Effect of oxygen isotope substitution on magnetic ordering in $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$

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Large isotope effect in metallic manganites

Decrease in \((T_C \sim t^*)\) by \(^{16}\text{O} \rightarrow ^{18}\text{O}\) exchange

\[
\alpha_0 \approx 0.9 \\
(T_C \sim M^{-\alpha_0})
\]

\[
\Delta T = 21 \text{ K}
\]

From G.-M. Zhao et al.
Nature 381(1996) 676

Oxygen isotope exponent \((T_C \sim M^{-\alpha_0})\)

\[
\alpha_0 = -\Delta \ln T_C / \Delta \ln M
\]

Polaronic narrowing\(^1-3\) of bandwidth \(t\)

\[
t^* = t \exp(-g^2)
\]

where \(g^2 = \lambda \cdot t / \omega\)

coupl. const

\[
\omega \sim M^{-0.5}
\]

\[
\alpha_0 = -\Delta \ln T_C / \Delta \ln M \sim 0.5E / \hbar \omega
\]

\(\alpha_0 \approx 0.8 - 1\)

can be theoretically estimated\(^1\)

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\(^2\) A.S.Alexandrov, N.F.Mott Int. J. Mod. Phys 8, 2075 (1994)
\(^3\) A.S.Alexandrov, V.V.Kabanov, D.K.Ray, PRB 49, 9915 (1994)
Isotope effect expected if:

Polaronic narrowing works:

- e-hopping time $\tau \sim 1/\omega$
- opt. phonon $\sim 20$ meV

Isotope effect expected?

**YES**
- double-exchange charge ordering
- $T_C \sim zt^*$
- $T_{CO} \sim t^*/V$, $V \sim 0.2$

**NO**
- Superexchange
  - $J_{AF} \sim -b^2/U$
  - $J_F \sim b^3/U^2$
  - $\tau = \hbar/U$, $U \sim 5$ eV

Isotope effect allows us to verify the type of interactions involved!
Giant isotope effect in intermediate-bandwidth manganites

\[ t^* = t \exp\left(-\frac{E_{pol}}{\omega}\right) \] is not enough!

\[ ^{16}\text{O} \rightarrow ^{18}\text{O} \]

\[ T_c \rightarrow 0 \text{ K?} \]

\[(\text{La}_{0.25}\text{Pr}_{0.75})_{0.7}\text{Ca}_{0.3}\text{MnO}_3\]


\[(\text{La}_{0.5}\text{Nd}_{0.5})_{0.67}\text{Ca}_{0.33}\text{MnO}_3\]

Guo-meng Zhao et al, SSC 104, 57 (1997)
\[ (\text{La}_{1-y}\Pr_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \] phase diagram

**A-cation**

- **Mott**
  - Insulator
  - FM double exchange metal

\[ b_\sigma \sim \cos(\phi) \sim \langle r_A \rangle \sim (1-\text{const} \cdot y) \]

Is increased with \( y \) resulting in the insulator-metal transition

\[ J_F \sim b_\sigma \]

\[ J_{AF} \sim -b_\pi^2/U \]

*Mesoscopic phase separation AFM + FM*

\[ \text{small} \quad \langle r_A \rangle = 1.319\text{Å} \quad \text{Pr} \]

\[ \text{large} \quad \langle r_A \rangle = 1.356\text{Å} \quad \text{La} \]
$(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ phase diagram

Mott insulator $\leftrightarrow$ FM double exchange metal

$T_C \sim \phi$

$(180^\circ - \phi)$

$b_\sigma \sim \cos(\phi)$
Questions

• How the Orbital (OO), charge (CO) and magnetic ordering (AFM, FM) depend on temperature and the effective bandwidth (Pr conc. y, oxygen mass)?
• What is the ground magnetic state? Factors controlling phase separation.
• Origin of the giant isotope effect?
• Microscopic mechanism of phase separation.
Experiment

1. Neutron (T=2-1400K) and synchrotron x-ray (room T) diffraction

High resolution HRPT diffractometer, Cold DMC (up to 4.2Å) at SINQ/PSI

2. ac-magnetic susceptibility, T=2K-400K, DSC
Crystal structure: pseudocubic-orthorhombic transition

\[(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3\]

A-cation

The micro-strains is an intrinsic property of this system due to:
1. A-cation radius dispersion
2. structure transformation
Orbital and charge ordering OO/CO (I)

\[(La_{1-y}Pr_y)_{0.7}Ca_{0.3}(Mn^{3+})_{0.7}(Mn^{4+})_{0.3}O_3\]

\[3t_{2g}1e_g\]

\[Mn^{3+} : Mn^{4+} = (70:30)\%\]

\[\theta = \frac{\theta}{2}\left|3z^2 - r^2\right| + \sin\frac{\theta}{2}\left|x^2 - y^2\right]\]

\[tg(\theta) = \frac{Q_2}{Q_3} = \frac{\sqrt{3}(l-s)}{(2m-l-s)}\]

pseudo-spin plane

“defect” CO model:

\[Mn^{4+} (%) = \frac{1}{2} - \frac{m-s}{l-s} \approx 26\%\]
Orbital and charge ordering OO/CO (II)

\[(La_{1-y}Pr_y)_{0.7}Ca_{0.3}(Mn^{3+})_{0.7}(Mn^{4+})_{0.3}O_3\]

CO is suppressed
Microstructure parameters

Bragg peak width
δd/d = δa/a ⊗ d/L ⊗ “instrument”

strain size

De-convolution of the pseudo-Voigt Bragg peaks width δ(2θ) = “Cagliotti” with the instrument resolution function.

T=290K
y=0.75

x-ray, 0.93 Å
HRPT, 1.9 Å

δd_{st}/d=0.23(2)%
δd_{st}/d=0.16(1)%
Anisotropic micro-strain - structure indicator of CO

Anisotropic micro-strain along [100] 
~ a measure of CO

\[ \frac{\delta d_{st}}{d} \]

Micro-strains as a function of Pr concentration (sp. gr. \textit{Pnma})

Picture rom D.E. Cox et al.,PRB (1998)
Magnetic ordering as a function of temperature

Mott

insulator ↔ FM double exchange metal

$y = 0.8$

$T_C, T_N (K)$

Mesoscopic phase separation AFM + FM

$y_c$

$T (K)$

$I(T) = I_0(1 - (T/T_N)^\alpha)^\beta$

DMC/SINQ

$\lambda = 2.56\text{Å}$

$y = 0.8$
Magnetic ground state of \((\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3\)
Magnetic ground state of (La$_{1-y}$Pr$_y$)$_{0.7}$Ca$_{0.3}$MnO$_3$

Effective magnetic moments = $\sqrt{\text{volume} \cdot \text{moment}}$

\[
\left(\frac{m_A}{M_A}\right)^2 + \left(\frac{m_F}{M_A}\right)^2 = \text{volume} = 1
\]

\[
m_F^2(m_A^2) = M_F^2\left(1 - \frac{m_A^2}{M_A^2}\right)
\]

\[
M_A = 2.26(1)\mu_B
\]

\[
M_F = 3.57(2)\mu_B
\]

Percolation threshold

FM volume (%)

y=0.9

y=0.8

y=0.5

y=1.0

AFM volume (%)

FM volume (%)

FMI, FMM, AFMI

3.

1.

2.

\[T_C\]

\[T_N\]

Mesoscopic phase separation AFM + FM
Magnetic ground state of \((\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3\)

Polaronic narrowing acts as the narrowing due to the increase in \(y\): the phase balance is shifted towards the AFM/CO phase.
Microstrains effect on phase separation

Phase separation is favored by internal micro-strains

Percolation

strain=0.23%

strain=0.15%

Phase separation is favored by internal micro-strains
Origin of mesoscopically inhomogeneous state

• *quenched disorder* enhances the fluctuation of the competing orders near the original bicritical point [e.g. J. Burgy, A. Moreo, M. Mayr, E. Dagotto et al, PRL, PRB 2000-2004]

• *lattice distortions* and the long-range strain similar to one observed at the martensite type structural transition [e.g. K. H. Ahn, T. Lookman, and A. R. Bishop, Nature 428, 401 (2004)]
Suppression of all types of ordering near M-I transition in \((\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3\)
Influence of quenched disorder on the competition between ordered states separated by a first-order transition


(La\(_{1-y}\)Pr\(_y\))\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\)

RFIM + correlated disorder

\[ H = -J\sum_{\langle ij \rangle} S_i S_j + J'\sum_{\langle ik \rangle} S_i S_k \]

\( J' \to J'_{ik} = J' + W_{ik} \)

\( \alpha \sim 3 \) elasticity mechanism of the distortion propagation (Khomskii, Kugel, 2001) \( \sim 1/d_{\langle ik \rangle}^{\alpha} \)

Typical random field distribution

Ising spin distribution

2D

3D
Summary

$\text{La}_{1-y}\text{Pr}_y\text{Ca}_{0.3}\text{MnO}_3$ ($y=0.2-1.0$) with $^{16}\text{O}$/ $^{18}\text{O}$

- At T=0, there are 3 distinct coexisting mesoscopically phase separated phases: CO/AFMI + (FMM, FMI)
- the carrier bandwidth ($m_\text{O}$, $y$) and the crystal lattice micro-strains control the volume fractions of the FM and AFMI clusters.
- quenched disorder is responsible for the formation of the long-scale phase separated state
The End
**Samples**

**Powders of \((La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3\)**

- **O-series** \((y=0.2, 0.5, 0.7, 0.75, 0.8, 0.85, 0.9, 0.95, 1.0)\): by the solid state synthesis from oxides and carbonates of respective metals. The \(^{18}\text{O}\) (>85%) samples as well as the final \(^{16}\text{O}\) samples were obtained via respective oxygen isotope exchange at the same conditions.

- **N-series\(^1\)**: by the “paper” synthesis starting from aqueous solutions of nitrates of the respective metals (N-series) with the final thermal treatment similar to the O-series.

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MO Imaging of Percolative Conduction Paths and Their Breakdown in Phase-Separated \((\text{La}_{0.3}\text{Pr}_{0.7})_{0.7}\text{Ca}_{0.3}\text{MnO}_3\)

(Faraday effect) magnetization

Magnetic ordering as a function of temperature

\[ y = 0.5 \]

\[ T_C, T_N (K) \]

Integrated intensity

DMC/SINQ \( \lambda = 2.56 \text{Å} \)

AFM + FM

Macro-phase separation

\( T_N, T_C \)
Orbital and Charge ordering

\((\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}(\text{Mn}^{3+})_{0.7} (\text{Mn}^{4+})_{0.3}\text{O}_3\)

- Satellite (to \textit{Pnma}) Bragg peaks due to a-axis doubling
- Anisotropic (along [100]) peak broadening due to the microstrains
- Mn-O bond length mismatch

Readily observed from NPD data

From D.E. Cox et al., PRB (1998)
\((\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3\) phase diagram

Mott

Insulator ≻ FM double exchange metal

\(y_c\)

Mesoscopic phase separation AFM + FM

\(T_c, T_N\)
Giant isotope effect in $(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3$, $y=0.75$

Neutron diffraction intensities

Increase in the $m_O$ leads to complete suppression of the FMM phase and hence to the insulating state

OO effects
(La$_{1-y}$Pr$_y$)$_{0.7}$Ca$_{0.3}$MnO$_3$: $\chi_{ac}(T) = \chi' (T) + i\chi'' (T)$

Pomjakushin et al, 2005, unpublished
OO/CO effects (I)

\[(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}(\text{Mn}^{3+})_{0.7}(\text{Mn}^{4+})_{0.3}\text{O}_3\]

\(\text{Mn}^{3+} : \text{Mn}^{4+} = 70:30\)

\(3t_{2g}1e_g\)

\(3t_{2g}\)

Mn-O bond lengths in LPCM (y=0.7)

Charge ordered

Orbitally ordered

Orbitally disordered

sp.gr. \(\text{Pnma}\)
Deconvoolution of the Bragg-peak widths

\[(La_{1-y}Pr_y)_{0.7}Ca_{0.3}MnO_3, \ y=0.75\]

**O-series**
- \(\delta a/a = 0.22(1)\%\)
- \(L=1800(60)\text{Å}\)

**N-series**
- \(\delta a/a = 0.15(1)\%\)
- \(L=4400(400)\text{Å}\)

\[\delta d/d = \delta a/a \otimes d/L\]

Deconvolution of the pseudo-Voigt Bragg peaks width \(\delta(2\theta) = "Cagliotti"\) with the instrument resolution function.

\[I_{\text{exp}} = \int_{-\infty}^{\infty} PV_{\text{sample}}(2\theta - \xi) PV_{\text{instrument}}(\xi)d\xi\]
T-dep of anisotropic strain

![Graph showing the temperature dependency of anisotropic strain.](image)
Thermal displacement parameters

B^{1/2} \sim T <1/\omega^2> 1/M
Magnetic state. Bragg I(T)

\(x = 0.8, 0.75, \text{“New” O-series}\)

\[\begin{align*}
\text{Intensity (counts)} & \quad 0 & 50 & 100 & 150 & 200 \\
\text{Temperature (K)} & \quad 0 & 800 & 1200 & 1600
\end{align*}\]

\(x = 0.75, \text{“Old” N-series}\)

\[\begin{align*}
\text{Intensity (counts)} & \quad 0 & 50 & 100 & 150 & 200 \\
\text{Temperature (K)} & \quad 0 & 400 & 800 & 1200 & 1600 & 2000 & 2400 & 2800 & 3200 & 3600 & 4000 & 4400 & 4800 & 5200 & 5600 & 6000 & 6400 & 6800 & 7200 & 7600 & 8000 & 8400 & 8800 & 9200 & 9600 & 10000 & 10400 & 10800 & 11200 & 11600 & 12000
\end{align*}\]

No FM

FM suppressed
Saturated effective magnetic moments in 
$(La_{1-y}Pr_{y})_{0.7}Ca_{0.3}MnO_3$

“New” O-series

Metallic FM+AFM separated state

\[ m_F^2(m_A^2) = M_F^2 \left( 1 - \frac{m_A^2}{M_A^2} \right) \]

\[ M_{FM} = 3.52(14)\mu_B \]

\[ M_{AFM} = 2.32(33)\mu_B \]

\[ \{ III_{AF} = V_{AF} \, IV_{AF} \} \]

Effective moments

\[ m_F = (1-v)^{1/2} M_F \]

Volume fraction
Saturated effective magnetic moments in $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$

Effective moments \( \left\{ \begin{array}{l} m_{AF} = \sqrt{\nu} M_{AF} \\ m_{F} = (1-\nu)^{1/2} M_{F} \end{array} \right. \) Volume fraction

"New" O-series

"Old" N-series

Metal \( \rightarrow \) insulator
What is the difference between two series? Crystal structure?

\((\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3, y=0.75\) from both N- and O-series

*Pnma, single phase at 290K*

SLS X-ray material beamline.
Ultra-high resolution. \(\lambda=0.9\text{A}\)

HRPT/SINQ diffraction pattern.
\(\lambda=1.9\text{A}, \text{HI-mode}\)

\(R_p=4\%\)

\(R_p=3.4\%, \chi^2=3\)
Comparison of lattice parameters

\[ (\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3, \]

\( \text{Pnma} \)

\[ r = \frac{200(a-c)}{(a+c)} \]

\( T = 290 \text{K} \)

O-series, "new"

40bar O\(_2\)

O-series, as prep

Ref [4] Radaelli

\( \text{Radaelli et al} \)

\( \text{N-series} \) ref [2,3]

\( \text{micro-LPCM ISIS, } r = 0.32 \)

\( y-\text{Pr} \)

\( a \)

\( b/\sqrt{2} \)

\( c \)

\( \text{Pnma} \)

\( \text{La}_{1-y}\text{Pr}_y\text{MnO}_3 \)
Bragg peak widths. Synchrotron X-ray, HRPT

Pseudo-cubic metrics:
Strong peak overlap

O-series
Deconvolution of the Bragg-peak widths. Comparison of HRPT and synchrotron

\[
I_{\text{exp}}(2\theta) = \int_{-\infty}^{\infty} \int PV_{\text{sample}}(2\theta - \xi) PV_{\text{instrument}}(\xi) d\xi
\]

Lorenzian $\otimes$ Gaussian

- **O-series**
  - $\delta a/a = 0.22(1)\%$
  - $L = 1800(60)\text{Å}$

- **N-series**
  - $\delta a/a = 0.15(1)\%$
  - $L = 4400(400)\text{Å}$

**HRPT, High Intensity**
- $\lambda = 1.9\text{Å}$

**Synchrotron, Ultrahigh Resolution**
- $\lambda = 0.9\text{Å}$
Thermal cycling through $T_C$

Data: Data13_MDCemu
Model: ExpDec1
Equation: $y = A1 \times \exp(-x/t1) + y0$
Weighting: y

Chi$^2$/DoF = 0.01685
R$^2$ = 0.93356

$y0$ = 0.00407 ± 0.00008
A1 = 0.00034 ± 0.00015
t1 = 2.70818 ± 2.81979

Latte parameters (Å):
- O-18
- O-16
- O-16/O-18
- $a$
- $b'$
- $c$

# of cycles

0 2 4 6 8 10
y=0.75
DMC pattern

\[ \sim 1 \mu_B \]