

Formation of Finite Antiferromagnetic Clusters and the Effect of Electronic Phase Separation in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$

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We report the first experimental evidence of a magnetic phase arising due to the thermal blocking of antiferromagnetic clusters in the weakened charge and orbital ordered system $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$. The third order susceptibility (χ_3) is used to differentiate this transition from a spin- or cluster-glass-like freezing mechanism. These clusters are found to be mesoscopic and robust to electronic phase separation which only enriches the antiphase domain walls with holes at the cost of the bulk, without changing the size of these clusters.

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Cuprates and manganites belong to the class of highly correlated electron systems, where the kinetic and potential energies share comparable scales resulting in a fascinating array of electronic and magnetic properties. The parent compounds in both these classes of materials are antiferromagnetic (AFM) insulators, and the physical properties evolve as a function of hole doping. The current consensus is that the AFM host has the tendency to expel away holes, an electronic phase separation (EPS) mechanism leading to regions with varying hole concentrations [1]. When coupled with other competing interactions like the Coulombic repulsion, this leads to various self-organized structures. In practical systems, this could take the form of an antiphase domain wall [2], along which the holes are concentrated and across which the antiferromagnetic order changes sign. An interesting experimental manifestation of this charge segregation is the formation of the *cluster spin-glass* phase in cuprates which has been the subject of intense scrutiny for many years and has been detected using a variety of measurements [3,4]. This phase is postulated to appear when AFM clusters encircled by the antiphase domain walls freeze, provided there is sufficient disorder in the system to prevent long range ordering. However, there has been no conclusive evidence of such a state arising purely out of EPS in the mixed valent manganites. Here, hole concentrations of close to 50% are most relevant for studies of this nature since Coulombic repulsive forces are known to stabilize the formation of a charge and orbital ordered (COO) AFM ground state [5]. A variety of relaxation effects possibly arising due to phase competition are observed in these compositions, but whether these *glassy* phases mimic the canonical spin glasses or whether EPS leads to a new form of *glassiness* remains to be understood in addition to their relation with those found in cuprates and other spin systems [6].

In manganites, the disorder necessary for prohibiting the long range order can be easily introduced in the form of impurities in the Mn-O-Mn network. The nature of the

dopant has a crucial bearing on the magnetism, as impurities with partially filled *d* bands (like Cr or Co) could participate in the broadening of the e_g bandwidth[7]. The bandwidth (W) of the host system is equally important as shown by the fact that substitution of Cr in the large W system $\text{La}_{0.46}\text{Sr}_{0.54}\text{MnO}_3$ is seen to induce a reentrant spin-glass phase [8], whereas when substituted in the narrow W system $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ the formation of a relaxor ferromagnet is speculated [9]. Co substitution in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ is reported to form an inhomogeneous magnetic state which also exhibits sharp magnetization steps as a function of applied field [10]. Substitution studies where the impurity has a nonmagnetic configuration (d^0 or d^{10}) would be particularly advantageous, since it would be expected to introduce random disorder in the COO state without introducing any magnetic interactions of its own. Ionic considerations also need to be taken into account, considering the fact that lattice distortions play a crucial role in stabilizing the physical properties of these systems.

In an attempt to observe the evolution of magnetic phases in a COO system with quenched nonmagnetic impurities, we have undertaken a detailed study of the compound $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$ using dc magnetization (DCM) and linear and nonlinear ac susceptibility ($ac\chi$). Since large applied fields can mask the intrinsic signatures of inhomogeneously magnetized systems, we have concentrated on *low field* measurements to discern the magnetic ground state. Nonmagnetic Al was selected on ionic considerations and polycrystalline samples were prepared using the solid state ceramic route, the details of which have been reported earlier [11]. In this Letter, we report the first conclusive observation of thermal *blocking* of AFM spin clusters in a weakened COO system, contrary to the cluster spin-glass *freezing* observed in the cuprates. Moreover, the size of these clusters is found to be robust within the experimental time scales against EPS, which only enriches the domain walls with holes at the cost of the antiferromagnetism of the bulk.

The parent $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, with a narrow W is known to be a prototype COO system, and a robust CO is seen to set in at $T \approx 240$ K [12]. This real space ordering of charge carriers, accompanied by an alternate ordering of the $d_{3x^2-r^2}/d_{3y^2-r^2}$ Mn^{3+} orbitals in the ab plane is manifested in bulk magnetic measurements in the form of a rapid fall of the susceptibility at T_{CO} . This COO is known to enhance antiferromagnetic fluctuations and long range AFM order sets in at $T_N \approx 175$ K. Interestingly, the correlation lengths for the orbital order (OO) is seen to be shorter than that of the CO, indicating the presence of an orbital (antiphase) domain state [13]. Al substitution in the Mn site of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ introduces random disorder in the COO state, as a result of which the strength of the CO reduces, as is shown in the inset of Fig. 1.

Dilution of the magnetic lattice using nonmagnetic Al causes the long range AFM transition temperature (T_N) to drop to ≈ 50 K, as is shown in Fig. 1. Interestingly, an additional feature is observed at lower temperatures as evidenced by a cusp in the zero field cooled (ZFC) DCM at $T_G \approx 26$ K. Moreover, a strong irreversibility in DCM is observed, as indicated by the large bifurcation in the ZFC and field cooled (FC) magnetization measurements. This history dependence is a generic feature of disordered systems and is seen in a variety of systems like spin glasses (SG), cluster glasses, and superparamagnets (SPM). It is interesting to note that unlike in a prototype SG [14], here the irreversibility is seen to commence at temperatures much higher than T_G . Also, below T_G the FC magnetization is seen to increase monotonically with decreasing temperature, where as in a spin glass, the FC magnetization would be expected to remain almost independent of temperature.

However, these observations are by no means conclusive; since it is known that both SG and SPM with large

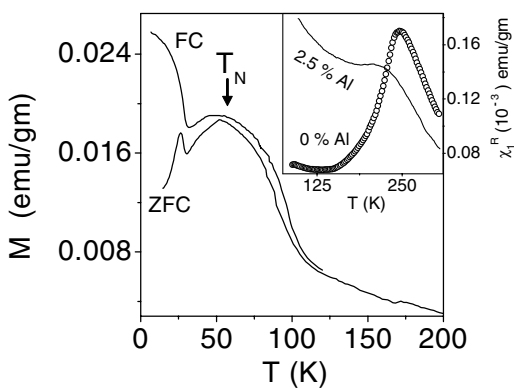


FIG. 1. Irreversibility in DCM as measured using ZFC and FC magnetization runs in the sample $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$ at a measuring field of 100 Oe. The inset shows the real part of χ_1 as measured at a field of 12.5 Oe and frequency of 133 Hz for the samples $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$ and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. The reduction of the CO strength with Al substitution is clearly seen.

dipolar interactions can show a bifurcation in FC and ZFC much above T_G and SPMs with a narrow volume distribution can exhibit a temperature independent FC below T_G similar to that of a prototype spin glass. Coupled with the fact that experimental signatures like a large history dependence in DCM, frequency dependence in $\text{ac}\chi$ and time dependence in remanant magnetization are exhibited by all of the above mentioned metastable systems makes identification among them a nontrivial exercise. Needless to say, the physics involved in these systems are totally different, since *freezing* is a cooperative phenomenon where spins (or clusters) are frustrated due to random competing ferro and antiferro interactions, whereas *blocking* is a purely dynamic phenomenon arising out of the competition between the thermal and the magnetic (volume and anisotropy) energies of the magnetic clusters.

We have circumvented this problem by using the third ordered susceptibility (χ_3) to determine the nature of the observed low temperature phase. χ_3 has long been used as a direct probe of the divergence of the Edward-Anderson order parameter, signifying the onset of a spin-glass transition [15]. It is well known that theoretically, χ_3 is expected to have a negative divergence in the limits $H \rightarrow 0$, and $T \rightarrow T_G$, where H denotes the magnetic field [16]. Though SPMs also show a negative cusp in χ_3 analogous to that exhibited by SGs, the crucial difference is that unlike for a SG, here χ_3 is not *critical* as a function of H or T . This intrinsic difference can be used to accurately differentiate a *freezing* from a *blocking* phenomenon [17]. This can be vividly demonstrated by plotting the peak value of χ_3 as a function of H as is shown in Fig. 2, where the peak value of χ_3 is plotted as a function of H for the sample $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$. Here, χ_3 is clearly seen to saturate in the limit $H \rightarrow 0$, indicating that this

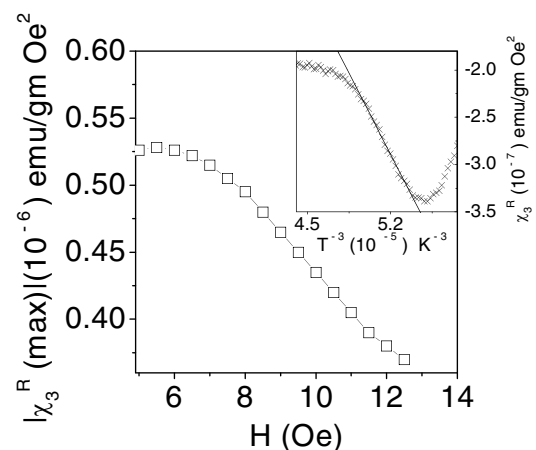


FIG. 2. The peak value of χ_3 plotted as a function of the applied ac field H , clearly indicating that χ_3 is not *critical* with H . The inset shows the temperature variation of χ_3 above T_G for $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$. The straight line is a T^{-3} fit to the data obtained at a field of 12.5 Oe at an exciting frequency of 133 Hz.

low temperature phase which we have observed occurs due to the *blocking* of the magnetic entities and is not a cooperative freezing phenomenon.

The total magnetization (M) of a system of noninteracting (single domain) SPM particles can be given as $M = n\langle\mu\rangle L(\langle\mu\rangle H/k_B T)$, where n is the number of particles per unit volume, $\langle\mu\rangle$ is the average magnetic moment of a single magnetic entity, k_B is the Boltzmann's constant, and $L(x)$ is the Langevin function. The linear and nonlinear susceptibilities above the blocking temperature can then be calculated to be $\chi_1 = n\langle\mu\rangle/3k_B T$ and $\chi_3 = -(n\langle\mu\rangle/45)(\langle\mu\rangle/k_B T)^3$. Thus the χ_3 is negative and proportional to T^{-3} [18]. The inset of Fig. 2 shows this T^{-3} dependence for the real part of the measured χ_3 for this sample, further substantiating the fact that the feature observed in our magnetic measurement arises due to the blocking of magnetic entities.

An estimation of $\langle\mu\rangle$ can be made using the ratio χ_3/χ_1 as is obvious from the above equations. Using fits to χ_3 and χ_1 , the value of $\langle\mu\rangle$ determined is of the order of 10^4 Bohr magneton. Here, it is important to note that a prototype SPM will have a large value of $\langle\mu\rangle$ due to the fact that it is made up of a large number of spins aligned in a single domain. However, the effective $\langle\mu\rangle$ in our case should have been miniscule, as here the clusters have AFM order within them. This value of $\langle\mu\rangle$ can arise partly due to the presence of uncompensated (free) spins on the surface of these entities. The existence of a finite dipolar interaction between these surface spins could also explain the experimental observation of the fact that the onset of irreversibility in DCM measurements is seen much above T_G . Here it is interesting to note that in our case, the AF clusters are blocked, whereas in the cuprates the AF clusters are known to be frozen. We believe that this contrasting behavior occurs due to the rather unique phase diagram exhibited by the narrow bandwidth $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ compounds, as it is well known that a ferromagnetic (FM) state is not known to occur anywhere in the vicinity of half doping [19]. Hence, in spite of EPS causing an appreciable spatial distribution of hole concentrations, there is no FM interaction which would facilitate a cooperative freezing mechanism. However, in the cuprates the presence of a finite FM exchange coupling between the Cu spins is well known [20], which would promote magnetic frustration. This absence of a FM component is also substantiated by the fact that throughout the temperature range of our measurements, the second order susceptibility (χ_2) which arises due to the presence of a symmetry-breaking field [21] was seen to be absent.

The following two important experimental observations we believe have a significant bearing on the nature of EPS in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ in particular and manganites in general: (i) T_G as measured in $ac\chi$ and DCM does not vary, in spite of the fact that the time scales of these probes are vastly different. This would imply that the clusters are reasonably large, and our preliminary esti-

mates show that they are of the order of 500 nm [22]. (ii) Figures 3 and 4 show the large hysteretic behavior of $ac\chi$ as a function of thermal cycling. It is to be noted that the direction as well as the range of thermal cycling is different for Fig. 3 and 4. However, there is no observable change in the T_G , indicating that the cluster volume does not change. Thus the size of these clusters is concluded to be robust against EPS. Figure 4 indicates that EPS reduces the hole concentration of the bulk in the cooling run, causing a corresponding reduction in T_N , an observation that is in agreement with both the phase diagram of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, as well as our current understanding of EPS. This reduction of holes in the bulk would enhance its concentration at the domain walls without any observable change in the size of the clusters. This is evident from our observation that a T^{-1} fit to χ_1 measured above T_G in the heating and cooling cycles indicates that the factor $n\langle\mu\rangle$ is larger in the cooling run by a factor of 1.3. Moreover, the magnetic loss as measured by χ_1^I is seen to be enhanced in the cooling run, presumably arising as a consequence of larger intercluster interactions across the hole enriched *antiphase* domain wall. The thermal hysteresis in χ_1 is seen to extend to the region $T > T_{CO}$, clearly indicating the presence of superheated CO clusters right up to 300 K and above. This is in agreement with studies indicating the existence of a new scale T^* where these correlations would form (or die out) [23]. Though it is obvious that $T^* > 1.3T_{CO}$ in our case, an accurate determination of T^* is not possible considering the fact that our measurements extend only up to 300 K. Prior reports have indicated that T^* is of the order of $1.9T_{CO}$ in a CO system, whereas it is $\approx 1.8T_C$ in optimally doped

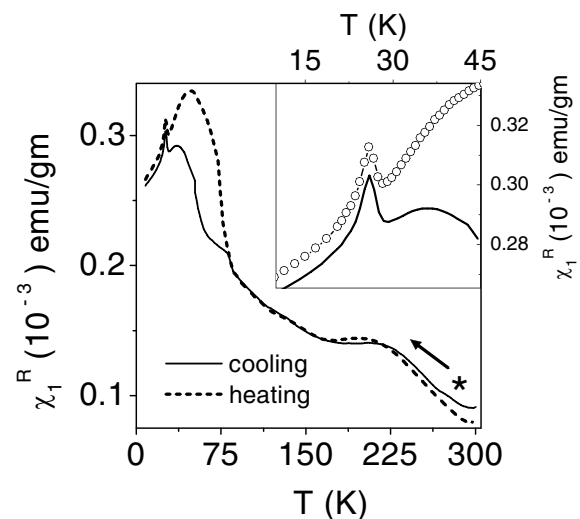


FIG. 3. The real part of χ_1 as measured in the cooling and heating runs at an exciting field and frequency of 12.5 Oe and 133 Hz, respectively, for $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$. The asterisk shows the beginning of the temperature cycle, with the arrow indicating the direction. The inset clearly shows that T_G does not vary with this thermal cycle.

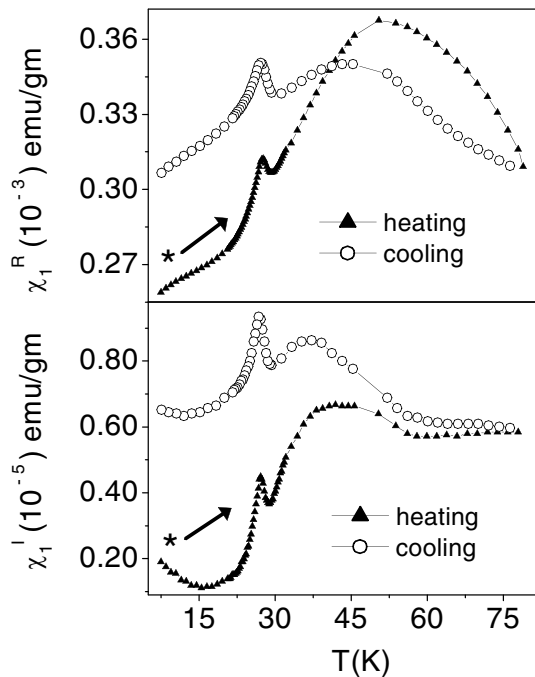


FIG. 4. The upper panel shows the real part of $ac\chi$ (χ_1^R) as measured at a field of 2.5 Oe and a frequency of 733 Hz for the sample $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$ in heating and cooling cycles. The lower panel shows the imaginary part of $ac\chi$ (χ_1^I) as measured during the same measurement run. The asterisk indicates the beginning of the thermal cycle with the arrow indicating the direction.

perovskite FM manganites and $2.5T_C$ in their layered analogs [24].

All our experimental observations can be qualitatively explained on the basis of a model incorporating the effects of clusters formed as a result of the destabilization of the pristine COO state. Al substitution in the COO $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ introduces random impurities in the Mn-O-Mn lattice and reduces the range of the CO interaction, resulting in the formation of (weakened) CO clusters. On cooling, an AFM order is stabilized *within* these clusters, and below T_G they become thermally blocked with respect to the time scales of our experimental probes. The important point to be noted in all our measurements is that though the magnitude of χ_1 changes during thermal cycling, the blocking temperature (T_G) *does not change*. This indicates that there are no appreciable changes in the size of the AFM clusters and that the change in susceptibility arises due to the change in the density of spins at the domain walls, this change being a function of the thermal/magnetic history of the system. A preliminary finite size scaling analysis substantiates this argument, indicating that the AFM correlation length (ξ) is limited to a maximum value of the order of the cluster size [25]. This spatial inhomogeneity in hole concentrations can account for the observation of CE and pseudo-CE phases as detected using neutron diffraction on a similar system [26]. A spin flip transition as a function of an applied dc

field can also explain the multiple magnetization steps seen in these systems [10], as the critical field required for triggering a metamagnetic transition would be different for the two phases.

In summary, we present a scenario of EPS in manganites where random nonmagnetic substitution in a COO matrix leads to robust mesoscopic AFM clusters, where the EPS changes only the hole concentration of the bulk of the cluster with respect to its domain walls without invoking any FM phase. This conclusion has significant impact on the EPS mechanism in transition metal oxides in the presence of disorder and calls for a proper identification of low temperature metastable features observed in these systems.

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