Micromagnetic Imaging to Determine the Nature of the Ferromagnetic Phase Transition in La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3}

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There is considerable controversy surrounding the nature of the paramagnetic to ferromagnetic phase transition in La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3}. We have used transmission electron microscopy to determine whether the phase transition is first or second order. On warming through the transition point, the ferromagnetic phase retreats from the sample surface as it is replaced by the paramagnetic phase. This coexistence of ferromagnetic and paramagnetic phases indicates a primarily first order transition. However, there is also continuous loss of magnetization which precedes the phase transition. We compare this with the phase transition in nickel, an archetypal second order ferromagnet.

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Nearly all paramagnetic to ferromagnetic phase transitions are second order. Only a few first order transitions have been observed, notably in MnAs where the Curie temperature is found to differ by 10 K on warming compared with cooling when the magnetization is measured as a function of temperature [1]. In conventional magnetization experiments, any such thermal hysteresis in La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3} is much smaller (see Fig. 1) and the magnetization in La\textsubscript{2/3}Ca\textsubscript{1/3}MnO\textsubscript{3} appears to diminish gradually and continuously as is conventional for a second order transition [2]. This is not conclusive evidence that the phase transition is second order, however, because the magnetization is averaged over the specimen and a gradual reduction in magnetization on warming could be caused either by a reduction in the local magnetization uniformly throughout the specimen (as in a second order transition) or the growth of paramagnetic patches within the ferromagnetic phase (a first order transition).

Biernacki [3] has reviewed the previous work on this subject and has found that there is no consensus as to the nature of the paramagnetic to ferromagnetic phase transition in La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3}. Thus we were motivated to study the phase transition using transmission electron microscopy and, in particular, Fresnel imaging and off-axis holography which gives a quantitative, local measure of the magnetization. A similar approach was used by Yoo et al. [4] to demonstrate that paramagnetic and ferromagnetic phases can coexist in La\textsubscript{0.81}Sr\textsubscript{0.19}MnO\textsubscript{3} despite the thermodynamic identification of a second order phase transition in La\textsubscript{0.80}Sr\textsubscript{0.20}MnO\textsubscript{3} which has the same structure and phases [5].

The polycrystalline (grain size 2 \(\mu\)m) La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3} sample used in this investigation was synthesized by a standard solid state reaction described in Ref. [6]. The single crystal nickel sample was synthesized by the Bridgman floating zone method [7].

The magnetic moment of La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3} was measured as a function of temperature with a vibrating sample magnetometer equipped with a liquid-helium-cooled cryostat under an applied field of 1 T as shown in Fig. 1. This was converted to a magnetization by dividing by the sample volume which was measured by weighing the sample with a four figure balance and converting this to a volume via the known density. The uncertainty in the sample mass was 0.5% and this was the principal uncertainty in the magnetization measurement.

It can be seen that the magnetization rises on cooling and has a value 3.71 ± 0.02\(\mu_B\)/Mn at 50 K (the theoretical spin-aligned value is 3.70\(\mu_B\)/Mn). The Curie temperature (judged by the inflexion point on the curve) was 257 K. The sample temperature was changed at 4 K/min in order to reduce thermal inertia as far as was practicable. Comparing warming and cooling curves gave an upper bound of 2 K on any thermal hysteresis. At 90 K, the lowest temperature accessible with the liquid nitrogen cooled specimen stage for the electron microscope, the average magnetization was 3.65 ± 0.02\(\mu_B\)/Mn.

FIG. 1. Magnetization vs temperature for La\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3} in a field of 1 T as measured by vibrating sample magnetometry. Warming and cooling curves are included in the plot although these very nearly coincide giving an upper bound of 2 K on any thermal hysteresis. Transmission electron microscopy revealed that the magnetization reduced homogeneously with increasing temperature in the range marked “homogeneous.” Above 242 K (marked by the dashed line), ferromagnetic and paramagnetic phases coexisted (see text).
We then measured the magnetization on a microscopic scale by electron holography. To acquire electron holograms [8,9], an electron biprism (a positively charged wire) is inserted into the column of the transmission electron microscope and used to interfere a reference electron wave passing through vacuum with one passing through the sample. A digital reconstruction allows both the amplitude and phase of the electron wave function to be determined as it exits the specimen. There are two contributions to the phase of the exit wave function: one electrostatic and the other magnetic. The magnetic contribution can be isolated by subtracting the phase obtained above the Curie temperature since only the electrostatic contribution is present when the specimen is paramagnetic. The magnetization can then be calculated from the magnetic contribution to the phase following the method described in Ref. [10]. For each hologram, we measured the magnetization in ten 0.1 \( \mu \)m square regions. From these we found the average magnetization and random error associated with this measurement which we quote. The values of the mean inner potential used in this calculation were 28.30 V for \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) and 28.70 V for nickel. These were taken from tables of theoretical scattering factors [11] and are likely to overestimate the mean inner potential and thus the magnetization, possibly by as much as 10\%, since atomic bonding is not taken into account.

Figure 2(a) shows the arrangement of magnetic domains at 90 K obtained by electron holography. It can be seen that they are separated by 180° domain walls and have triangular 90° closure domains at the specimen edge. This is a typical magnetic structure of a ferromagnet. The magnetization measured by electron holography at this temperature was 3.61 \( \pm 0.08 \mu_B/\text{Mn} \), in good agreement with the bulk magnetization of 3.65 \( \pm 0.02 \mu_B/\text{Mn} \) measured by vibrating sample magnetometry.

As the specimen was warmed, the domain structure changed very little. At 242 K there has been a net movement of the domains with respect to the configuration at 90 K but the shapes and sizes of the domains are very similar. We found that such rearrangements in the magnetic structure frequently occurred in both this sample and in nickel as the temperature was changed. It will also be noted that there is a small black region near the edge of the specimen indicating that the specimen has become paramagnetic in this region. The most striking difference is that the apparent local magnetization has reduced to 1.67 \( \pm 0.04 \mu_B/\text{Mn} \) in the ferromagnetic regions. We refer to this measurement as an “apparent” magnetization because it is likely that there were paramagnetic regions above and below the ferromagnetic phase which reduced the apparent magnetization since our measurements assumed that the magnetization was uniform throughout the thickness of the specimen (discussed later).

Only 1 K higher at 243 K [Fig. 2(b)], the ferromagnetic regions began a more rapid withdrawal from the edge of the specimen. At 243 K the apparent local magnetization in the ferromagnetic regions was 1.46 \( \pm 0.04 \mu_B/\text{Mn} \) [Fig. 2(c)] and at 244 K, 1.23 \( \pm 0.03 \mu_B/\text{Mn} \) [Fig. 2(d)]. Above 244 K, the ferromagnetic phase was no longer visible in this region of the sample.

We found that to within 2 K, the thermocouple on the liquid nitrogen cooled specimen stage recorded the same temperature when the phase transition took place both on warming and cooling. Changing the convergence angle of the electron beam did not have any significant effect on the temperature at which the transition took place indicating

![Image](https://example.com/figure2.png)

FIG. 2 (color online). (a)–(d) The disappearance of ferromagnetism in \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) measured by electron holography as the sample was warmed towards its Curie point of 257 K. Ferromagnetic regions are colored with the direction of magnetization indicated by the color wheel in the inset to (b) as well as by arrows superimposed. The strength of the magnetization is indicated by the intensity of the color. Note that electron holograms only give information near the specimen edge and the specimen continues into the lower right-hand corner of each panel marked “specimen interior.” The temperature (\( T \)) and the average apparent magnetization (\( M^r \)) in each image is (a) \( T = 90 \text{ K}, M^r = 3.61 \pm 0.08 \mu_B/\text{Mn} \), (b) \( T = 242 \text{ K}, M^r = 1.67 \pm 0.04 \mu_B/\text{Mn} \), (c) \( T = 243 \text{ K}, M^r = 1.46 \pm 0.04 \mu_B/\text{Mn} \), (d) \( T = 244 \text{ K}, M^r = 1.23 \pm 0.03 \mu_B/\text{Mn} \). (e)–(h) The development of magnetization in single crystal nickel. (e) \( T = 294 \text{ K}, M = 0.59 \pm 0.02 \text{ T} \), (f) \( T = 447 \text{ K}, M = 0.56 \pm 0.03 \text{ T} \), (g) \( T = 632 \text{ K}, M = 0.17 \pm 0.01 \text{ T} \), (h) \( T = 634 \text{ K} \), no detectable ferromagnetism.
that heating by the electron beam was not significant for the conditions used here. We are thus confident that the temperatures recorded here are an accurate measurement of the specimen temperature to within 2 K.

It is clear from Figs. 2(a)–2(d) that the paramagnetic phase forms at the sample edges. We now consider the possibility that the paramagnetic phase forms at all sample surfaces, i.e., above and below the ferromagnetic region as illustrated by the schematic cross section in Fig. 3. We can estimate the thickness, \( t \), of the paramagnetic layer from the width, \( w \), of the paramagnetic region surrounding the ferromagnetic region observed by electron holography via

\[
t = w \sin(\theta/2),
\]

where \( \theta \) is the wedge angle found from holograms taken above the Curie temperature where the phase shift can be directly related to the sample thickness. Knowing the thickness of the paramagnetic region, \( t \), and the total sample thickness, the true magnetization, \( M \), can be estimated from the apparent magnetization, \( M^* \), as summarized in Table I. This analysis shows that the corrected magnetization in the ferromagnetic phase is in reasonable agreement with the bulk magnetization of \( 2.50 \pm 0.01 \mu_B/\text{Mn} \) measured by vibrating sample magnetometry. It is thus likely that the paramagnetic phase forms at all sample surfaces before spreading into the bulk of the material.

Our microscopic investigation has shown that only a thin layer (<20 nm) of the paramagnetic phase is present at temperatures below 242 K and thus the bulk magnetization measured by vibrating sample magnetometry gives the magnetization of the ferromagnetic phase in this temperature range. Above 244 K, the bulk magnetization is averaged over both the ferromagnetic and paramagnetic phases. We have indicated this in Fig. 1 with a dashed line: at temperatures below the dashed line the volume fraction of the paramagnetic phase is so small that the measured magnetization is that of the ferromagnetic phase. The magnetization curve shows that as the specimen is warmed, the magnetization reduces continuously before phase separation occurs. This continuous reduction in magnetization anticipates the first order transition: a so-called premonitory effect [12]. We therefore describe the transition as a combination of first and second order processes.

![Schematic cross section of the La\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\) sample showing the relationship between the width of the paramagnetic region measured in projection by electron holography, \( w \), and the thickness of the paramagnetic layer, \( t \), assuming that the paramagnetic layer grows from all surfaces. FM and PM stand for ferromagnetic and paramagnetic, respectively.](image)

In order to further check the validity of our interpretation, we performed a similar experiment with single crystal nickel which should display a conventional second order ferromagnetic to paramagnetic phase transition which should be readily distinguishable from the phase transition observed in La\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\). Nickel has a Curie temperature of 631 K and a saturation magnetization of 0.60 T at 300 K [13] and the magnetization tends towards a limit of 0.61 T as the temperature approaches 0 K [14].

At room temperature (296 K), the magnetization measured by electron holography was \( 0.60 \pm 0.02 \) T, in good agreement with the bulk value. It can be seen from Figs. 2(c)–2(h) that like the manganite sample, the magnetization fades gradually and uniformly and rearrangements of the magnetic structure take place during this process. However, unlike the manganite sample, there is no withdrawal of the domains from the specimen edge: the magnetization simply fades to zero with increasing temperature as expected in a second order phase transition.

In order to gain a better insight into the processes that took place in La\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\) near the Curie point, Fresnel images were recorded at video rate. In the Fresnel method [15] the sample is imaged out of focus with a coherent beam of electrons. Lorentz forces in the sample cause magnetic domain walls to appear as bright interference fringes where the electrons converge and dark regions where the electrons diverge. Fresnel images are less quantitative than holograms, they can be acquired faster from larger areas.

The nucleation and growth of magnetic domains is shown in Figs. 4(a)–4(h). As the specimen was cooled through its Curie temperature, magnetic domains formed first on a grain boundary and then spread into the bulk of the specimen. Further Fresnel measurements showed that as the specimen was warmed, this process was reversed: magnetic domains withdrew from the specimen edge towards grain boundaries where they finally disappeared. The growth of the domains is not a continuous process but proceeds by a series of discontinuous expansions which take place faster than the frame rate of the video (<1/15 s). We have also found that the slower the temperature is changed, the slower the transition takes place.

Figure 4 also demonstrates that the phase coexistence reported here is not caused solely by ion damage to the specimen surface during sample preparation resulting in a lower Curie temperature near the surface. If this were the case, the electron holograms taken above the Curie temperature would show an abrupt transition. The transition is much more gradual as shown in Fig. 4.

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Table I. For La\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\), the average apparent magnetization, \( M^* \), can be corrected for the thickness of the paramagnetic layer, \( t \), to give an estimate of the true magnetization \( M \) as described in the text.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Width (nm)</th>
<th>Thickness (nm)</th>
<th>Apparent Magnetization ( M^* ) (( \mu_B/\text{Mn} ))</th>
<th>True Magnetization ( M ) (( \mu_B/\text{Mn} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>242 ( \pm 2 )</td>
<td>120 ( \pm 30 )</td>
<td>16 ( \pm 4 )</td>
<td>1.67 ( \pm 0.04 )</td>
<td>2.1 ( \pm 0.5 )</td>
</tr>
<tr>
<td>243 ( \pm 2 )</td>
<td>180 ( \pm 40 )</td>
<td>23 ( \pm 6 )</td>
<td>1.46 ( \pm 0.04 )</td>
<td>2.1 ( \pm 0.5 )</td>
</tr>
<tr>
<td>244 ( \pm 2 )</td>
<td>300 ( \pm 70 )</td>
<td>40 ( \pm 10 )</td>
<td>1.23 ( \pm 0.03 )</td>
<td>2.2 ( \pm 0.5 )</td>
</tr>
</tbody>
</table>
The magnetic phase has been observed in single crystal absence of suitable surfaces, point nucleation of the ferromagnetic first followed by thinner areas as the specimen was cooled. However, the magnetic domains appear first in a thin region at the bottom right of Fig. 4(b) and then spread along the grain boundary into a thicker region of the specimen. Furthermore, one would have to argue that atomic disorder due to ion thinning reduced the Curie temperature and yet atomic disorder due to the presence of a grain boundary increased the Curie temperature above that of the bulk. Instead, we believe that this is clear evidence of a first order nucleation-and-growth process by which La$_{0.7}$Ca$_{0.3}$MnO$_3$ becomes ferromagnetic.

We conclude that the ferromagnetic to paramagnetic transition which takes place in La$_{0.7}$Ca$_{0.3}$MnO$_3$ is primarily a first order transition. The transition itself is preceded by a continuous reduction in magnetization. This anticipation of the first order transition is reminiscent of the premonitory effects observed in other first order phase transitions [12] such as the appearance of tweed which precedes a martensitic phase transformation [16].

We find that both ferromagnetic and paramagnetic phases form on surfaces (either grain boundaries or the specimen surface) before spreading into the bulk of the specimen. This is expected as the new phase can grow via heterogeneous nucleation and growth which has a lower energy cost than nucleation and growth from points of a grain boundary increased the Curie temperature above that of the bulk. Instead, we believe that this is clear evidence of a first order nucleation-and-growth process by which La$_{0.7}$Ca$_{0.3}$MnO$_3$ becomes ferromagnetic.

It is rather surprising that the ferromagnetic phase forms at grain boundaries but the paramagnetic phase forms on specimen surfaces: one might have thought that the same nucleation sites would serve for either phase. At present, we are unclear as to why this is the case but in the future we plan to investigate grain boundaries which are closer to the specimen edge so that electron holography can be used to obtain the magnetization distribution of the ferromagnetic phase as it forms.

From this work we expect the magnetic properties of La$_{0.7}$Ca$_{0.3}$MnO$_3$ to change as the grain size of the sample changes. Indeed, López-Quintela et al. [18] have found that the onset temperature of ferromagnetism is higher for polycrystals composed of grains of size 150 nm and 250 nm than for samples with a grain size of 500 nm. This could be the result of having a higher number of grain boundaries on which the nucleation of the ferromagnetic phase can take place but it is difficult to disentangle the effects of grain boundaries from other effects such as chemical nonstoichiometry due to the different specimen preparation procedures necessary to produce samples with different grain sizes.

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