0.66(2)</td>
<td>0.737(3)</td>
<td>0.937(3)</td>
<td>3.76(4)</td>
<td>-3.80(4)</td>
</tr>
<tr>
<td>Quenched</td>
<td>8.3733(2)</td>
<td>0.3814(1)</td>
<td>0.15(2)</td>
<td>0.66(2)</td>
<td>0.727(3)</td>
<td>0.947(3)</td>
<td>3.74(4)</td>
<td>-3.85(4)</td>
</tr>
</tbody>
</table>

3. CATION DISTRIBUTION IN DEFECT CO-MN FERRITES

Admitting from the work of Chassaing et al. [1] the following structural formula:

Co$_2^+$Fe$_{1-y}$[Fe$_{0.665+y}$Mn$_{0.287}$Mn$_{0.068}$Co$_{0.936-y}$]O$_{11.044}$O$_4$

neutron diffraction gives cation distributions accurately from the average scattering lengths $<b_{tetra}>$ and $<b_{octa}>$ on tetrahedral and octahedral sites (Table 1).

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jp4:19971214
The average cation to anion distances \( R_{\text{tetra}} = \sqrt{3} (u - \frac{1}{4}) \) and \( R_{\text{octa}} = a \left( 3u^2 - \frac{11}{4}u + \frac{43}{64} \right)^{\frac{1}{2}} \) calculated from the cell parameter \( a \) and the oxygen positional parameter \( u \) (Table 1), can also be estimated from the above cation distributions from \( R_{\text{tetra}} = \sum_{i} x_i (C_{A_i} - O) \) and \( R_{\text{octa}} = \frac{1}{2} \sum_{i} y_i (C_{B_i} - O) \), where \( x_i \) and \( y_i \) are the cation concentrations on A and B sites respectively, and \( C_{A_i} - O \) and \( C_{B_i} - O \) are the cation to anion distances, sums of ionic radii [2, 3]. Table 2 shows a good agreement confirming cationic distributions.

### Table 2: Average cation to anion distances calculated from a (cell parameter) and \( u \) (oxygen position) and from cationic distributions (estimated standard deviations are given in parentheses)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( y )</th>
<th>A site [Co(^{2+})]</th>
<th>( R_{\text{tetra}} ) ( \AA )</th>
<th>( R_{\text{octa}} ) ( \AA )</th>
<th>( M_{A} ) (( \mu_B ))</th>
<th>( M_{B} ) (( \mu_B ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slowly cooled</td>
<td>0.299 (4)</td>
<td>1.906 (1)</td>
<td>1.888 (10)</td>
<td>2.041 (1)</td>
<td>2.057 (10)</td>
<td>3.76 (4)</td>
</tr>
<tr>
<td>Quenched</td>
<td>0.314 (4)</td>
<td>1.906 (1)</td>
<td>1.890 (10)</td>
<td>2.041 (1)</td>
<td>2.056 (10)</td>
<td>3.74 (4)</td>
</tr>
</tbody>
</table>

### 4. MAGNETIC MOMENTS

The magnetic reliability factors are \( R_{\text{mag}} = 2.33 \) for the slowly cooled sample and \( R_{\text{mag}} = 2.80 \) for the quenched sample. Neutron diffraction reveals a classical collinear ferrimagnetism with the A-site moments opposed to the B-site moments. The sum of the A-site moments and the sum of the B-site moments supposed in a parallel alignment have been calculated from the above cation distribution formulas and from the following values for the moments assigned to the several ions (Mn\(^{3+}\) : 4 \( \mu_B \); Mn\(^{4+}\) : 3 \( \mu_B \); Fe\(^{3+}\) : 5 \( \mu_B \); Co\(^{2+}\) : 3.2 \( \mu_B \)). These calculated values are greater than the experimental ones determined from neutron diffraction data as shown in Table 3, which probably results from fluctuations in the alignments of the magnetic moments.

### Table 3: Calculated (from cationic distributions) and experimental (from neutron diffraction) magnetic moments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M_A ) (( \mu_B )) neutron diffract.</th>
<th>( M_A ) (( \mu_B )) cationic distrib.</th>
<th>( M_B ) (( \mu_B )) neutron diffract.</th>
<th>( M_B ) (( \mu_B )) cationic distrib.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slowly cooled</td>
<td>3.76 (4)</td>
<td>4.46</td>
<td>3.80 (4)</td>
<td>4.04</td>
</tr>
<tr>
<td>Quenched</td>
<td>3.74 (4)</td>
<td>4.43</td>
<td>3.85 (4)</td>
<td>4.05</td>
</tr>
</tbody>
</table>

### 5. CONCLUSION

This study shows that the difference between the coercivities of the two samples has a purely local origin, an anisotropic arrangement [4, 5] of cobalt ions being probably favoured by the multiple valence states of manganese and defects on octahedral sites, a very slow cooling allowing to create the maximum of these anisotropic configurations.

### References