

# Anomalous Thermal Expansion in $(\text{Pr}, \text{Ca})\text{MnO}_3$ due to Orbital Ordering

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## Abstract

The monoclinic lattice parameters of the perovskite manganites  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  were systematically measured by XRD at the Ca doping levels  $x = 0.4, 0.5$  and  $0.1$  at temperatures from  $83\text{ K}$  to  $403\text{ K}$ . The orbital ordering transition observed around  $250\text{ K}$  at  $x = 0.4$  and  $x = 0.5$ , located by SQUID magnetometry, was associated with a transient cell volume expansion of order  $0.1\%$ , during which the CO-related monoclinic distortion set in. The anomalous cell expansion, arguably driven by electrostructural disorder, was of sufficient magnitude to locally dominate the thermal expansion.

*Keywords:* manganite orbital charge ordering thermal expansion

## 1 Introduction

The perovskite manganite family  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  (PCMO) can be seen as the set of arbitrary solid solutions between  $\text{PrMnO}_3$  and  $\text{CaMnO}_3$ . It contains ceramics with a variety of functional properties, such as colossal magnetoresistance (CMR) [1, 2], colossal electroresistance (CER) [3], photosensitive magnetization [4, 5, 6] and even a strong low temperature magnetocaloric effect (MCE) [7, 8]. The majority of these properties are most prominent at the Ca concentrations in the "optimal doping region", roughly  $0.3 \leq x \leq 0.5$ , where PCMO can exhibit a dynamic mixture of an orbital ordered (OO), charge ordered (CO), insulating antiferromagnetic (AFM) phase and an electronically disordered, metallic ferromagnetic (FM) phase [1, 6, 9, 10, 11].

Despite the importance of lattice strain effects in manganite thin films [12, 13, 14] and reports of significant magnetostructural anomalies associated with the CO-OO transitions [9, 10, 11, 15, 16, 17], including the dynamic electromagnetic phase separation [1], very few systematic studies have been conducted regarding the temperature dependence of the basic crystallographic lattice parameters of PCMO below room temperature where the said anomalies occur [18].

In this work, we have used X-ray diffraction to systematically measure the temperature dependence of the lattice constants of polycrystalline bulk PCMO at the Ca concentrations

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$x = 0.4$  and  $0.5$ , where CO and OO are known to be present [1, 9, 10, 11, 17], and uncovered a transient anomalous expansion of the unit cell volume coincident with the OO-CO transition observed at  $T \approx 250$  K in each material. To give a more realistic and coherent picture of the average unit cell geometries than previous literature can present, and to take into account the presence of intrinsic phases which break the commonly assumed orthorhombic  $Pnma$  symmetry, we have performed the entire analysis in the more general monoclinic space group  $P2_1/m$ .

## 2 Materials and Methods

Polycrystalline bulk samples of  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  were synthesized by the ceramic method at the Ca doping levels  $x = 0.1$  (control sample),  $x = 0.4$  and  $x = 0.5$ . The process has been described elsewhere in more detail [19]. The sintered samples were powderized for characterization using non-ambient XRD (Philips *X'Pert Pro* diffractometer and Anton Paar *TTK 450* sample chamber with LN<sub>2</sub> cooling) and SQUID magnetometry (Quantum Design *MPMS XL* magnetometer).

Diffractograms were recorded in the temperature range from 83 K to 403 K at intervals of 40 K, in a technical vacuum ( $< 1$  mbar), using Cu K $_{\alpha}$  radiation, at diffraction angles  $20^\circ \leq 2\theta \leq 110^\circ$ . The angular spacing of data points was set to  $\Delta(2\theta) = 0.013^\circ$ . The counting times were such that the peak group (121)(200)(002) (per space groups  $Pnma$  and  $P2_1/m$ ) always reached ca. 4000 counts. The temperature dependence of magnetization,  $M(T)$ , was measured at intervals of  $\Delta T = 1.0$  K in field-cooled cooling mode over the same temperature range as the diffractograms, using an external magnetic field  $\mu_0 H_{\text{ext}} = 10$  mT.

After an initial phase confirmation using Rietveld refinement, crystallographic unit cell parameters were conveniently extracted from the diffractograms by Le Bail analysis in the monoclinic space group  $P2_1/m$  using the FullProf program package [20]. The magnetization data were not refined further for the purposes of this work.

## 3 Results

Figure 1 shows the raw non-ambient X-ray diffractograms of the sample with the Ca concentration  $x = 0.5$ . The variation of the diffraction pattern as a function of temperature is very subtle, but an indication of the low-temperature monoclinic distortion can be seen in the splitting of the (161)(323) peak group. As verified by initial Rietveld refinement of the  $T = 283$  K dataset, no impurity peaks are present, except for a multiplet from the sample holder at  $2\theta \approx 42^\circ$ . The situation was the same at the other Ca concentrations,  $x = 0.1$  and  $x = 0.4$  (diffractograms not shown).

The Le Bail fits in the monoclinic space group  $P2_1/m$  systematically converged to give a good match between the observed and calculated diffraction intensities. The  $\chi^2$  goodness-of-fit figures fell within the range from 1.1 to 1.5, indicating that the data were well explained by the fit in all cases. A selection of obtained  $P2_1/m$  cell parameters are stated for reference in the table 1 at different temperatures, and the complete datasets are shown graphically in figure 2. Transient anisotropic thermal expansion is observed in the samples at  $x = 0.4$  and  $x = 0.5$  below room temperature, giving a motivation to our present work.

It should be noted that, as usual in Le Bail and Rietveld fits of this complexity, the initial value sensitivities of the parameters were of the same order of magnitude as the calculated standard deviations. The 283 K values are within ca. 1% of previously published room-temperature parameters obtained in the corresponding orthorhombic space group  $Pbnm$  [19,

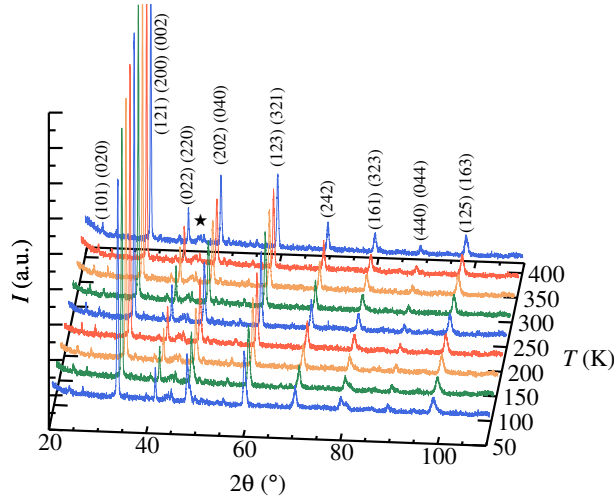


Figure 1: The raw x-ray diffractograms at Ca doping  $x = 0.5$ . The most prominent reflections have been indexed in accordance with the monoclinic space group  $P2_1/m$ . The star marks a multiplet originating from the sample holder, all other peaks are associated with PCMO. The projection is isometric to allow a visual comparison of the peak intensities and positions at different temperatures.

Table 1: The experimental  $P2_1/m$  cell parameters of the PCMO samples at the extremal accessed temperatures,  $T = 403$  K and  $83$  K, and near room temperature, at  $T = 283$  K. The numbers in the brackets correspond to the standard deviations of the least significant digits of the parameter values as calculated by FullProf [20].

		$x = 0.1$	$x = 0.4$	$x = 0.5$
$T = 403$ K	$a$ (Å)	5.5604(2)	5.4335(2)	5.4066(3)
	$b$ (Å)	7.6651(3)	7.6739(2)	7.6449(3)
	$c$ (Å)	5.4528(2)	5.4202(2)	5.3985(3)
	$\beta$ (°)	90.148(4)	90.352(5)	90.259(5)
$T = 283$ K	$a$ (Å)	5.5774(2)	5.4290(3)	5.4031(2)
	$b$ (Å)	7.6570(2)	7.6743(2)	7.6540(2)
	$c$ (Å)	5.4531(2)	5.4203(2)	5.3960(2)
	$\beta$ (°)	90.103(6)	90.353(4)	90.253(4)
$T = 83$ K	$a$ (Å)	5.5826(2)	5.4241(3)	5.4033(3)
	$b$ (Å)	7.6464(3)	7.6728(3)	7.6539(2)
	$c$ (Å)	5.4524(2)	5.4178(2)	5.3945(2)
	$\beta$ (°)	90.122(6)	90.514(4)	90.692(4)

21] from which  $P2_1/m$  is a direct generalization after a permutation of the labels  $a, b$  and  $c$ . Most of the discrepancy can be attributed to differences in synthesis history and measurement temperatures, leaving the difference in symmetries as a tertiary factor.

Figure 3 shows the  $P2_1/m$  unit cell volume,  $V_{\text{cell}} = abc \sin \beta$ , the monoclinic angle,  $\beta$ , and a normalized magnetization curve as functions of temperature,  $T$ , for our control sample,  $x = 0.1$ . The cell volume decreases sharply above  $T \approx 300$  K, consistently with earlier reports of

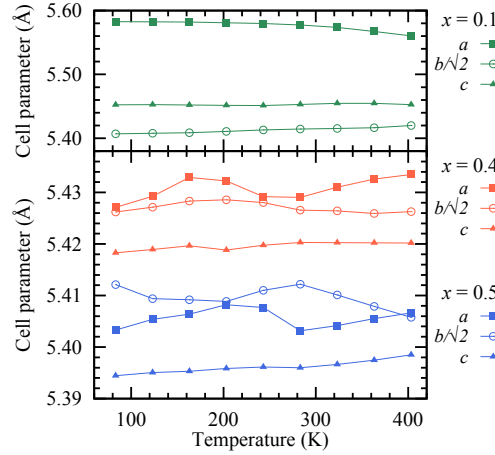


Figure 2: The experimental  $P2_1/m$  cell parameters  $a$ ,  $b/\sqrt{2}$  and  $c$  of the PCMO samples as functions of temperature. The standard deviations of the parameters, as calculated by FullProf [20], were smaller than the plot symbols.

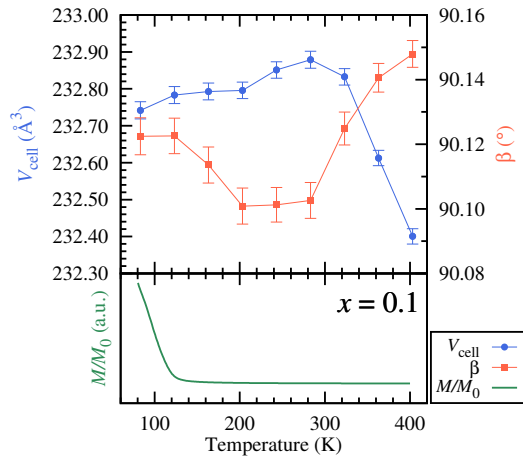


Figure 3: The unit cell volume,  $V_{\text{cell}}$ , monoclinic cell angle,  $\beta$ , and normalized magnetization,  $M/M_0$ , as functions of temperature at the Ca doping level  $x = 0.1$ . The error bars are based on standard deviations calculated by FullProf [20], composed by the total differential approximation for  $V_{\text{cell}}$ . The line width exceeds the error in  $M/M_0$ .

an orthorhombic-to-pseudocubic transition caused by the relaxation of cooperative Jahn-Teller distortion [21, 22]. Otherwise, however, the thermal expansion is regular and the monoclinic distortion (the deviation of  $\beta$  from  $90^\circ$ ) small, less than  $0.2^\circ$ . The magnetic Curie transition and a very slight associated increase in  $\beta$  can be identified around 100 K [21].

The samples at the Ca concentrations  $x = 0.4$  and  $x = 0.5$  (figure 4) differ dramatically from the control in that they exhibit a distinct magnetic anomaly at  $T \approx 250$  K, caused by the condensation of Mn spins into FM-coupled chains due to the onset of OO and CO [11, 17]. Our experiments reveal that this magnetic transition is accompanied by a transient increase in

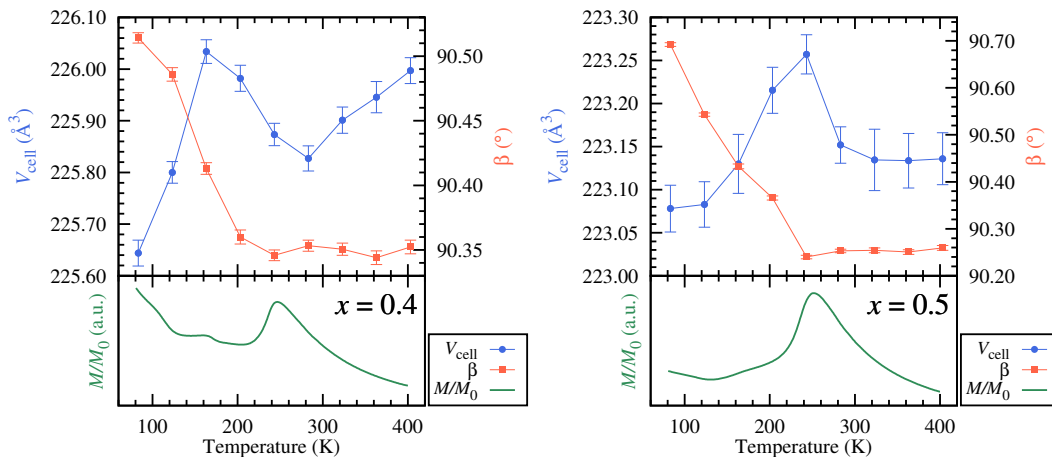


Figure 4: The unit cell volumes,  $V_{\text{cell}}$ , monoclinic cell angles,  $\beta$ , and normalized magnetizations,  $M/M_0$ , as functions of temperature at the Ca doping levels  $x = 0.4$  and  $x = 0.5$ . The error bars are based on standard deviations calculated by FullProf [20], composed by the total differential approximation for  $V_{\text{cell}}$ . The line width exceeds the error in  $M/M_0$ .

$V_{\text{cell}}$  (0.13% at  $x = 0.4$ , 0.07% at  $x = 0.5$ ) which locally dominates the thermal expansion, but gradually dies out as long-range CO sets in below the Néel transition around  $T_N = 170$  K [6, 21]. The low- $T$  CE-AFM CO phase, which can coexist with FM clusters [1, 17, 6], is associated with a monoclinic distortion of the approximately  $Pnma$ -orthorhombic cell [4, 6]. This distortion is reflected by the observed increase in  $\beta$  towards lower temperatures.

## 4 Discussion

The main result of our present study was to show that the OO of PCMO at the Ca concentrations  $x = 0.4$  and  $x = 0.5$  below  $T = 250$  K is accompanied by a 0.1% transient increase in  $V_{\text{cell}}$ , during which the monoclinic distortion, reflected by  $\beta$ , begins to increase linearly vs. temperature to accommodate a long range CO [4, 6]. No such effects are present in our  $x = 0.1$  control sample, in the absence of OO and CO. It is worth noting about  $x = 0.4$  and  $x = 0.5$  in figure 2 that whereas the cell parameters  $a$  and  $b$  oscillate anomalously around  $T = 250$  K, the temperature evolution of  $c$  remains practically linear throughout the anomaly. Such a decorrelation between the basal parameters  $a$  and  $c$  is compatible with CE-type OO [17], although a change in  $b$  is a stronger signature of this type of order [23].

It is quite apparent from the literature that the anomalous thermal expansion, whose magnitude is similar to the magnetostriction observed during the high-field breakdown of the CO-OO state in PCMO [15], is driven, like the particular magnetostriction effect, by the electrostructural competition between ordered CE-AFM and disordered FM clusters [1, 6, 17]. The transient increase in  $V_{\text{cell}}$  is proportionally much larger at  $x = 0.4$  than at  $x = 0.5$ , whereas the observed monoclinic distortion is stronger at  $x = 0.5$  at low temperatures. This is in line with the view that the most stable and symmetric checkerboard CO state can only be realized in the half doped species, i.e.  $x = 0.5$ , and any deviation from this ideal stoichiometry will make the development of a more disordered, and therefore less dense, electronic structure energetically favourable [1, 6, 9, 10]. A charge disproportionation scenario, such as what has been reported

at  $x = 0.4$  [17], is then likely for PCMO instead of the checkerboard CO.

Earlier neutron diffraction studies show very few if any signs of a transient cell volume anomaly near  $T = 200$  K in the  $x = 0.5$  material [18], a matter which could be explained by a minute stoichiometric fault in our sample. The variation in  $x$  that might have resulted from our synthesis conditions has been estimated at  $\Delta x = 0.02$ , and a similar standard deviation was obtained by Rietveld refinement of  $x$ .

Our Le Bail fits in the rather general space group  $P2_1/m$  confirmed that a slight monoclinic distortion of the PCMO unit cell is already present at room temperature, although  $Pnma$  and  $Pbnm$  (where effectively  $\beta = 90^\circ$ ) remain very good practical approximations. A single  $P2_1/m$  structural phase was technically sufficient for indexing and explaining all observed XRD reflections to a good  $\chi^2$ , even in the ordered states of the samples  $x = 0.4$  and  $x = 0.5$  despite the probable presence of electromagnetic phase separation [1, 6, 17]. Realistic averages of the cell parameters were therefore arguably obtained.

## 5 Conclusions

Non-ambient XRD and SQUID magnetometry of PCMO at the Ca doping levels  $x = 0.4$  and  $x = 0.5$  revealed an anomalous transient expansion of the unit cell volume (0.13% at  $x = 0.4$  and 0.07% at  $x = 0.5$ ) as a function of temperature in coincidence with the magnetic OO-transition around  $T \approx 250$  K. The magnitude of this effect, arguably driven by electrostructural disorder, was similar to that of the magnetostriction reportedly observed during the high-field breakdown of the CO-AFM state, and sufficient to locally dominate the thermal expansion.

Le Bail fits in the space group  $P2_1/m$  confirmed a slight monoclinic distortion of the PCMO unit cell already at room temperature. A single  $P2_1/m$  phase was technically sufficient for indexing and explaining all observed XRD reflections to a good  $\chi^2$ , even in the electromagnetically ordered states of the samples  $x = 0.4$  and  $x = 0.5$ .

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## References

- [1] E. Dagotto, T. Hotta, and A. Moreo. *Phys. Rep.*, 344:1–153, 2001.
- [2] H. Yoshizawa, H. Kawano, Y. Tomioka, and Y. Tokura. *Phys. Rev. B*, 52:R13145–R13148, Nov 1995.
- [3] A. Asamitsu, Y. Tomioka, H. Kuwahara, and Y. Tokura. *Nature*, 388:50–2, 1997.
- [4] P. Beaud, A. Caviezel, S. O. Mariager, L. Rettig, G. Ingold, C. Dornes, S-W. Huang, J. A. Johnson, M. Radovic, T. Huber, T. Kubacka, A. Ferrer, H. T. Lemke, M. Chollet, D. Zhu, J. M. Glownia, M. Sikorski, A. Robert, H. Wadati, M. Nakamura, M. Kawasaki, Y. Tokura, S. L. Johnson, and U. Staub. *Nat. Mater.*, 13:923–927, 2014.
- [5] S. Majumdar, T. Elovaara, H. Huhtinen, S. Granroth, and P. Paturi. *J. Appl. Phys.*, 113:063906, 2013.
- [6] D. E. Cox, P. G. Radaelli, M. Marezio, and S-W. Cheong. *Phys. Rev. B*, 57:3305–3314, Feb 1998.
- [7] M. S. Reis, V. S. Amaral, J. P. Araújo, P. B. Tavares, A. M. Gomes, and I. S. Oliveira. *Phys. Rev. B*, 71:144413, 2005.

- [8] J. Tikkanen, H. Huhtinen, and P. Paturi. *IEEE Trans. Magn.*, 50(11):1–4, Nov 2014.
- [9] C. Frontera, J. L. García-Muñoz, A. Llobet, M. Respaud, J. M. Broto, J. S. Lord, and A. Planes. *Phys. Rev. B*, 62:3381–3388, Aug 2000.
- [10] J. P. Hill et al. *Appl. Phys. A*, 73:723–30, 2001.
- [11] Masatoshi Imada, Atsushi Fujimori, and Yoshinori Tokura. *Rev. Mod. Phys.*, 70:1039–1263, Oct 1998.
- [12] Dipak Kumar Baisnab, T. Geetha Kumary, A.T. Satya, Awadhesh Mani, J. Janaki, R. Nithya, L.S. Vaidhyanathan, M.P. Janawadkar, and A. Bharathi. *J. Magn. Magn. Mater.*, 323(22):2823 – 2827, 2011.
- [13] K. H. Ahn, T. Lookman, and A. R. Bishop. *Nature*, 428:401–404, 2004.
- [14] W. Prellier, A.M. Haghiri-Gosnet, B. Mercey, Ph. Lecoeur, M. Hervieu, Ch. Simon, and B. Raveau. *Appl. Phys. Lett.*, 77:1023, 2000.
- [15] M. Tokunaga, N. Miura, Y. Tomioka, and Y. Tokura. *Phys. Rev. B*, 57:5259–5264, Mar 1998.
- [16] Michael A. Carpenter, Christopher J. Howard, Ruth E. A. McKnight, Albert Migliori, Jon B. Betts, and Victor R. Fanelli. *Phys. Rev. B*, 82:134123, Oct 2010.
- [17] Huali Yang, Yiwei Liu, Jiandi Zhang, Xiangqun Zhang, Zhaohua Cheng, Yali Xie, Baomin Wang, Qingfeng Zhan, B. G. Shen, E. W. Plummer, and Run-Wei Li. *Phys. Rev. B*, 91:174405, May 2015.
- [18] Z. Jirák, F. Damay, M. Hervieu, C. Martin, B. Raveau, G. André, and F. Bourée. *Phys. Rev. B*, 61:1181–1188, Jan 2000.
- [19] T. Elovaara, H. Huhtinen, S. Majumdar, and P. Paturi. *J. Phys.: Condens. Matter*, 24:216002, 2012.
- [20] Juan Rodríguez-Carvajal. *Physica B*, 192(1–2):55–69, 1993.
- [21] Z. Jirák, S. Krupička, Z. Šimša, M. Dlouhá, and S. Vratislav. *J. Magn. Magn. Mater.*, 53:153–66, 1985.
- [22] J. A. Alonso, M. J. Martínez-Lope, M. T. Casais, and M. T. Fernández-Díaz. *Inorg. Chem.*, 39(5):917–923, 2000.
- [23] Y. Tomioka and Y. Tokura. *Phys. Rev. B*, 66:104416, Sep 2002.