Effect of magnetic field and pressure on charge-orbital ordering in $\text{Pr}(\text{Sr}_{1-x}\text{Ca}_x)_2\text{Mn}_2\text{O}_7$ ($x = 0.4$ and 0.9) single crystals

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The magnetic properties of half-doped $\text{Pr}(\text{Sr}_{1-x}\text{Ca}_x)_2\text{Mn}_2\text{O}_7$ ($x = 0.4$ and 0.9) single crystals have been investigated under magnetic field (H) and hydrostatic pressure (P). Analysis of magnetization data reveals that, for $x = 0.4$ sample, only one charge-orbital ordering (CO-OO) transition occurs which decreases very slowly with P , while the antiferromagnetic ordering transition shifts towards higher temperature with the increase of P . For $x = 0.9$ sample, with the increase of P , the low-temperature CO-OO transition temperature decreases and the high-temperature CO-OO transition remains unaffected while antiferromagnetic and structural transition temperatures increase. © 2011 American Institute of Physics. [doi:10.1063/1.3657848]

I. INTRODUCTION

Layered manganites exhibit many unusual and interesting physical properties such as colossal magnetoresistance, charge-orbital ordering (CO-OO), and metal-insulator transition similar to those of three-dimensional perovskite manganites. However, the key property of the layered manganites distinct from the three-dimensional one is their high degree of anisotropy due to the presence of rock salt layer in between bilayers.¹ Recent studies on single crystals of bilayered manganites have revealed that the physical properties are anisotropic even within the MnO_2 plane.²⁻⁵ In half-doped bilayer manganites, the ferromagnetic metallic state competes with various other charge, orbital, and spin ordered phases, and CO-OO phase often results in the formation of checkerboard type alternation of $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions and staggered type alternation of e_g orbitals of Mn^{3+} ions.^{2,3} Such an ordering pattern gives rise to anisotropic physical properties with respect to the crystallographic axis.³⁻⁸

The layered $\text{Pr}(\text{Sr}_{1-x}\text{Ca}_x)_2\text{Mn}_2\text{O}_7$ crystallizes in a distorted orthorhombic structure.⁴ As the average ionic size of A-site cations of this system is relatively small, the tolerance factor is smaller than 1. The deviation of tolerance factor from unity often results in the tilt of MnO_6 octahedra, producing an orthorhombic distortion from the tetragonal structure even in the charge-orbital disordered phase. The investigation of magnetic property shows that there exists two successive long-range CO-OO transitions in $\text{Pr}(\text{Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7$ with different orbital stripe directions, one is the high-temperature charge ordering (CO1) phase with $T_{\text{CO1}} = 370$ K and the other is low-temperature charge ordering (CO2) phase with $T_{\text{CO2}} = 300$ K (315 K) in cooling (warming) cycle.²⁻⁵ In the high-temperature phase, the orbital stripe is directed along the a axis, whereas it is along the b axis in the low-temperature phase, i.e., when the system is cooled down, the CO-OO phase initially formed at T_{CO1} experiences a rotation of orbital stripe at T_{CO2} .² This

rotation of orbital stripe is associated with the structural phase transition.²

As the orbital degree of freedom couples strongly with the lattice, any change in structural parameter is expected to modify the orbital state of $\text{Pr}(\text{Sr}_{1-x}\text{Ca}_x)_2\text{Mn}_2\text{O}_7$.³⁻⁵ Indeed, it has been shown that the direction of the orbital stripe can be changed with the application of uniaxial pressure.³ Apart from the CO-OO ordering, as the system is highly anisotropic due to its layered-like stacking, a significant change in electronic and magnetic properties with the application of hydrostatic pressure may take place. So far there is no report on physical properties of this system under hydrostatic pressure. For this reason, we have investigated the effect of hydrostatic pressure on CO-OO ordering, antiferromagnetic ordering, and structural transition from magnetic measurements on $\text{Pr}(\text{Sr}_{1-x}\text{Ca}_x)_2\text{Mn}_2\text{O}_7$ for $x = 0.4$ and 0.9 compositions. We have chosen these two compositions because of their unique position in the phase diagram.⁴ At $x = 0.4$, the magnetic and electronic phase diagram splits into two different regions. For $x < 0.4$, no CO-OO occurs and a pseudometallic A-type magnetic ordering emerges at low temperature. Also, the difference between two CO-OO transition temperatures is quite small for x close to 0.4. Above $x = 0.4$, two consecutive CO-OO transitions occur and the nature of magnetic ordering changes from A- to CE-type. As the effect of uniaxial pressure on two CO-OO transitions has already been studied for $x = 0.9$ sample, we can compare and contrast the present hydrostatic results with the reported uniaxial one.³

II. SAMPLE PREPARATION, CHARACTERIZATION, AND EXPERIMENTAL TECHNIQUE

The single crystals of $\text{Pr}(\text{Sr}_{0.6}\text{Ca}_{0.4})_2\text{Mn}_2\text{O}_7$ (PSCMO4) and $\text{Pr}(\text{Sr}_{0.1}\text{Ca}_{0.9})_2\text{Mn}_2\text{O}_7$ (PSCMO9) were grown by traveling solvent floating zone technique. We prepare polycrystalline powder sample by standard solid-state reaction method using high purity oxides and carbonates. The powder was then pressed into feed and seed rods. The apparatus used for

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crystal growth was an image furnace equipped with four 1000 W halogen incandescent lamps and focusing mirrors. The molten zone of the feed rod was vertically scanned at a rate of 4 mm/h. The crystal with $x=0.4$ was grown under a 5 bar 90% Ar+ 10% O₂ gas flow, while the other sample was grown under a 10 bar pure oxygen atmosphere. The magnetization measurements at ambient and hydrostatic pressures were performed by using the vibrating sample magnetometer module of a physical properties measurement system (Quantum Design) in fields up to 9 T. A clamp type miniature hydrostatic pressure cell (M Cell of Easylab, UK) made of nonmagnetic Cu-Be alloy was used for the high-pressure magnetization measurements. The mixture of flourinert 70 and flourinert 77 was used as a pressure transmitting medium. The value of hydrostatic pressure was estimated from the shift of the superconducting critical temperature of pure Sn with applied pressure.⁹ The quality of the crystals was carefully checked by various techniques such as energy dispersive x-ray analysis, x-ray powder diffraction, and the Laue diffraction. We have determined T_{CO1} and T_{CO2} from the peak position of the anomaly in $M(T)$ curve. As the anomaly is very weak at T_{CO} and T_N , we have used $dM(T)/dT$ vs T plot for their determination.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the temperature dependence of magnetization (both the cooling and heating cycles) in an applied field of 0.5 T along the three crystallographic axes a , b , and c for PSCMO4 and PSCMO9 single crystals. The magnetization for PSCMO4 shows complicated but qualitatively similar temperature dependence along the three axes. It gradually increases on cooling in the high-temperature range from 300 to 195 K, and then decreases rapidly as temperature decreases from 195 to 100 K, and finally shows an increase below 100 K. These three main temperature ranges roughly correspond to the three magnetic or CO-OO states, i.e., non-CO-OO paramagnetic state, CO-OO paramagnetic state, and antiferromagnetic ordered state from high to low temperature. Below T_N , A- and CE-type antiferromagnetic ordering coexists.⁴ The decrease of magnetization in the intermediate temperature range may be attributed to the occurrence of CO-OO phenomenon around $T_{CO} = 196$ K. Similar kind of decrease in magnetization in the vicinity of CO-OO has also been reported for other manganites.^{10–12} In all the

three axes, the CO-OO transition is accompanied by a thermal hysteresis, indicating the first order nature of the transition.

The temperature dependence of magnetization curves along the three axes for PSCMO9 shows qualitatively similar behavior as that observed in PSCMO4 with quite distinct features in the high temperature region [Fig. 1(b)]. For PSCMO9, the CO transition splits into two: $T_{CO1} = 370$ K and $T_{CO2} = 295$ K (310 K) in cooling (warming) cycle. The qualitative behavior of temperature dependence of magnetization for this sample is similar to that reported earlier.² As the temperature is decreased, CO-OO initially formed along the a axis at T_{CO1} tends to rotate the orbital stripe direction along the b axis when the temperature approaches T_{CO2} .^{2,3} The CO-OO transition at T_{CO2} shows a strong thermal hysteresis, whereas no thermal hysteresis has been observed for the CO-OO transition at T_{CO1} [inset of Fig. 1(b)]. We would like to mention that the temperature dependence of resistivity for this sample also shows a strong hysteresis at T_{CO2} but not at T_{CO1} (not shown). No other peaks or anomalies are observed in the orthorhombically distorted structure between T_{CO1} and T_{CO2} . The system undergoes a CE-type antiferromagnetic ordering below $T_N \sim 155$ K. On further cooling below T_N , another anomaly is observed around $T_S = 100$ K with a thermal hysteresis in magnetization along the a axis only [Fig. 1(b)]. This anomaly is due to the structural phase transition from orthorhombic to lower symmetry monoclinic accompanying the rotation of the MnO₆ octahedron. The presence of thermal hysteresis at T_S suggests that this structural transition is first order in nature. The experimental data in Figs. 1(a) and 1(b) show that both the samples are magnetically anisotropic. We believe that this magnetic anisotropy stems from the structural distortion.

The magnetic coupling between bilayers in $\text{Pr}(\text{Sr}_{1-x}\text{Ca}_x)_2\text{Mn}_2\text{O}_7$ may enhance and lead to the realization of isotropic three-dimensional spin ordered state with the increase of magnetic field strength.¹³ Figure 2 shows the temperature dependence of magnetization for different magnetic fields up to 9 T. At low fields, the anisotropy was observed between in-plane and out-of-plane magnetization for both the samples (Fig. 1). This is quite usual in bilayer systems because of the large difference in lattice parameters. For PSCMO4 sample, the magnetization with field along the three crystallographic axes are almost same above T_{CO} , but the in-plane magnetization is significantly smaller than the out-of-plane magnetization for

FIG. 1. (Color online) Temperature dependence of magnetization with an applied field of 0.5 T along all the three axes for PSCMO4 (a) and PSCMO9 (b) samples. The solid lines correspond to cooling cycle data, while the dotted lines correspond to heating cycle data of magnetization. Inset shows the positions of CO-OO ordering, magnetic ordering, and structural transitions for PSCMO9 sample.

$T < T_N$ and the magnetization along all the three axes increases below T_N . One can see that the anisotropy between in-plane and out-of-plane magnetization decreases systematically with increasing field strength [Figs. 2(a)–2(d)]. The ratio of out-of-plane and in-plane magnetization decreases from 2 to 1.2 as the field increases from 0.5 to 9 T. Unlike cubic perovskite manganites, the dependence of T_{CO} on H is very weak. T_{CO} decreases at the rate of ~ 0.4 K/T.

In the case of PSCMO9 sample, there is a significant anisotropy in magnetization even within the ab plane, i.e., between M_a and M_b . On the other hand, the anisotropy between in-plane and out-of-plane magnetization is smaller in PSCMO9 as compared to PSCMO4. This could be due to the difference in their structural parameters. In the CO1 phase, the lattice parameter b becomes double, whereas in the CO2 phase the lattice parameter a becomes double; c parameter increases slowly with the decrease of temperature. For both PSCMO4 and PSCMO9, at low temperatures below T_N , M_c increases at a much faster rate than M_a and M_b . It is clear from Fig. 2 that though magnetization increases rapidly with applied field for both the samples, the decrease of magnetic anisotropy (M_c/M_a) is faster in the case of PSCMO9. Due to the rapid decrease of anisotropy, the system becomes almost isotropic at 9 T, i.e., $M_a \approx M_b \approx M_c$ [Figs. 2(e)–2(h)]. It may be mentioned that the disappearance of anisotropy between in-plane and out-of-plane magnetization in $\text{La}_{2-2x}\text{Sr}_{1-2x}\text{Mn}_2\text{O}_7$ at high magnetic field has been attributed to the metamagnetic transition.¹⁴ For PSCMO9 sample, we observe that T_{CO2} decreases very slowly with the increase of H , while T_{CO1} is insensitive to H .

During the magnetic measurements on PSCMO9, a strong thermal hysteresis has been observed in the b -axis magnetization (M_b) in the vicinity of structural transition for applied field of ~ 7 T. This observation forced us to concentrate for further measurements with fields close to 7 T. So, we have carried out magnetic measurements for some additional fields both below and above 7 T with a field interval of 0.5 T. These measurements reveal some interesting results which are shown in Figure 3. A small hysteresis opens up

between cooling and warming cycles around T_S above 5.0 T. This hysteresis becomes more and more pronounced with the increase of field up to 7 T and then reduces with further increase of H . The nature of anomaly at T_S also changes significantly with the increase of field strength. Below 6.0 T, M_b shows a profound minimum at T_S . At 6 T, a shoulder-like feature appears slightly above T_S which transforms into a sharp peak, shifts towards lower temperature, and pins at T_S with increasing H in the range $6 \text{ T} < H \leq 7.5 \text{ T}$. Though the size of this anomaly decreases rapidly above a critical field and disappears for $H > 7.5 \text{ T}$, T_S is almost field-independent (Fig. 3).

The temperature dependence of magnetization under hydrostatic pressure has been measured for both the compositions. The data have been collected only during the heating cycle. Figures 4(a) and 4(b) show the temperature dependence of magnetization at some selected hydrostatic pressures for PSCMO4 and PSCMO9, respectively. The sample orientation with respect to applied magnetic field cannot be determined precisely because the pressure-applying procedure can change the initial sample orientation. Comparing the magnetization results at ambient pressure and its evolution with pressure, we find that the direction of magnetic field is almost parallel to c axis for PSCMO4 and parallel to ab plane for PSCMO9 samples. For PSCMO4, the magnetization-temperature curves show that magnetization increases and T_N shifts towards higher temperature upon increasing hydrostatic pressure [Fig. 4(a)]. T_N increases from 98 K at ambient pressure to 107 K at 0.56 GPa. Such a substantial change in antiferromagnetic ordering temperature may be due to the increase of the magnetic coupling between the neighboring Mn ions as a result of the shrinkage of the inter-ionic distance. On the other hand, the CO temperature decreases with the increase of hydrostatic pressure at the rate 8 K/GPa.

For PSCMO9, we observe that both T_N and T_S increase very slowly [Inset Fig. 4(b)] with the increase of pressure. The anomaly at T_N decreases with the increase of pressure and is not clearly visible at high pressure. Similarly, the CO-OO transition at T_{CO2} becomes sluggish at high pressure,

FIG. 2. (Color online) Temperature dependence of magnetization with fields 2, 5, 7, and 9 T for PSCMO4 (a)–(d) and PSCMO9 (e)–(h). Inset: Thermal hysteresis between heating cycle (dotted line) and cooling cycle (solid line) data in the vicinity of structural phase transition of PSCMO9 at $H = 7$ T.

FIG. 3. (Color online) Temperature dependence of b -axis magnetization (M_b) for PSCMO9 at (a) 5.0 T, (b) 5.5 T, (c) 6.0 T, (d) 6.5 T, (e) 7.0 T, and (f) 7.5 T. The evolution of anomaly at T_S is clearly reflected with the increase of field but no appreciable change in T_S is observed.

as a result, it is difficult to determine the dependence of T_{CO2} on pressure above 0.54 GPa. On the other hand, the anomaly at structural transition is quite sharp and the sharpness does not change with the increase of pressure [Fig. 4(b)]. Unlike T_{CO2} , we observe that the dependence of T_{CO1} on P is very weak. T_{CO2} and T_{CO1} decrease at the rate of 49.82 and 1.89 K/GPa, respectively. (All the transition temperatures are determined from the weak anomaly either in the $M(T)$ curve or in the dM/dT curve.) The present results on hydrostatic pressure for PSCMO9 sample may also be compared and contrasted with the uniaxial pressure effect reported by Tokunaga *et al.*⁵ As in the present case, T_{CO1} and T_N do not change significantly with uniaxial pressure. However, T_{CO2} shows a nonmonotonic dependence on uniaxial pressure. Initially T_{CO2} decreases with uniaxial pressure, then increases and saturates above 0.1 GPa. This is due to the rotation of CO-OO stripe with applied pressure.²⁻⁵ The CO-OO stripe in CO1 phase which was directed along the a axis at ambient pressure rotates along the b axis above a critical value of pressure due to the stress-induced interchange between a and

b axes. Such a change in the direction of CO-OO stripe is unlikely to occur for hydrostatic pressure. Normally, all the lattice parameters a , b , and c shrink continuously with hydrostatic pressure and hence a monotonous change in characteristic temperatures with P .

The above results show that the effects of hydrostatic pressure on electronic, magnetic, and structural phase transitions are not same for two samples. In particular, the pressure dependence of T_N is quite different. T_N increases rapidly with P in PSCMO4, while there is almost no change in T_N with P for PSCMO9. Such a difference in magnetic property in response to external perturbation can be explained considering the $(x - T)$ phase diagram of $\text{Pr}(\text{Sr}_{1-x}\text{Ca}_x)_2\text{Mn}_2\text{O}_7$.⁴ It has been shown that CO-OO disappears and a pseudometallic state emerges below T_N for samples with $x < 0.4$. The emergence of such a weak metallic state suggests that the magnetic ground of the system is canted antiferromagnetic. The sharp increase of magnetization below $x = 0.4$ also supports the slight canting of magnetic moments of Mn ions. This is expected because the substitution of larger size Sr ion

FIG. 4. (Color online) Temperature dependence of magnetization ($H = 0.5$ T) for PSCMO4 (a) and PSCMO9 (b) at some selected pressures. Insets show the pressure dependence of several transition temperatures for both the samples.

for Ca enhances ferromagnetic double-exchange interaction due to the increase of Mn-O bond angle and decrease of Mn-O bond length. As PSCMO4 sample is close to metal-insulator phase boundary, the effect of hydrostatic pressure on magnetic transition can be significant as in the case of other perovskite manganites with ferromagnetic ground state.^{15–24}

In conclusion, we have investigated the effect of hydrostatic pressure and magnetic field on magnetic, CO-OO, and structural transitions for $\text{Pr}(\text{Sr}_{1-x}\text{Ca}_x)_2\text{Mn}_2\text{O}_7$ ($x=0.4$ and 0.9). At low field, both the systems are magnetically highly anisotropic but the anisotropy decreases systematically with the increase of H . For $x=0.4$ sample, CO-OO transition is insensitive to both H and P , while the antiferromagnetic transition shifts towards higher temperature with the increase of P . For $x=0.9$ sample, with the increase of P , though the high-temperature CO-OO transition does not get affected significantly, the low-temperature CO-OO transition decreases rapidly. Both antiferromagnetic and structural transition temperatures increase very slowly with P .

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- ¹Y. Moritomo, A. Asamitsu, H. Kuwahara, and Y. Tokura, *Nature (London)* **380**, 141 (1996).
- ²Y. Tokunaga, T. Lottermoser, Y. Lee, R. Kumai, M. Uchida, T. Arima, and Y. Tokura, *Nature Mater.* **5**, 937 (2006).
- ³Y. S. Lee, Y. Tokunaga, T. Arima, and Y. Tokura, *Phys. Rev. B* **75**, 174406 (2007).
- ⁴Y. Tokunaga, T. J. Sato, M. Uchida, R. Kumai, Y. Matsui, T. Arima, and Y. Tokura, *Phys. Rev. B* **77**, 064428 (2008).
- ⁵Y. Tokunaga, R. Kumai, N. Takeshita, Y. Kaneko, J. P. He, T. Arima, and Y. Tokura, *Phys. Rev. B* **78**, 155105 (2008).

- ⁶Y. Moritomo, Y. Maruyama, T. Akimoto, and A. Nakamura, *Phys. Rev. B* **56**, R7057 (1997).
- ⁷F. Wang, A. Gukasov, F. Moussa, M. Hennion, M. Apostu, R. Suryanarayanan, and A. Revcolevschi, *Phys. Rev. Lett.* **91**, 047204 (2003).
- ⁸S. Arumugam, K. Mydeen, N. Manivannan, M. K. Vanji, D. Prabhakaran, A. T. Boothroyd, R. K. Sharma, and P. Mandal, *Phys. Rev. B* **73**, 212412 (2006).
- ⁹Y. Uwatoko, M. Kosaka, K. Umeo, T. Takabatake, G. Oomi, and N. Mori, *Rev. High Pressure Sci. Technol.* **2**, 1113 (2000).
- ¹⁰Y. Moritomo, Y. Tomioka, A. Asamitsu, and Y. Tokura, *Phys. Rev. B* **51**, 3297 (1995).
- ¹¹C. Martin, A. Maignan, M. Hervieu, and B. Raveau, *Phys. Rev. B* **60**, 12191 (1999).
- ¹²P. Mandal, A. Hassen, and A. Loidl, *Phys. Rev. B* **69**, 224418 (2004).
- ¹³S. Arumugam, K. Mydeen, M. Fontes, N. Manivannan, M. K. Vanji, K. U. R. Tulasi, S. M. Ramos, E. B. Saitovitch, D. Prabhakaran, and A. T. Boothroyd, *Solid State Commun.* **136**, 292 (2005).
- ¹⁴T. Kimura, A. Asamitsu, Y. Tomioka, and Y. Tokura, *Phys. Rev. Lett.* **79**, 3720 (1997).
- ¹⁵J.-S. Zhou, J. B. Goodenough, and J. F. Mitchell, *Phys. Rev. B* **58**, R579 (1998).
- ¹⁶J.-S. Zhou, J. B. Goodenough, and J. F. Mitchell, *Phys. Rev. B* **61**, R9217 (2000).
- ¹⁷D. N. Argyriou, J. F. Mitchell, J. B. Goodenough, O. Chmaissem, S. Short, and J. D. Jorgensen, *Phys. Rev. Lett.* **78**, 1568 (1997).
- ¹⁸K. Mydeen, S. Arumugam, P. Mandal, A. Murugeswari, C. Sekar, G. Krabbes, and C. Q. Jin, *J. Appl. Phys.* **106**, 103908 (2009).
- ¹⁹H. Y. Hwang, T. T. M. Palstra, S. W. Cheong, and B. Batlogg, *Phys. Rev. B* **52**, 15046 (1995).
- ²⁰Y. Tokura, H. Kuwahara, Y. Moritomo, Y. Tomioka, and A. Asamitsu, *Phys. Rev. Lett.* **76**, 3184 (1996).
- ²¹I. V. Medvedeva, Yu. S. Bersenev, K. Brner, L. Haupt, P. Mandal, and A. Poddar, *Physica B* **229**, 194 (1997).
- ²²P. Postorino, A. Congeduti, P. Dore, A. Sacchetti, F. Gorelli, L. Ulivi, A. Kumar, and D. D. Sarma, *Phys. Rev. Lett.* **91**, 175501 (2003).
- ²³K. Mydeen, P. Sarkar, P. Mandal, A. Murugeswari, C. Q. Jin, and S. Arumugam, *Appl. Phys. Lett.* **92**, 182510 (2008).
- ²⁴P. Sarkar, S. Arumugam, P. Mandal, A. Murugeswari, R. Thiagarajan, S. E. Muthu, D. M. Radheep, C. Ganguli, K. Matsubayashi, and Y. Uwatoko, *Phys. Rev. Lett.* **103**, 057205 (2009); P. Sarkar, P. Mandal, K. Mydeen, A. K. Bera, S. M. Yusuf, S. Arumugam, C. Q. Jin, T. Ishida, and S. Noguchi, *Phys. Rev. B* **79**, 144431 (2009); S. Dash, K. Kumar, A. Banerjee, and P. Chaddah, *ibid.* **82**, 172412 (2010).