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Magnetic properties of cobalt and manganese oxide spinel ceramics

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Abstract. Magnetic susceptibility measurements, magnetization and neutron diffraction results at low temperature for cobalt and manganese oxide spinel ceramics are presented. The Curie temperature varies similarly with the sample composition in ceramics and powders. The experimental molar Curie constant variation is explained by the presence of Co\textsuperscript{2+}, Co\textsuperscript{III}, Mn\textsuperscript{3+} and Mn\textsuperscript{4+}, and possibly Co\textsuperscript{3+} in the octahedral sites for the cobalt rich phases. The magnetic moments of the cations in tetrahedral and octahedral sites are not collinear and the global magnetization is oriented in a third direction.

Introduction

Cobalt and manganese oxides Mn\textsubscript{3-x}Co\textsubscript{x}O\textsubscript{4} (0≤x≤3), which crystallize in the spinel structure, are multiferroics that can be used in various technological applications (batteries, memory devices, NTC thermistors…) thanks to their thermal, optical, electrical and magnetic properties.

We have recently undertaken a detailed study of the structural properties of Mn\textsubscript{3-x}Co\textsubscript{x}O\textsubscript{4} ceramics over the whole solid solution range in relationships with their electrical properties [1]. Such materials exhibit very interesting properties due to the multiplicity of each cation that can be present on the tetrahedral \textit{A} and octahedral \textit{B} sites, with various possible oxidation numbers, spin states and orbital moments. Magnetic measurements can help to describe the cation distribution of cobalt and manganese in spinels thanks to their different scattering factors and characterize their magnetically ordered state at low temperature.

Below \(T_N = 42K\), Mn\textsubscript{3}O\textsubscript{4} is ferrimagnetic [2]. Following Yafet-Kittel’s theory, the haussmanite magnetic structure can be described by a double crystal structure along the \textit{b}-axis. The Mn\textsuperscript{2+} magnetic moments for the \textit{A} sites are ordered in the [010] direction with a moment of 4.2\(\mu_B\) [3]. For the \textit{B} sites, the magnetic moments are sub-divided in two non collinear sub-lattices in the (100) plane with a resulting moment of 1.96\(\mu_B\) oppositely aligned to the tetrahedral moment. At 33K, the magnetic and crystallographic structures become identical with antiferromagnetic couplings. The \textit{B-B} interaction is predominant due to the low distances separating the Mn\textsuperscript{3+}. This allows a direct interaction exchange by Mn\textsuperscript{3+} ions orbital covering. For the \textit{A-A} and \textit{A-B} interactions, a superexchange can take place through the oxygen ions.

On the other end of the Mn\textsubscript{3}O\textsubscript{4}-Co\textsubscript{3}O\textsubscript{4} system, the cobalt oxide spinel is antiferromagnetic below \(T_N = 40K\) [4]. Structural, thermodynamic and magnetic calculations usually agrees with a high spin Co\textsuperscript{2+} on the \textit{A} sites and low spin Co\textsuperscript{III} on the \textit{B} sites [5-7]. For the \textit{A} sites, the Co\textsuperscript{2+} magnetic moments are spread out on two equal sub-lattices of opposite orientations. Each Co\textsuperscript{2+} ion is surrounded by four neighbors in tetrahedral environment with anti-parallel moments compared to the central ion. The macroscopic global magnetization is then equal to zero. In comparison with other direct spinels, Co\textsubscript{3}O\textsubscript{4} exhibits strong interactions between the Co\textsuperscript{2+} in the \textit{A} sites that are probably due to Co\textsuperscript{III}-O-Co\textsuperscript{III} super-exchange interactions [8]. When substituting Co for Mn, large ferromagnetic components appear and a material taken from the Mn\textsubscript{3-x}Co\textsubscript{x}O\textsubscript{4} series (0<x≤3) is usually ferrimagnetic [9,10].
Sample preparation

Mixed manganese and cobalt oxalic powders were prepared by the co-precipitation method using ammonium oxalate and cobalt and manganese nitrates in stoichiometric proportions [11]. Oxalic powders were then heated for 4 hours in air at 800°C for sample decomposition. The resulting mixed manganese and cobalt oxide powders were either mixed with an organic binder before a 2×6mm (height×diameter) disc was put under 500MPa for 30s and left overnight at a sintering temperature 1160≤T1≤1300°C (conventional sintering technique), or prepared as ceramics using a Spark Plasma Sintering apparatus in the P = 50MPa for 5min and 700≤T≤750°C conditions (SPS technique) [1]. The thermal cycles are schematized in Figure 1. The conventional sintering technique was applied to the samples for which x<1.78 and the SPS technique for x≥1.78 in order to prepare high density pellets of single phase ceramics. For the former technique, samples were slowly cooled down from T1 to T2 and left for 1 hour before quenching in water to prevent sample cracking (see Fig. 1), while for the latter technique a (Co,Mn)O thin layer formed on both sides of each pellet was removed by polishing before measurements.

![Figure 1: Phase diagram for Mn$_{3-x}$Co$_x$O$_4$ with 0< x ≤3. TS and CS correspond to Tetragonal and Cubic Spinel structures, respectively. Open squares symbolize the T$_1$ temperature and close squares T$_2$ (conventional sintering) or T (SPS) used in the preparation of ceramics.](image)

Structural characterization

For x<1.78, a pure tetragonal phase was evidenced by XRD at room temperature for each oxide spinel ceramic while a pure cubic phase was characterized for any further x values.

Room temperature neutron diffraction measurements allowed us to determine the cation distributions for tetrahedral and octahedral sites of the manganese and cobalt oxide spinel ceramics [1]. For 0≤x≤1, Mn$^{2+}$ on the A sites are progressively replaced by Co$^{2+}$ while Mn$^{3+}$ remain on the B sites. For 1<x≤3, Co$^{2+}$ and low spin Co$^{3+}$ (Co$^{3+}$) appear on the B sites in the presence of Mn$^{3+}$ and Mn$^{4+}$. This cation distribution, confirmed by thermogravimetric analysis performed on the starting oxide powders [12], is original in ceramics and was, to our knowledge, only mentioned earlier for Mn$_{1-x}$Co$_x$O$_3$ (0≤x≤1) thin films and CoMn$_2$O$_4$ nanocrystals [13,14], while both manganese and cobalt oxidation states have recently been reported in RE-perovskites [15,16]. Our ceramics show the highest electrical conductivity in the region where a maximum of couples Co$^{2+}$/Co$^{3+}$ and Mn$^{3+}$/Mn$^{4+}$ concentrations are present in the B sites [1]. Presence of two oxidation states for each element drives to specific conduction mechanisms and double-exchange magnetic interactions.
Magnetic susceptibility measurements

10 to 20 mg of each sample powder, obtained after grinding of the ceramic, was introduced into a transparent diamagnetic pharmaceutical holder for magnetic susceptibility measurements with a MPMS-XI Quantum Design magnetometer put under vacuum. A magnetic field of 3000Oe was applied during measurements in the [2-300K] temperature range. Except for Co$_3$O$_4$, which is antiferromagnetic below the magnetic ordering temperature $T_N$, the thermal variation of the inverse molar magnetic susceptibility is associated with a ferrimagnetic behavior. The variation of the $T_C$ Curie temperature as a function of the cobalt amount in the manganite spinel ceramics (see Table 1) is very close to that previously observed for powders [17].

For our Co$_3$O$_4$ ceramic, $T_N$ is equal to 33K while Roth found a value of 40K [4]. The variation of $T_C$ obtained for ceramics is very similar to those reported earlier for sample powders of same composition despite different thermal treatments, especially with slower cooling in the case of powders. For an increasing cobalt content up to $x \approx 2$, $T_C$ increases, then it decreases. Therefore, this is where the concentrations of manganese and cobalt couples are the highest that the magnetic interactions are the strongest. For all ceramics, the paramagnetic temperatures $\theta_p$, which are characteristics of the strongest magnetic interactions, are negatives with relatively high values, in accordance with predominant antiferromagnetic interactions (see Table 1).

Experimental molar Curie constant $C_m$ extracted from the magnetic susceptibility variations versus temperature were compared to those reported earlier in the literature with various cation distributions (see Table 1). $C_m$ of Mn$_{3-x}$Co$_x$O$_4$ ($1.54 \leq x \leq 3$) ceramics decreases when the cobalt content increases, in relation with the appearance of diamagnetic Co$^{3+}$ in octahedral sites. In order to explain the experimental $C_m$ values, it is necessary to use the magnetic orbital contribution of Co$^{2+}$ as mentioned in previous works [18,19]. Therefore, $C_m$ is equal to 2.18 and 4.07emu.mol$^{-1}$.K$^{-1}$ for Co$^{2+}$ in tetrahedral and octahedral environment, respectively. For the trivalent cobalt in octahedral sites, the structural and electrical properties relationships showed that high spin Co$^{3+}$ would exist in the structure, with a maximum concentration corresponding to the one for Co$^{2+}$ in the same sites, the main part being of low spin Co$^{3+}$. In Table 1, the $C_m$ theoretical values for only Co$^{3+}$, and (Co$^{3+}$ +Co$^{3+}$) are given for comparison. The experimental $C_m$ values are closer from the theoretical ones in the latter case, which still remains to be confirmed by using spectroscopic techniques, for instance. However, if the usual cation distributions proposed in the literature are taken into account with either (Co$^{3+}$ and Mn$^{3+}$) or (Co$^{2+}$, Co$^{3+}$ and Mn$^{4+}$) on the B sites, the experimental $C_m$ values can never be explained. Only, the presence of Co$^{2+}$, Co$^{3+}$, Co$^{3+}$, Mn$^{3+}$ and Mn$^{4+}$ can justify the values obtained in our ceramics for $1 < x < 3$.

**Table 1: Curie temperatures and molar Curie constants for Mn$_{3-x}$Co$_x$O$_4$ ceramics**

<table>
<thead>
<tr>
<th>x</th>
<th>$T_C$ [K]</th>
<th>$\theta_p$ [K]</th>
<th>$C_m$ exp [uem.mol$^{-1}$.K$^{-1}$]</th>
<th>$C_m$ theo (Co$^{3+}$$_B$ 100%) [uem.mol$^{-1}$.K$^{-1}$]</th>
<th>$C_m$ theo ((Co$^{3+}$Co$^{3+}$)$_B$) [uem.mol$^{-1}$.K$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.54</td>
<td>158</td>
<td>-371</td>
<td>7.05</td>
<td>6.63</td>
<td>6.90</td>
</tr>
<tr>
<td>1.78</td>
<td>185</td>
<td>-348</td>
<td>6.82</td>
<td>6.13</td>
<td>6.52</td>
</tr>
<tr>
<td>2.22</td>
<td>148</td>
<td>-613</td>
<td>6.53</td>
<td>5.47</td>
<td>6.52</td>
</tr>
<tr>
<td>2.60</td>
<td>100</td>
<td>-142</td>
<td>4.09</td>
<td>3.78</td>
<td>4.38</td>
</tr>
<tr>
<td>2.77</td>
<td>77</td>
<td>-160</td>
<td>3.35</td>
<td>3.26</td>
<td>3.29</td>
</tr>
<tr>
<td>3</td>
<td>33</td>
<td>-108</td>
<td>2.36</td>
<td>2.14</td>
<td>3.18</td>
</tr>
</tbody>
</table>
Magnetization measurements were performed on each grinded ceramic with the MPMS-XI Quantum Design magnetometer at 5K with a magnetic field H varying from 500 to 70000Oe. First magnetization variation $I$ vs field for $\text{Mn}_{0.78}\text{Co}_{2.22}\text{O}_4$ ceramic is represented in Fig. 2, for example.

For all compositions under study, the variations become linear at high field (H>20000Oe) and the saturation could never be reached, even for the highest field applied. Therefore, our ceramics exhibit a strong magneto-crystalline anisotropy and the magnetic moments of cations in $A$ and $B$ sites are not collinear. The spontaneous magnetization $I_0$ was determined by extrapolating to H=0 the linear variation of the magnetization vs field. Fig. 2 shows the complex $I_0$ variation as a function of the cobalt content for our ceramics, which is very similar to the variations observed by previous authors on oxide powders of the same compositions [9,17]. The sample thermal treatment has therefore no real influence on the magnetic ordering. The spontaneous magnetizations are very small compared to the values determined for a collinear model with two sub-lattices of Néel by considering the average distributions usually given in the literature with the presence of $\text{Co}^{III}$ or ($\text{Co}^{III}$ and $\text{Co}^{3+}$) in $B$ sites. This result was already observed in other manganese oxide spinels such as $\text{NiMn}_2\text{O}_4$ and $\text{FeMn}_2\text{O}_4$ with $I_0 = 1.63$ and $1.55\mu_B$.mol$^{-1}$ and $M_s = 3.83$ and $3.82\mu_B$.mol$^{-1}$, respectively [20,21]. The lack of saturation of the experimental magnetization and the complex magnetic structures of Yafet-Kittel type in the tetragonal phase or of ‘star’ type in the cubic phase can explain these differences. Thus, from a simple consideration of a saturation moment it seems difficult to have a complete cation distribution over the $A$ and $B$ sites in the $\text{Mn}_3\text{O}_4$-$\text{Co}_3\text{O}_4$ system.

Neutron diffraction at 10 K

The macroscopic measurement of magnetization is not the only technique that can show evidence for the presence of a spontaneous magnetic order in ferromagnetic samples. Neutron diffraction can also be a really interesting technique thanks to the neutron spin that can interact with the electron spin. Besides the structural information given by neutron diffraction measurements, the location and orientation of the magnetic moments for each $A$ and $B$ network can be determined below the $T_C$ magnetic ordering temperature, in relation with the cation distributions and oxidation states.

Four samples of $\text{Mn}_{3-x}\text{Co}_x\text{O}_4$ ceramics, with $x = 1.54, 1.78, 2.22$ and 2.77, were measured by neutron diffraction at 10 K with a Helium cryostat on the Super-D2B instrument (wavelength of 1.594Å) at the ILL in Grenoble, France. Fig. 3 shows the neutron diffraction patterns of $\text{Mn}_{1.46}\text{Co}_{1.54}\text{O}_4$ (tetragonal phase) and $\text{Mn}_{0.78}\text{Co}_{2.22}\text{O}_4$ (cubic phase) ceramics. There is a good
agreement between the observed and calculated intensities obtained by Rietveld refinements with the FULLPROF program. The magnetic and structural cells are always identical. The magnetic moments for each crystallographic site were determined and compared with values reported elsewhere for manganites of spinel structure, namely NiMn$_2$O$_4$ and FeMn$_2$O$_4$ (see Table 2). The spontaneous magnetization values determined at 5 K and previously discussed in this paper are also presented for comparison. For the sample compositions where $x$ is closer to 2, the magnetic moments for the $A$ and $B$ sites are close to the values obtained by Boucher et al. [9]. In particular, $M_A \sim 3 \mu_B$.mol$^{-1}$ is to be related to the magnetic moment of Co$^{2+}$. For those compositions, a ferromagnetic $A$ sub-lattice can be envisaged with an almost complete alignment of the Co$^{2+}$ magnetic moments. Whereas the resulting magnetic moments for the $B$ sites are lower than those calculated with all Co$^{2+}$, Co$^{3+}$, Mn$^{3+}$ and Mn$^{4+}$ ions supposed to be aligned in the same direction. As a matter of fact, the $M_B$ resulting moment is an average value of non-aligned magnetic moments usually described in the manganese oxide spinels (see [22], for instance). The magnetic structure is thus composed of two sub-lattices of magnetization $M_A$ and $M_B$ forming an angle lower than 180° between each other. The resulting magnetization is then situated in a third direction.

Table 2: Magnetic moments on the $A$ and $B$ sites of some Mn$_{3-x}$Co$_x$O$_4$ ceramics determined using neutron diffraction measurements at 10 K. Spontaneous magnetizations determined at 5 K and literature data for NiMn$_2$O$_4$ and FeMn$_2$O$_4$ are given for comparison.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x$</th>
<th>$M_A$ [µB.mol$^{-1}$]</th>
<th>$M_B$ [µB.mol$^{-1}$]</th>
<th>$I_o$ exp [µB.mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_{3-x}$Co$_x$O$_4$</td>
<td>1.54</td>
<td>0.77 (1)</td>
<td>1.39 (2)</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>1.78</td>
<td>3.03 (5)</td>
<td>4.67 (9)</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>2.22</td>
<td>3.06 (4)</td>
<td>3.25 (6)</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>2.77</td>
<td>1.00 (5)</td>
<td>2.38 (9)</td>
<td>0.75</td>
</tr>
<tr>
<td>NiMn$_2$O$_4$ [20]</td>
<td>3.83 (6)</td>
<td>2.76 (12)</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>FeMn$_2$O$_4$ [21]</td>
<td>4.30</td>
<td>3.10</td>
<td>1.55</td>
<td></td>
</tr>
</tbody>
</table>

For the other two ceramic compositions ($x = 1.54$ and 1.77) studied by neutron diffraction at very low temperature, the magnetic structures are more complex according to the low magnetization values obtained for the Co$^{2+}$ in the tetrahedral sites (see Table 2). This result can be interpreted by the occurrence of two sub-lattices of Co$^{2+}$ ions non-collinear in the $A$ sites and at least two sub-lattices of manganese and cobalt ions in the $B$ sites. The resulting magnetizations for each site will then form an angle lower than 180° and the global magnetization will be oriented in a third direction with non-collinear structures.
Conclusion

Magnetic properties of dense and single phase Mn\textsubscript{3-x}Co\textsubscript{x}O\textsubscript{4} (0 \leq x \leq 3) ceramics were characterised. These properties are strongly related to the cation distribution of the material which depends upon the preparation method and thermal treatment. Our ceramics present similar magnetic properties to those reported for powders of the same compositions. The Curie constant decrease as the cobalt content increase is in agreement with a larger proportion of trivalent cobalt ion on the octahedral sites. The magnetic structure of Mn\textsubscript{3-x}Co\textsubscript{x}O\textsubscript{4} (0 \leq x < 3) is ferrimagnetic. At low temperature, the magnetic ordering is characterised by a non-collinear arrangement of spins, as described by Yafet-Kittel for the tetragonal phases or the ‘star’ type for the cubic phases.

References