Phase separation in Pr$_{0.7}$Ca$_{0.3}$MnO$_{0.3}$: a case of weak quenched disorder

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Abstract. Phase separation (PS) in manganites has been suggested to arise as a consequence of quenched disorder due to the size mismatch of the A-site cations in the perovskite lattice. In this paper, we have used single crystal x-ray and in-field neutron diffraction measurements to investigate PS in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$, a compound with weak quenched disorder. Above the charge/ordering transition, our measurements show CE-type clusters with a coherence length of $\sim$20 Å. At $T_{CE} = 220$ K the coherence length of the diffuse scattering diverges as a long-range ordered CE state is formed. Concurrently, the Huang scattering abruptly decreases at $T_{CE}$ as the diffuse CE-type reflections develop into Bragg reflections, suggesting that the transition to the CE-state is of the disorder–order type. Our neutron measurements of the ferromagnetic (FM) and antiferromagnetic (AF) ordering in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$, show the presence of FM 200 Å clusters coexisting with long range AF and FM phases. Application of field after zero-field-cooling leads to the reduction of the diffuse FM scattering. We argue that PS in this compound arises as a consequence of the Jahn–Teller strain from Mn$^{3+}$ centres that act like quenched disorder.

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1. Introduction

The resolution of competing interactions in complex transition metal oxides in the form of mesoscopic and microscopic phase separation (PS) continues to test our understanding of the underlying physics of these materials. Competing interactions arise in the manganites in a natural way. In undoped manganese perovskites (such as LaMn$^{3+}$O$_3$), the Mn$^{3+}$ ion has three $d$ electrons in the $t_{2g}$ states that are Hund’s rule exchange-coupled to form a $S = 3/2$ core spin, and one additional electron in a higher-energy doubly degenerate $e_g$ orbital ($S = 2$). The energy of the occupied $e_g$ level can then be lowered by distorting the octahedron. The doping of charge into the system by the introduction of divalent ions such as Ca$^{2+}$ for La$^{3+}$ removes an equal number of $e_g$ electrons to introduce JT (Jahn–Teller)-inactive Mn$^{4+}$ ions and at the same time allow for ferromagnetic (FM) double-exchange coupling between Mn$^{3+}$ and Mn$^{4+}$ ions.

The effect of doping charge into LaMnO$_3$ has an additional structural effect apart from the introduction of undistorted Mn$^{4+}$O$_6$ octahedral. Burgy et al [1] have recently suggested that chemical doping leads to an intrinsic inhomogeneity that arises from the size mismatch among the various trivalent and divalent A-site cations. The effect of the average A-site cation on the electronic properties of the material is reflected in the ideas of band width control via the tolerance factor [2]. This idea has been qualified by Rodriguez-Martinez and Attfield [3] by pointing out that the variance of the ionic size is also of key importance. Here the large discrepancy in the local variation of the tolerance factor is recognized to affect directly the effective charge transfer between Mn$^{4+}$ and Mn$^{3+}$, so that materials with a large ionic size variance remain insulating even if the average tolerance factor is the same as for other ferromagnetic metallic (FMM) compositions.

The relationship between intrinsic inhomogeneities in manganites and PS has been examined using quantum Monte Carlo models [1, 4]. In these models, the absence of intrinsic inhomogeneities results in a phase diagram of two homogeneous phases (FMM and antiferromagnetic (AF) insulator) separated by a first-order phase transition as a function of doping. The introduction of an inherent or quenched disorder in the system results in a low-temperature regime that consists of coexisting ordered clusters of both phases, with randomly oriented order parameters. This state is analogous to PS found in many manganites, where the cluster size can range from microscopic to mesoscopic. Although these simulations do not address...
the origins of the intrinsic inhomogeneities (that is treated as a quenched disorder), they do point to the possible origin of PS.

Of the many manganite systems that exhibit PS, the Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ compound is one of the most exciting and at the same time least understood. In this material the competition between charge, spin and lattice degrees of freedom leads to a CE-type charge and orbital ordering that coexists with a ferromagnetic insulating (FMI) phase at low temperature, but application of magnetic field [5, 6], exposure to light [7, 8] or x-rays [9] can melt both states to stabilize an FMM state [10]. The behaviour of this material, both in terms of structure and magnetism, over the temperature range where PS occurs is very complex. But according to quantum Monte Carlo modelling discussed above, this compound should correspond to the case of weak quenched disorder and therefore no PS. This arises from the fact that the sizes of the A-site cations are almost identical (Ca$^{2+}$ ($r_{\text{ion}} = 99$ pm) and Pr$^{3+}$ ($r_{\text{ion}} = 100$ pm)) and the variance of their ionic size is essentially zero. In this context, PS in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ is not expected and provides an opportunity to study PS in the presence of very weak quenched disorder.

The Pr$_{1-x}$Ca$_x$MnO$_3$ system has been studied extensively in terms of both charge and magnetic degrees of freedom. In the $x = 0.35$ compound, neutron scattering from FM clusters with coherence length of $\sim 20$ Å has been shown to sharply decrease at the onset of a CE-type charge and orbitally ordered phase at $T_{CE} = 230$ K and again at $T_N \sim 160$ K [11]. For a doping of $x = 0.3$, the magnetic properties of these manganites are somewhat different. Here the CE-type charge and orbital ordering is observed at $T_{CE} \sim 180$ K and CE-type AF ordering is found at $T_N = 140$ K [12]. However, instead of the collapse of FM correlations at $T_N$, a fully ordered FM state is observed below $T_C \sim 120$ K [12]. Initially, these FM reflections were interpreted as spin canting in the CE-phase; however Cox et al. [12] showed that they belong to a new FMI phase that coexists at low temperatures with the CE-type phase. The application of magnetic field not only results in the melting of the CE-phase as reported by Yoshizawa et al. [13] but also melts the FMI phase giving rise to a third FMM phase with a much smaller unit cell volume [10]. These structural observations are consistent with bulk resistivity and magnetization measurements [14].

Measurements in powder samples with composition $x = 0.3$ show clearly that the FM transition in this manganite is very much akin to a spin-glass transition [10]. Quasi-elastic small-angle neutron scattering (QSANS) measurements show evidence of spin diffusion well above $T_C$, within the CE stability region. However, close to $T_C$ the ratio of the elastic to inelastic contribution of the QSANS signal diverges, similar to that for a spin-glass. Interestingly, these measurements also suggest that the magnetization of clusters (amount of FM clusters) decreases close to $T_C$, but does not disappear completely and frozen FM clusters are still present as low as 4 K [10].

In this paper we report a detailed investigation of PS in the absence of quenched disorder in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$, using single crystal diffuse x-ray and in-field neutron diffraction measurements. Above $T_{CE}$, we find clusters of the CE-phase with a coherence length of $\sim 20$ Å. At $T_{CE} = 220$ K the coherence length of the diffuse scattering from these clusters diverges as a long-range CE state is formed. Concurrently, the Huang scattering (that arises from local JT distortions) abruptly decreases at $T_{CE}$ as the diffuse CE-type reflections develop into Bragg reflections, suggesting that the transition to a charge- and orbital-ordered state is akin to a disorder–order transition. In our x-ray measurements, at 115 K the intensity of the CE-type reflections begins to decrease, suggestive of a photo-induced charge melting. Our neutron measurements of the FM and AF ordering in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$, show the presence of FM 200 Å clusters coexisting with a long-range AF and FM phases. Application of field after zero-field-cooling (ZFC) measurements leads to the reduction of the diffuse FM scattering. Field-cooled measurements at $H = 7$ T surprisingly
show that local CE correlations persist at high fields and to low temperatures. We argue that PS in Pr\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3} cannot be considered to occur in a homogeneous background, as suggested by the negligible size mismatch of the A-site cation. Rather the order–disorder nature of the transition into the CE-phase results in a state in which regions that are not amalgamated into the CE-phase, while cooling through $T_{CE}$, develop into the glassy JT state [10]. We suggest that this glassy state is FM in nature, with a distribution of FM cluster sizes over multiple length scales, which results in an apparent PS in Pr\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3}.

2. Experimental setup

A single crystal of Pr\textsubscript{0.7}Ca\textsubscript{0.3}MnO\textsubscript{3} was prepared via the travelling floating-zone method. The crystal used for the neutron experiments had a diameter of 5 mm and height of 10 mm. A small piece of this crystal was cut and used for the x-ray scattering measurements. Single crystal x-ray diffraction measurements were made on the BESSRC 11ID-C beamline at Argonne’s Advanced Photon Source as a function of temperature from 300 to 50 K using a close cycle refrigerator. For this experiment we used an incident energy of 115 keV, while intensity measurements were made using a Ge solid state detector. Neutron diffraction measurements were made using a cryomagnet mounted on the BT-2 thermal triple axis at the NIST Center for Neutron Research.

For the neutron diffraction data integrated intensities and FWHM were computed by a least-squares fit of a Gaussian peak plus a linear background to the measurements. For the x-ray measurements, a similar approach was used but a squared Lorentzian line shape was used instead. To extract the contribution of the Huang scattering from the diffuse x-ray data, scans along H or K were made starting close to either the (6,0,0) or (5,0,0) reflection. The scans included both the Huang scattering close to the Bragg reflection as well as the diffuse CE-type super lattice reflection (or Bragg reflection below $T_{CE}$). The measurements were then fit as already described with the addition of the an $A/q^2$ term, centred at the middle of the Brillouin zone to describe the Huang scattering. Here $A$ is a scalar constant proportional to the contribution of the Huang scattering. The thermal diffuse scattering (TDS) component was estimated from the temperature dependence of the scattering (see below).

3. Results

3.1. Short-range charge correlations

X-ray diffraction is the probe of choice to examine diffuse scattering arising from charge correlations in manganites. Single crystal neutron and x-ray diffraction measurements have shown that anomalies in the temperature dependence of the TDS [15, 16] arises from Huang scattering from the long-range strain field induced on the lattice by local JT distortions [15]–[17]. While Huang scattering is distributed as a smooth symmetric function centred around Bragg reflections in reciprocal space, correlations between lattice displacements due to the local ordering of JT active Mn\textsuperscript{3+} results in diffuse satellite reflections [15, 18, 19]. We remark here that TDS that arises from low-energy phonons close to the centre of the Brillouin zone has a $1/q^2$ dependence (where $q$ is a point in the first Brillouin zone), the same as Huang scattering. However, the temperature dependence of these two effects is significantly different as the TDS contribution scales directly with $k_BT$. 

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In figure 1 we show sections of reciprocal space around the (6, 0, 0) Bragg reflection for 250 and 210 K and around the (8, 0, 0) reflection at 100 K. Our measurements show the presence of Huang-like scattering at 250 K that is very similar to the measurements of Shimomura et al [20]. Apart from the \(1/q^2\) dependence of the Huang scattering along the [0, k, 0] direction at 250 K, we also find additional scattering centred close to \(k = 0.45\). This is evident in a section through our reciprocal space map at 250 K along [6, k, 0] shown in figure 2. Below the transition to the CE-phase at 210 K (figure 1) we see clearly the presence of the superlattice reflections with propagation vector \((0, \frac{1}{2}, 0)\) at 210 and 100 K (assuming the \(Pbnm\) setting for this higher temperature orthorhombic perovskite). In addition to this scattering we also find satellite reflections with propagation vector \((\frac{1}{2}, 0, 0)\) both around the (6, 0, 0) and (8, 0, 0) reflections above and below \(T_{CE}\) (see figure 1), that arise from another minor domain of the CE-phase. Scattering at \((\frac{1}{2}, \frac{1}{2}, 0)\) type positions arises from twin domains.

Diffuse \((0, \frac{1}{2}, 0)/\left(\frac{1}{2}, 0, 0\right)\) superlattice reflections as seen in figure 1 at 250 K, indicate that short-range charge and orbital correlations of the CE-type are present above \(T_{CE}\). These correlations have a coherence length of \(\sim 20\) Å as obtained from their width in reciprocal space. To follow the evolution of the diffuse scattering through the transition to the CE-phase we have repeated the same scan shown in figure 2 as a function of temperature. The results are shown in figure 3 (upper panel), where we plot along the \(x\)-axis the \(k\) position in reciprocal space along (6, k, 0) and along the \(y\)-axis the temperature of the measurement. The intensity is shown both in the form of contours and colour. As seen from this figure, on cooling through the transition to the CE-phase we clearly observe the reduction of the diffuse scattering close to the (6, 0, 0) Bragg reflection while concurrently the intensity of the (6, \(\frac{1}{2}, 0\)) reflection increases rapidly giving a transition temperature for the CE-phase at \(T_{CE} = 220\) K. Accompanying this increase in intensity, the width of the same reflection decreases to the resolution limit of the instrument at \(T_{CE}\) as shown in the inset of figure 3 (lower panel), indicating that the correlation length diverges at the transition.

To separate the TDS contribution from the Huang scattering we plot the intensity of the combined contributions as obtained from fitting our scans as described in section 2. The variation of the diffuse scattering intensity as a function of temperature is shown in figure 3 (lower panel). We find that at low temperature the variation of the diffuse scattering close to the Bragg reflection is essentially linear, consistent with TDS. However, at high temperature, we find significant deviations from linear behaviour associated with the transition to the CE-phase at 220 K. The linear temperature dependence of the TDS allows us to extrapolate the phonon contribution and subtract it from the total diffuse intensity, thus providing only the Huang scattering contribution as shown in the lower curve of figure 3 (lower panel). From this analysis it is evident, that above \(T_{CE}\), the local structure of \(Pr_0.7Ca_{0.3}MnO_3\) consists of short-range CE-type correlations (as indicated by diffuse \((0, \frac{1}{2}, 0)\) reflections) and local lattice distortions that result from long-range deformations around JT-active Mn\(^{3+}\) ions. We note here that from the nature of the Huang scattering itself the lattice distortions from both correlated and uncorrelated JT-active Mn\(^{3+}\) ions contribute here.

The evolution of the diffuse scattering as a function of temperature is shown in the rapid reduction of the Huang scattering contribution at \(T_{CE}\), as the weak \((6, \frac{1}{2}, 0)\) CE-type reflection rapidly increases in intensity (see figure 4). This indicates that the local structure of \(Pr_0.7Ca_{0.3}MnO_3\) undergoes significant changes during the ordering of the CE-phase as CE-regions grow rapidly below \(T_{CE}\). We believe that these measurements indicate that the transition to the CE-phase is a disorder–order transition on cooling. In this picture, local JT interactions...
Figure 1. A section of reciprocal space around the \((6, 0, 0)\) and \((8, 0, 0)\) reflections, perpendicular to the \([0, 0, 1]\) axis (the \(\text{Pbnm}\) setting of space group no. 62 is used to describe the crystallographic axis). Measurements were made at 250 and 210 K around the \((6, 0, 0)\) and 100 K around the \((8, 0, 0)\) reflections. The colour contour maps were made by interpolations between measurements which are shown as white points. The Huang scattering around the Bragg reflection is evident above \(T_{CE}\) in the 250 K map. Below \(T_{CE}\) at 210 and 100 K the CE \((0, \frac{1}{2}, 0)\)-type reflection is observed. For all maps, superlattice reflections with propagation vector \((\frac{1}{2}, 0, 0)\) are observed to arise from a minor CE-phase domain. Colour scales of intensity are shown for the measurements centred around \((6, 0, 0)\) and \((8, 0, 0)\) reflections. Measurements at Bragg or at \((\frac{1}{2}, \frac{1}{2}, 0)\) type positions were not made and consequently the interpolation routines do not provide correct results. Scattering at \((\frac{1}{2}, \frac{1}{2}, 0)\) type positions arises from twin domains in our crystal. For example the \((\frac{10}{3}, \frac{1}{3}, 0)\) reflection arises from the \((11, 1, 0)\) Bragg peak of another domain. This scattering is sufficiently distant in reciprocal space to give no contribution to the Huang scattering close to the Bragg reflections of the main domain we are investigating.
Figure 2. A scan through the diffuse scattering along the \([0, k, 0]\) direction from \((6, 0, 0)\) clearly shows the Huang scattering and a pronounced shoulder centred at \(\sim (6, 0.47, 0)\) at 260 K. The line through the data is a fit using a \(1/q^2\) term for the Huang scattering and a Gaussian peak to model the diffuse scattering arising from CE correlations. The Huang scattering and CE-peak contributions obtained from the least-squares fit are also shown individually on the figure.

lead to the formation of CE-clusters that increase in size close to \(T_{CE}\), while uncorrelated JT distorted MnO\(_6\) are incorporated into the growing clusters as the correlation length diverges.

On cooling, below \(T_{CE}\) the intensity of the \((6, 1/2, 0)\) reflection increases with decreasing temperature until 115 K, where it then begins to decrease again. We believe that the decrease in intensity of this reflection below 115 K is due to a photo-induced effect as we find the opposite effect by measuring the \((3, 7/2, 0)\) reflection using neutrons (see figure 4).

3.2. Magnetic ordering

Two magnetic phases were detected in our \(Pr_{0.7}Ca_{0.3}MnO_3\) single crystal using neutron single-crystal diffraction, an FM phase and an AF phase associated with the CE-type charge and orbital ordering (AF(CE)). The temperature dependence of the magnetic ordering is shown in figure 4, where we plot the AF(CE) and FM order parameters measured using the \((1/2, 0, 0)\) and \((2, 0, 0)\) reflections, respectively. We find that the AF(CE) ordering occurs at \(T_N = 130\) K while FM long-range order is observed at \(T_C = 115\) K. These measurements are consistent with previous neutron measurements of the magnetic ordering in \(Pr_{0.7}Ca_{0.3}MnO_3\) which report that the FM-phase coexists with the CE-phase [12, 13].

3.3. Field dependence of FM and CE-phases

The stability of the FM and CE phases under a magnetic field applied along the \(c\)-axis was investigated in our \(Pr_{0.7}Ca_{0.3}MnO_3\) crystal using neutron diffraction, utilizing a vertical field cryomagnet on the BT-2 triple axis spectrometer. For these experiments, the sample was first ZFC to 5 K and then the field was applied in 0.5 T increments to 7 T and then released again.
in 0.5 T steps to 0 T, and then the sample was warmed. Scans of the FM (2, 0, 0) and AF-CE ($\frac{1}{2}, \frac{1}{2}, 0$) reflections were made as a function of temperature and field. For field-cooling (FC) measurements, the sample was brought to a temperature of 250 K were field was applied again in 0.5 T increments to 7 T. The sample was then cooled to 5 K, where the field was reduced to 0 T again in 0.5 T steps.
Figure 4. Temperature dependence of the characteristic pseudo-CE (pCE) (6, 1/2, 0) reflection measured using x-ray diffraction and the FM and AF-CE characteristic reflection ((2, 0, 0) and (1/2, 1/2, 0)), respectively measured using neutron diffraction. All measurements shown here were made in zero field.

In figure 5, we show measurements as a function of temperature and field for the FM (2, 0, 0) and AF(CE) (1/2, 1/2, 0) reflections, respectively. On ZFC, the intensity of the FM reflection shows a significant increase, indicative of FM ordering at $T_C = 115$ K. On further cooling below $T_C$ the magnetic scattering does not saturate and a positive slope is found even below 10 K. The temperature dependence of the AF(CE) reflection suggests the onset of AF ordering at $T_N = 110$ K, and as with the FM scattering there is no saturation of the AF moment at low temperatures.

The application of magnetic field parallel to the $c$-axis, at 5 K has a significant effect on the stability of both magnetic phases. We find the intensity of the FM reflection to increase by a factor of $\sim 2.4$, while the AF(CE) reflection decreases to 8% of its ZFC value at 5 K. We note that for this reflection a change in slope occurs at 3 T as the field is applied, which was also observed by Yoshizawa et al [13].

Decreasing the field from 7 to 0 T at 5 K, we find a significant hysteresis in the intensity of the FM and AF(CE) reflections. The FM intensity does not return to its previous ZFC value but remains 1.5 times higher in intensity. The intensity of the AF(CE) shows only a small increase from its 7 T value, on ramping down the field. The hysteresis exhibited by these magnetic reflections demonstrates the first-order nature of the field induced AF(CE) to FM transition.

A noteworthy feature of the scans of the FM phase is the presence of field-dependent diffuse scattering around the (2, 0, 0) reflection as shown in figure 6(a). Here we find that the diffuse scattering around the (2, 0, 0) reflection can be modelled by a Lorentzian providing a correlation length of $\sim 200$ Å at 5 K in ZFC. The field dependence of the FM diffuse scattering at 5 K (see figure 6(b)) shows the opposite behaviour to the intensity of the FM (2, 0, 0) reflection. Here the FM diffuse scattering decreases with applied field to 7 T and increases once the field is released to 0 T but only to 70% of its original 0 T value. The zero field result is in agreement with previous powder measurements in that a significant amount of frozen FM clusters exists in the
Figure 5. Temperature and field dependence of (a) the FM \((2, 0, 0)\) reflection and (b) the \(\text{AF(CE)}\) \(\left(\frac{1}{2}, 0, 0\right)\) reflection. ZFC measurements are indicated by filled symbols, while FC in 7 T are indicated by open symbols.

material \cite{10}. The application of the magnetic field essentially allows the remaining clusters to participate in a mesoscopic FM phase, as suggested by the decrease in the diffuse scattering and the increase in the \((2, 0, 0)\) FM reflection. However, on the release of field, the cluster behaviour appears to return and suggests that the state of the material after cycling field to 7 T still exhibits ferromagnetism over multiple length scales.
Figure 6. (a) A scan along \((h, 0, 0)\) after ZFC at 5 K in a field of 0 and 7 T. Intensity is plotted on a logarithmic scale to better highlight the diffuse scattering around the FM \((2, 0, 0)\) reflection. (b) Integrated intensity of the diffuse scattering as a function of field after ZFC to 5 K.

After the field cycle to 7 T and back down to 0 T at 5 K, the FM \((2, 0, 0)\) reflection was measured on warming. We found that the intensity of the FM reflection shows hysteresis, with a \(T_C\) on warming of 120 K, 10 K higher than \(T_C\) on cooling. In addition, a pronounced anomaly was observed at \(\sim 60\) K as shown in figure 5. We suggest that this anomaly is due to the melting of the FM-metallic phase in preference to the FM-insulating phase [10].

On warming the sample to 250 K we again applied a magnetic field parallel to the \(c\)-axis up to 7 T and we monitored the FM and CE-AF reflections. At 250 K and 7 T we find that the intensity of the FM \((2, 0, 0)\) reflection has increased by a small amount suggesting that a small FM moment has been induced by the field. Surprisingly, we also measure a weak CE-AF reflection at 7 T and 150 K as shown in figure 5. On cooling, this reflection showed a weak temperature dependence.
to 5 K while the FM reflection showed a smooth increase to a value almost twice that in the ZFC measurements. The intensity of the FM reflection is much higher compared to ZFC measurements suggesting that more Mn-spins contribute to the FM phase. At 5 K after FC, the release of field results in the decrease in the intensity of the FM reflection, to the same value as found with ZFC at \( H = 7 \) T and 5 K, indicating that the FM-metallic phase remains stable with the release of field, while the intensity of the AF reflection does not show any significant change and remains overall quite small. Although no detailed investigation was made of the changes of the FM and AF(CE) intensities on warming after FC and release of field, preliminary measurements indicate that the intensity of the FM reflections decreases rapidly while the AF(CE) intensity increases (see figure 5), suggesting that the field-induced FMM-phase is not stable at low temperatures on warming, once the field has been released.

4. Discussion

Our measurements describe the competing interactions in \( \text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) as the driving force for its unusual properties. At high temperatures \( T > 230 \) K we find evidence of short range CE-type correlations. With decreasing temperature and through the charge/orbital ordering transition, these correlations increase in size and their correlation length diverges at the transition. Similarly, Huang scattering suggests that long-range lattice deformations from locally distorted \( \text{Mn}^{3+}\text{O}_6 \) octahedra reach a maximum at \( T_{CE} \) and decrease rapidly with decreasing temperature for \( T < T_{CE}. \) These latter two observations suggest that the transition to the CE-phase in \( \text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) is of an order–disorder type. We suggest here that the significant local disorder driven by JT active \( \text{Mn}^{3+} \) can act as like nucleation centres for the CE phase. In this respect, the JT active \( \text{Mn}^{3+} \) ions act to induce a quenched disorder into the system driven by charge localization—as electronic degrees of freedom—as opposed to simple steric effects that arise from the size mismatch between A-site cations. Furthermore, this JT disorder differs from steric effects as described by Rodriguez-Martinez and Attfield [3] in that it introduces a highly displacive component.

Indeed an order–disorder model has been suggested for the cooperative JT distortion for LaMnO\(_3\) by Millis [21] and Ishihara and Maekawa [22], while Chatterji et al [23] describe neutron diffraction experiments that support this model. In order–disorder transitions, a strong anharmonic behaviour is required for the atomic potential and is known to lead to correlations above the ordering temperature. Thus, in the context of our measurements, the observation of correlations above \( T_{CE} \) is consistent with such a mechanism, as opposed to PS.

The magnetic PS into FM and AF(CE) phases in \( \text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) is interesting in that while the AF(CE) phase appears to be confined within the CE phase, the FM phases appear to exist over a range of length scales. The FM phase has been attributed to a JT glass state, that is separate from the CE phase [10]. In our work we find that the diffuse scattering around the FM reflections suggests that the FM state is not homogeneous, but exists over mesoscopic (resolution-limited FM Bragg reflections) and microscopic length scales as indicated by the presence of 200 Å FM clusters. Indeed Radaelli et al [10] using SANS measurements found evidence for 16 Å FM clusters at similarly low temperatures in ZFC measurements [10]. That ferromagnetism in \( \text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) occurs over a variety of length scales may reflect the glassy nature of the structural host phase. With respect to the order–disorder nature of the charge/orbital ordering transition at \( T_{CE} \), the FM phase may reflect varying size regions in which the growth of the CE phase, from clusters to long-range regions, was impeded. Indeed evidence for this idea is found.
in a minor domain of the CE phase that we found during our x-ray diffraction measurements that showed a divergence of its correlation length at the much lower ordering temperature of 150 K. This would suggest that local strain can frustrate the development of the CE phase partially or completely, possibly leading to an orbitally disordered insulating FM phase.

Our ZFC measurement to 5 K shows that the application of field leads to the melting of the AF state and the enhancement of the FM state. Interestingly, the FM diffuse scattering decreases with applied field at 5 K but increases as the field is released indicating that although a glassy JT phase may be incorporated into an FMM phase, it is not completely stable and disorder returns as indicated by the return of FM diffuse scattering as the field is decreased from 7 to 0 T after ZFC.

For compounds where the size mismatch between A-site cations is zero, no quenched disorder is expected, and PS models predict a true bi-critical behaviour with a sharp phase boundary. Phases on either side of the boundary are expected to be single phase and homogeneous. Quenched disorder arising from the mismatch of the A-site cations would result in the broadening of such a phase boundary with phase-coexistence and competition dominating in the region close to the critical compositions. Such PS has recently been discussed by Blake et al [24]. The manganite that we have investigated here falls in this class of materials where the size mismatch gives little or no quenched disorder and thus PS is not expected, although it is observed. In this work, we have shown that, in addition to the well known PS effects in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$, at temperatures above any magnetic or charge/orbital-ordering transition, the lattice is disordered on a local scale, not from steric effects but from the localization of charge, leading to local distortions from JT active Mn$^{3+}$ ions. Therefore, the phase transitions in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ cannot be considered to occur in a homogenous lattice background, as would be suggested by the PS picture of Burgy et al [1]. The order–disorder transition into the CE phase that we describe here and the tendency towards charge localization results in a state in which matter that is not amalgamated into the CE phase while cooling through $T_{CE}$, can develop into the glassy JT-state [10]. This glassy state we suggest is FM, and as suggested by the length scale of FM clusters, occurs over multiple length scales. The type of PS that occurs in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ we believe is different from what occurs for example in the Pr$_{0.35}$(Ca$_{1−\gamma}$Sr$_{1−\gamma}$)$_{0.65}$MnO$_3$ system [25, 26], where clear evidence of competing mesoscopic FM and CE(AF) phases is found. We argue rather that in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ PS is in essence accidental in that it arises from the frustration of the growth of the CE-type phase from CE-type clusters. We note finally that the ferromagnetism of the JT glass is not surprising, as Rodriguez-Martinez and Attfield [3] demonstrated that samples with large A-site variance, but with tolerance factor and electronic doping identical to FM metallic materials, were indeed insulating and FM also. Recent theoretical modelling has also indicated that the FM state is more resilient to disorder in comparison to charge/orbital-ordered states [27].

We note here that Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ is distinctly different to A-site ordered cation perovskites such as R$\text{Ba}_2$Mn$_2$O$_6$, R = Sm, Nd, Pr [28, 29]. Here, the relatively large size mismatch of the R and Ba ions results in a double perovskite structure of chemically homogeneous RO and BaO sheets. In this arrangement, the quenched disorder within a sheet is zero, but there are strain effects resulting from the tolerance factor between different A-site layers. Regardless, glassy behaviour appears to be observed in double perovskite samples in which quenched disorder is introduced during synthesis [28]. For well-ordered compositions such as R = Sr and Nd, FM- and charge-ordered phases are found as the tolerance factor is tuned [29].
5. Conclusions

In this paper, we have investigated the ordering of the CE phase in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ using single crystal diffuse scattering and find that it is akin to an order–disorder transition (on cooling) as indicated by the temperature dependence of the diffuse scattering. The investigation of the magnetic ordering in the same single crystal suggests that ferromagnetism arises over varying length scales. We argue that the order–disorder nature of the CE transition allows for regions in the material that are not amalgamated into the CE phase to remain in a charge/orbital disordered (insulating) state also over varying length scales. This JT glass state is FM giving rise to coexisting FM and AF phases at low temperature.

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