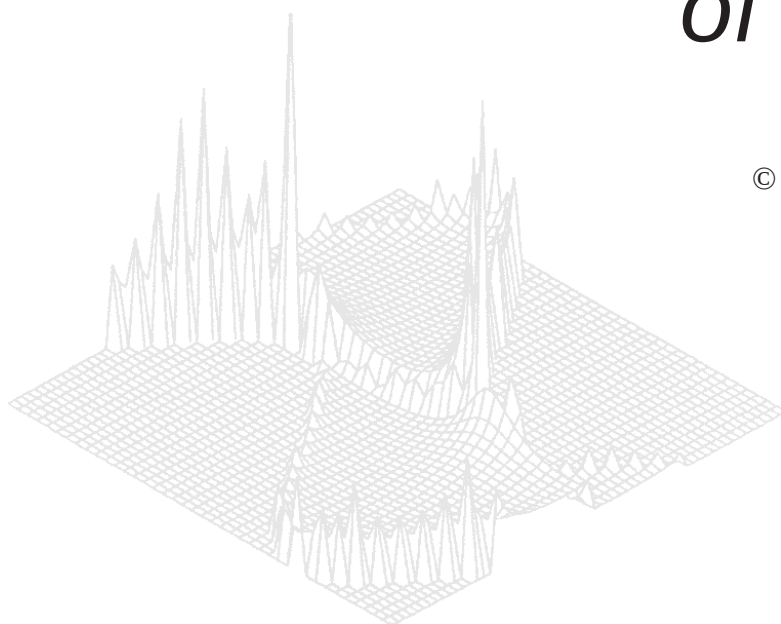

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Colossal Isotope Shift of the Metal–Insulator Transition Temperature in Epitaxial Thin Films of $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ *

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Abstract

A colossal shift of the maximum resistivity temperature induced by oxygen isotope exchange was registered for 60 nm thick films of the solid solution $\text{La}_{0.35}\text{Pr}_{0.35}\text{Ca}_{0.3}\text{MnO}_3$ on perovskite substrates. The magnitude of the effect depends on lattice strain resulting in the largest shift for the film on LaAlO_3 : the ^{16}O sample showed a metal–insulator transition at 182 K, whereas the ^{18}O sample was insulating down to 4.2 K, which is the highest difference ever reported for CMR manganites. An XRD and Raman spectrometry study indicates no difference in chemical composition or structure for the ^{18}O and ^{16}O samples at room temperature. The results are consistent with the model coupling the metal–insulator transition in the perovskite manganites to the lattice dynamics.

1. Introduction

The $\text{R}_{1-y}\text{M}_y\text{MnO}_3$ perovskites, where R^{3+} is a rare earth cation and M is a doubly charged cation of large ionic radius, with both R and M occupying A sites of the ABO_3 perovskite lattice, have become a highlight of modern solid state physics due to the recent discovery of colossal magnetoresistance (CMR) in such compounds (the main new results have been reviewed by Rao *et al.* 1996 and Ramirez 1997). The CMR accompanies the phase transitions resulting in the half-metallic ferromagnetic phase. The formation of such a ferromagnetic state on doping of RMnO_3 was explained by the mechanism of double exchange (Zener 1951). However, the models involving only double exchange cannot explain the observed resistivity. The resistivity above the Curie temperature T_c is much larger than the Mott limit and, moreover, rapidly increases as T decreases. Scattering produced by spin disorder is simply not large enough to cause such insulating behaviour. It was proposed that crucial additional physics is involved in terms of strong electron–phonon coupling in a Jahn–Teller form, which localises the conduction electrons as polarons at $T > T_c$ (Millis 1996). For polarons, a classical description involving particles incoherently hopping from site to site is appropriate.

The electric properties of the manganites are very sensitive to a variation of their composition and ambient pressure. Both influence the tolerance factor

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$t = d(\text{A-O})/\sqrt{2}d(\text{Mn-O})$, where d denotes the interatomic distance. The former varies the mean ionic radii of the cations in the A and B positions, while the latter exposes the different compressibility of the A-O and B-O bonds. A tolerance factor value of 0.91 was found to be critical for σ -bonding of the oxygen $2p$ orbitals with e_g orbitals of the Mn ions (Hwang *et al.* 1995; De Teresa *et al.* 1996). At the lower value, itinerant carriers become localised. The localisation affords conditions for charge ordering (ordering $\text{Mn}^{+3}/\text{Mn}^{+4}$).

Besides the static effects, the importance of the lattice dynamics was established. The isotope exchange in the oxygen sublattice, when ^{18}O is inserted instead of ^{16}O , was found to produce a huge effect on the electrical and magnetic properties of the ceramic solid solution with the tolerance factor of ≈ 0.91 for $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ($y = 0.75$), $(\text{La}_{1-y}\text{Nd}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ($y = 0.5$) (Zhao *et al.* 1997; Babushkina *et al.* 1998a, 1998b). The ^{16}O samples being metallic below T_c became insulating if ^{16}O was replaced by ^{18}O . Local structure Jahn-Teller distortions were found by EXAFS and neutron pair-density function (PDF) analysis (Tyson *et al.* 1996; Louca *et al.* 1997). The results imply that the metal-insulator transition in $\text{R}_{1-y}\text{M}_y\text{MnO}_3$ is a lattice dynamics transition at the same time.

To take into account the dynamic effects, the value of the resonance integral t_{ij} for e_g electron transfer between neighbouring Mn^{+4} and Mn^{+3} sites is averaged over related lattice vibrations. Crossing of the Jahn-Teller schemes in the non-adiabatic limit leads to a correlation between t_{ij} and the mean square displacement of the oxygen atom in the Mn-O chain (Kresin and Wolf 1997), with the latter related to the isotope mass. But the variation of t_{ij} in the model is rather modest. The variation can be crucial only with the involvement of a trigger mechanism. We mention just two possible mechanisms. First, the t_{ij} values can influence the competition between the ferromagnetic itinerant state and charge ordering (Babushkina *et al.* 1998a). On the other hand, the formation of polarons implies narrowing of the conduction bandwidth. The effective conduction bandwidth W_{eff} can be deduced as the product of the unperturbed bandwidth W and a corrective factor (Aleksandrov and Mott 1994):

$$W_{\text{eff}} = W \exp(-\gamma E/\hbar\omega), \quad (1)$$

where E is the polaron formation energy and the characteristic frequency of the optical phonons. A self-correlation is determined by the term γ , which is a function of the ratio E/W and characterises the mechanism of the electron-phonon coupling in the particular material. Depending on the $\gamma(E/W)$, a change of ω by the variation of the oxygen isotope mass could produce a cut-off for W_{eff} . At any rate, the involvement of a trigger mechanism implies that at a critical value $t_{ij} = t_c$ itinerant carriers in Mn-O chains become localised.

Until now the isotope effect has been studied only in the bulk manganites. It is very interesting to measure it for thin films on the perovskite substrates. The perovskite cell in the film is deformed, compared to the bulk material, to match the atomic positions of the substrate lattice. The remarkable feature of the epitaxial manganite films is that the strain is sustained even if the film thickness exceeds the perovskite lattice constant by a factor of 1000. Such films were grown by a variety of the vapour deposition technique (Eckstein *et al.* 1996;

Yeh *et al.* 1997; Gorbenko *et al.* 1997; Koo *et al.* 1997). The strain in the films influences the electric properties as well. In the present work we study the isotope effect in the thin perovskite films of $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$.

2. Experimental Details

Aerosol MOCVD used to prepare thin films includes deposition from a vapour produced by the evaporation of precursor solution nebula in the carrier gas flow (Gorbenko *et al.* 1994). Volatile precursors were as follows: $\text{La}(\text{thd})_3$, $\text{Pr}(\text{thd})_3$, $\text{Sr}(\text{thd})_2$, $\text{Ca}(\text{thd})_2$ and $\text{Mn}(\text{thd})_3$, where thd is 2,2,6,6-tetramethylheptan-3,5-dionate. Single crystalline (001) LaAlO_3 (pseudocubic cell) and (001) SrTiO_3 were used as substrates. Deposition runs were carried out at 750°C with a total pressure of the Ar–O₂ mixture of 6 mb (O₂ partial pressure of 3 mb) (note: 1 mb = 100 Pa). The $\text{La}_{0.35}\text{Pr}_{0.35}\text{Ca}_{0.3}\text{MnO}_3$ films prepared were 60 and 300 nm thick. Directly after the deposition at 750°C the reactor was filled with oxygen up to a pressure of 10^3 mb and films as-grown were annealed for 0.5 h at the deposition temperature. SEM was accomplished by CAMSCAN equipped with an EDAX system for quantitative chemical analysis of the films. SNMS depth profiling for metal components and ^{18}O was carried out with an INA-3 system. XRD with a four-circle diffractometer Siemens D5000 with secondary graphite monochromator (Cu K $_{\alpha}$ radiation) was applied to determine the phase composition, orientation and lattice parameters. Then θ – 2θ scans (including measurements of the tilted samples over the reflection poles found by φ – and χ -scanning), φ scans and out-of-plane rocking curve measurements were used. Reflections of the substrates were used as the inner standard. Calculations were made with reference to the lattice constants 0.3905 nm for SrTiO_3 and 0.3792 nm for LaAlO_3 . The XRD study was repeated after the isotope exchange experiments. For isotope exchange, pairs of $1\times 8\text{ mm}^2$ strips were cut from the samples and put into alumina boats which were placed in two quartz tubes mounted in the furnace. The quartz tubes formed parts of two identical closed loops where enforced circulation of gas was applied. All samples were treated simultaneously: one part of each sample was heated in $^{16}\text{O}_2$ atmosphere and the other part of the sample was heated in an $^{18}\text{O}_2$ enriched atmosphere (with molar fraction of $^{18}\text{O}_2$ of 85%). The diffusion annealing was carried out for 4 h at the temperature 750°C under an oxygen pressure of 10^3 mb.

The oxygen isotope ratio of the films was checked by Raman spectrometry. An isotope exchange process causes a line shift of the Raman phonon bands generated by lattice vibrations dominated by the mass of these isotopes. The line shift follows the isotope mass ratio according to

$$\frac{\omega_1}{\omega_2} = \sqrt{\frac{m_2}{m_1}} \quad (2)$$

in the absence of perturbing effects such as lattice deformations. The study was performed with a triple monochromator system and in a backscattering geometry of the incident laser light. Measurements made at various places on the sample surface lead to similar results in all cases.

Table 1. Structural characteristics of the $\text{La}_{0.35}\text{Pr}_{0.35}\text{Ca}_{0.3}\text{MnO}_3$ films on the perovskite substrates, studied in the present work

Substrate	Film thickness (nm)	Parameters ^A		Tetragonal distortion ^B (%)
		$a/2, b/2$	$c/2$	
LaAlO ₃	60	3.846 ± 0.003	3.872 ± 0.002	0.7
	300	3.848 ± 0.003	3.869 ± 0.002	0.5
SrTiO ₃	60	3.879 ± 0.003	3.823 ± 0.002	-1.5
	300	3.862 ± 0.003	3.848 ± 0.002	-0.4

^A Parameters are scaled to the perovskite cell dimension.^B Calculated from $[2(c-a)/(c+a)] \times 100\%$.

3. XRD Characterisation

The XRD study revealed that the films prepared were highly strained (Table 1). The films were epitaxial (an out-of-plane rocking curve of FWHM 0.17–0.25 and in-plane orientation defined φ -scans of FWHM 0.4–0.8) with pure cube-on-cube growth mode (see Fig. 1). The difference in the perovskite lattice constants results in a strain of the film lattice in the interface plane. The lattice constant of SrTiO₃ is larger, and consequently the tensile strain in the film demands an in-plane expansion of the perovskite cube. Deformation of the lattice normal to the substrate is proportional to the in-plane strain components. Thus, the films on SrTiO₃ are contracted along the normal. The opposite is true for the films on LaAlO₃.

One can expect a perturbation of the intrinsic buckling of the MnO₆ octahedra array under the strain (Fig. 2). In fact, the lattice mismatch between the perovskite substrate and manganite films can be compensated by a 1–2° anisotropic perturbation of the buckling (the mean value of the Mn–O–Mn bond angle differs from the undistorted value 180° by about 20° at a tolerance factor of ≈ 0.9). The balance of the formation energy of a misfit dislocation at the interface of the two perovskite lattices and lattice strain energy changes with the film thickness. Thus, thicker films are partly relaxed.

The high temperature annealing during the isotope exchange could cause further relaxation of the strain. But the XRD study after the isotope exchange revealed only a small relaxation for the 300 nm thick films and practically no relaxation for the 60 nm thick films (Fig. 3). The SNMS depth profiling revealed that the isotope exchange was not completed in 300 nm thick films, resulting in a lower ¹⁸O content at the film–substrate interface compared to the film surface by a factor of two. This fact is a result of very slow oxygen diffusion in the nearly stoichiometric $\text{R}_{1-y}\text{M}_y\text{MnO}_3$ owing to the lack of oxygen vacancies (van Hassel *et al.* 1993). No penetration of ¹⁸O into the substrate was detected by SNMS depth profiling.

4. Raman Spectrometry Characterisation

All $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films show first order Raman active phonon bands with A_g symmetry near 80 cm⁻¹, a doublet structure between 220–290 cm⁻¹ and a further band near 440 cm⁻¹ with B_g like character. Similar bands were

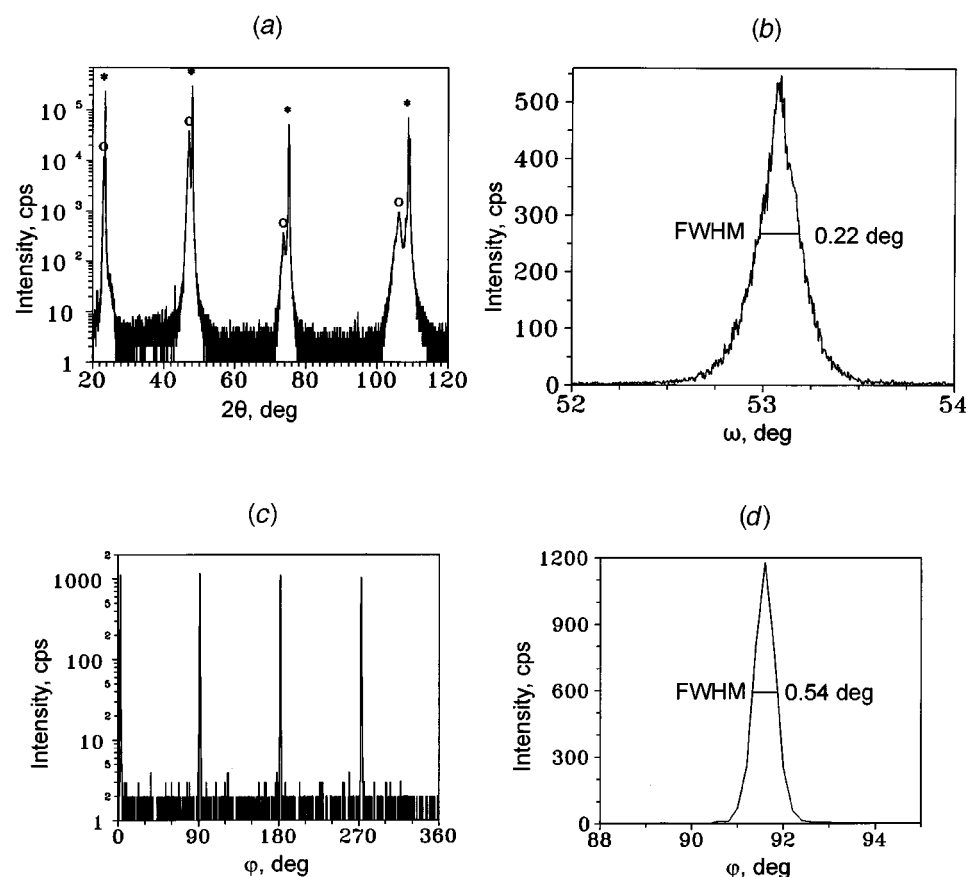


Fig. 1. (a) XRD characterisation of epitaxial quality of 300 nm thick $\text{La}_{0.35}\text{Pr}_{0.35}\text{Ca}_{0.3}\text{MnO}_3$ film on LaAlO_3 with θ - 2θ scan; (b) the rocking curve for pseudocubic reflection (004); (c) and (d) the φ scan for pseudocubic reflection (220). Marked reflections belong to the substrate (*) and the film (o). The instrumental broadening was 0.04° and 0.10° for the rocking curve and φ scan respectively.

found in films with thicknesses of 60 and 300 nm. The bands are superimposed by a strong background scattering with broad maxima near 490 and 610 cm^{-1} (Guettler *et al.* 1998). The bands between 220 – 290 cm^{-1} and 440 cm^{-1} were unambiguously identified as oxygen bands by isotope exchange experiments. The features near 490 and 610 cm^{-1} are also of phononic origin as they also show an oxygen isotope shift. They are, thus, assigned to second order Raman scattering mainly due to oxygen vibrational modes. No difference in the band position was registered for the films of the same composition on LaAlO_3 and SrTiO_3 . The result means that the geometry of individual MnO_6 octahedra, including Mn–O bondlengths, is not affected by the lattice strain.

The spectra of the thinner films are dominated by substrate lines (near 120 , 150 and 485 cm^{-1} for LaAlO_3 as can be seen in Fig. 4). This substrate spectrum is absent in the films with a thickness 300 nm exceeding the penetration depth of the excitation laser wavelength of 514.5 nm .

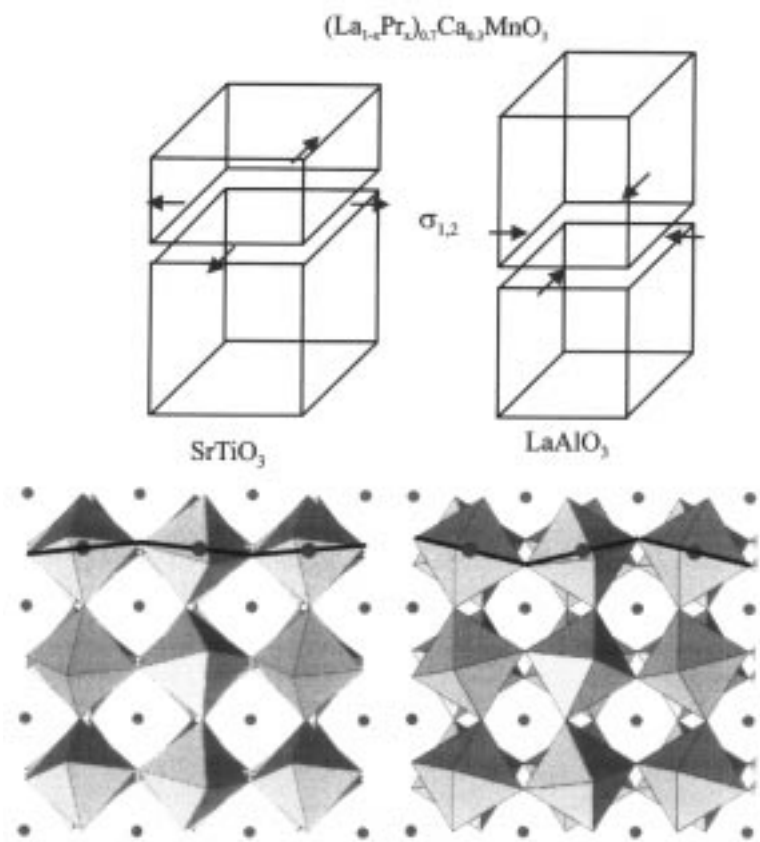


Fig. 2. Buckling of the MnO_6 octahedra network perturbed by lattice strain with in-plane expansion (left) and in-plane contraction (right) of the perovskite film lattice in $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ film on a SrTiO_3 and LaAlO_3 substrate respectively. The bold lines denote infinite Mn–O chains.

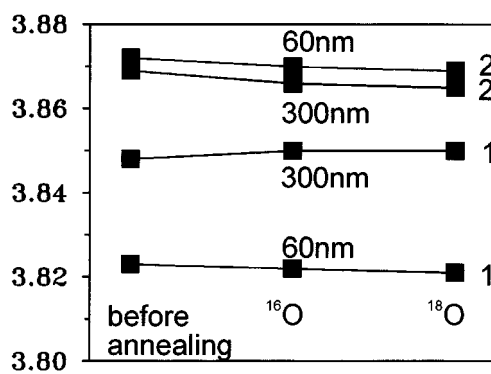


Fig. 3. Effect of the annealing in $^{18}\text{O}_2$ and $^{16}\text{O}_2$ on the strain relaxation in films of different thickness on (1) LaAlO_3 and (2) SrTiO_3 . The size of the black rectangles corresponds to the rms error of the lattice parameter $c/2$.

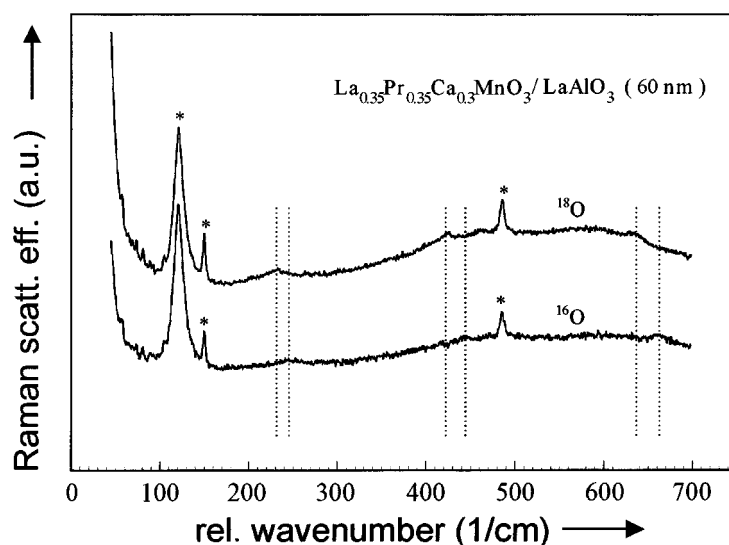


Fig. 4. Raman spectra ($\lambda = 514.5$ nm) of $\text{La}_{0.35}\text{Pr}_{0.35}\text{Ca}_{0.3}\text{MnO}_3$ films after oxygen isotope exchange (^{16}O and ^{18}O). As a guide for the eye, the positions of the bands referred to the scattering from $\text{La}_{0.35}\text{Pr}_{0.35}\text{Ca}_{0.3}\text{MnO}_3$ are marked by the dotted lines.

An additional line near 660 cm^{-1} was found in ^{16}O films. It has also been found in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films by Malde *et al.* (1998). The band near 660 cm^{-1} is, however, absent in ceramics and has varying scattering efficiencies in films with similar chemical composition. Therefore, it could be an impurity band most probably caused by Mn_2O_3 . Due to the very weak Raman scattering of CMR manganites caused by their small deviation from the non-Raman-active cubic structure, even small amounts of impurities lead to comparatively strong Raman bands. Taking into account the precision of EDX and SNMS analysis and the sensitivity of XRD, the upper limit of the impurity level is some 2–3%.

Table 2. Observed oxygen isotope shifts of the Raman bands near 660 and 439 cm^{-1} in $\text{La}_{0.35}\text{Pr}_{0.35}\text{Ca}_{0.3}\text{MnO}_3$ films

Film thickness (nm)	$\omega\text{ (cm}^{-1}\text{)}$ (^{16}O)	$\omega\text{ (cm}^{-1}\text{)}$ (^{18}O)	$\Delta\omega$	$-\Delta\omega/\omega$	$^{18}\text{O}/^{16}\text{O}+^{18}\text{O}$
60	664	634	30	0.045	0.78
	443	423	20	0.046	0.78
	243	232	11	0.045	0.77

The 660 cm^{-1} line can therefore be used as an inner standard in the isotope exchange experiments. A significant isotope effect was found for the modes near 240 , 440 and 660 cm^{-1} and is listed in Table 2. It corresponds to an $^{18}\text{O}/(^{16}\text{O}+^{18}\text{O})$ ratio of 0.8 ± 1 . This is in good agreement with the ratio of 0.85 in the exchange gas mixture used in our experiments. No shift for substrate bands was observed in accordance with SNMS depth profiling data. The line shift induced by the isotope exchange can be quantitatively related to the mass change involved. This indicates a complete gas exchange. Also, there are no

significant contributions from other potential factors resulting from the isotope exchange process, such as strain effects or the oxygen non-stoichiometry.

Table 3. Comparison of the maximum resistivity temperatures T_p (K) for the 60 nm thick $\text{La}_{0.35}\text{Pr}_{0.35}\text{Ca}_{0.3}\text{MnO}_3$ films

Substrate	As-grown film	T_p (K)	
		After 4h annealing in $^{16}\text{O}_2$	After 4h annealing in $^{18}\text{O}_2$
LaAlO_3	168.0	182.3	No T_p down to 4.2 K
SrTiO_3	176.6	190.1	125.2

5. Electrical Properties

The electrical measurements results were rather surprising. The long-term annealing in $^{16}\text{O}_2$ atmosphere resulted in a small increase in the maximum resistivity temperature T_p (Table 3). A similar behaviour was reported by Jin *et al.* (1995) and Krishnan *et al.* (1996) for $\text{R}_{1-y}\text{M}_y\text{MnO}_3$ perovskite films [we have also seen it for most $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films prepared by us]. We have found no relaxation of the strain for 60 nm thick films, and thus it cannot be responsible for the shift of T_p . No oxygen non-stoichiometry or $\text{Mn}^{3+}/\text{Mn}^{4+}$ variation is involved in the process as $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ solid solutions are nearly stoichiometric in oxygen at a not too low oxygen pressure ($>10^{-10}$ atm; 1 atm = 101.3 kPa). The probable reasons for the shift of T_p could be micro-heterogeneity effects related to the low deposition temperature or micro-twinning as the true lattice symmetry of $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ is orthorhombic. Both phenomena are definitely important for the electrical properties and both are sensitive to the post deposition heat treatment of the manganite films, but their study is still in progress (Hervieu *et al.* 1996; Zandbergen *et al.* 1998).

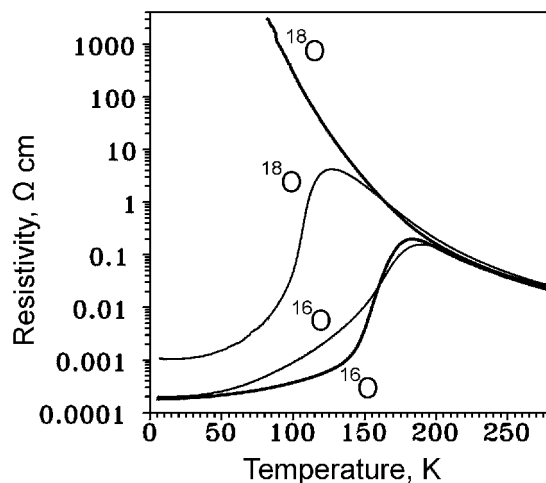


Fig. 5. Temperature dependence of the resistivity for $\text{La}_{0.35}\text{Pr}_{0.35}\text{Ca}_{0.3}\text{MnO}_3$ films after annealing in $^{16}\text{O}_2$ and in $^{18}\text{O}_2$. Bold lines are for the film on LaAlO_3 and thin lines for the film on SrTiO_3 .

In contrast to the small increase of T_p after annealing in $^{16}\text{O}_2$, a drastic decrease of T_p was observed after the parallel annealing in $^{18}\text{O}_2$ (Fig. 5). The effect was higher for the film on LaAlO_3 and no transition to the metallic state was detected down to 4.2 K for the ^{18}O sample.

The following qualitative consideration can explain the huge isotope effect in the thin films and its dependence on the substrate material. The localisation of the itinerant electrons implies a narrowing of the conduction band. The value of W depends on the cosine of the Mn–O–Mn bond angle. If W is about the cut-off value then even an anisotropic perturbation of the bond angles in the structure caused by the lattice strain would result in a drastic variation of the sensitivity to the oxygen isotope mass.

Because of the strain, the film on LaAlO_3 is actually closer to the critical state for the localisation of itinerant carriers than the film on SrTiO_3 . Actually, the strain increases the Mn–O–Mn bond angles in the plane of the film on SrTiO_3 . On the contrary, in the plane of the film on LaAlO_3 the Mn–O–Mn bond angles are decreased (see Fig. 2). The gain in the kinetic energy of itinerant carriers is higher, and W is larger, with double exchange assisted in the plane of the film and suppressed across the film. The opposite is true if it is suppressed in the plane of the film and assisted across the film, i.e. only in one dimension. The approach is supported by the variation of T_p for $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films as a function of y : owing to a decrease of the mean value of the Mn–O–Mn bond angle T_p decreases with the growth of y , but more rapidly for the films on LaAlO_3 than for those on SrTiO_3 (Gorbenko *et al.* 1998).

6. Conclusion

To sum up, we have found a colossal oxygen isotope shift of the maximum resistivity temperature for thin films of $(\text{La}_{1-y}\text{Pr}_y)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. The effect depends on the substrate material because of the strain in thin films. The highest magnitude of the effect in the film on LaAlO_3 is a result of the closer approximation to the localisation of the itinerant carriers.

Acknowledgments

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References

- Aleksandrov, A. S., and Mott, N. F. (1994). *Int. J. Mod. Phys. B* **8**, 16491.
- Babushkina, N. A., Belova, L. M., Ozhogin, V. I., Gorbenko, O. Yu., Kaul, A. R., Khomskii, D. I., and Kugel, K. I. (1998a). *J. Appl. Phys.* **83**, 7369.
- Babushkina, N. A., Belova, Gorbenko, O. Yu., Kaul, A. R., Bosak, A. A., Ozhogin, V. I., and Kugel, K. I. (1998b). *Nature* **391**, 159.
- De Teresa, J. M., Ibarra, M. R., Garcia, J., Blasco, J., Ritter, C., Algarabel, P. A., Marguina, C., and del Moral, A. (1996). *Phys. Rev. Lett.* **76**, 3392.
- Eckstein, J. N., Bozovic, I., O'Donnell, J., Onellion, M., and Rzechowski, M. S. (1996). *Appl. Phys. Lett.* **69**, 1312.
- Gorbenko, O. Yu., Fuflyigin, V. N., Erokhin, Y. Y., Graboy, I. E., Kaul, A. R., Tretyakov, Yu. D., Wahl, G., and Klippe, L. (1994). *J. Mater. Chem.* **4**, 1585.

- Gorbenko, O. Yu., Babushkina, N. A., Belova, L. M., Bosak, A. A., Amelichev, V. A., Kaul, A. R., and Wahl, G. (1997). Proc. XIV Int. Conf. on CVD and EuroCVD-11 (Eds M. D. Allendorf and C. Bernard), p. 1101 (Electrochemical Society: Pennington).
- Gorbenko, O. Yu., Bosak, A. A., Kaul, A. R., Babushkina, N. A., and Belova, L. M. (1998). In 'Chemical Aspects of Electronic Ceramics Processing', MRS Proceedings, Vol. 495, p. 333.
- Guettler, B., Skuja, L., Gorbenko, O. Yu., Kaul, A. R., Novozhilov, M. A., Babushkina, N. A., and Belova, L. M. (1998). In 'High Density Magnetic Recording and Integrated Magneto-optics', MRS Proceedings, Vol. 517, p. 111.
- Hervieu, M., Van Tendeloo, G., Caignaert, V., Maignan, A., and Raveau, B. (1996). *Phys. Rev. B* **53**, 14274.
- Hwang, H. W., Cheong, S. W., Radaelli, P. G., Marezio, M., and Batlogg, B. (1995). *Phys. Rev. Lett.* **75**, 914.
- Jin, S., Tiefel, T. H., McCormack, M., O'Bryan, H. M., Chen, L. H., Ramesh, R., and Shurig, D. (1995). *Appl. Phys. Lett.* **67**, 557.
- Koo, T. Y., Park, S. H., Lee, K. B., and Jeong, Y. H. (1997). *Appl. Phys. Lett.* **71**, 977.
- Kresin, V. Z., and Wolf, S. A. (1997). *Philos. Mag. B* **76**, 241.
- Krishnan, K. M., Modak, A. R., Lucas, C. A., Michel, R., and Cherry, H. B. (1996). *J. Appl. Phys.* **79**, 5169.
- Louca, D., Egami, T., Brosha, E. L., Roeder, H., and Bishop, A. R. (1997). *Phys. Rev. B* **56**, 8475.
- Malde, N., de Silva, P., Akther Hossain, A. K. M., Cohen, L. F., Thomas, K. A., MacManus-Driscoll, J. L., Mathur, N. D., and Blamire, M. G. (1998). *Solid State Commun.* **105**, 643.
- Millis, A. J. (1996). *Phys. Rev. B* **53**, 8434.
- Ramires, A. P. (1997). *J. Phys. Cond. Matter* **9**, 8171.
- Rao, C. N. R., Cheetham, A. K., and Mahesh, R. (1996). *Chem. Mater.* **8**, 2421.
- Tyson, T. A., Mustre de Leon, J., Conradson, S. D., Bishop, A. R., Neumeier, J. J., Roeder, H., and Zang, J. (1996). *Phys. Rev. B* **53**, 13985.
- van Hassel, B. A., Kawada, T., Sakai, N., Yokokawa, H., Dokiya, M., and Bouvmeester, H. J. M. (1993). *Solid State Ionics* **66**, 295.
- Yeh, N. C., Vasquez, R. P., Beam, D. A., Fu, C. C., Huynh, J., and Beach, G. (1997). *J. Phys. Cond. Matter* **9**, 3713.
- Zandbergen, H. W., Aarts, J., Freisem, S., Graboy, I. E., Gorbenko, O. Yu., and Kaul, A. R. (1999). In 'High-temperature Superconductors and Novel Inorganic Materials Engineering', NATO series (Ed. G. Van Tendeloo), p. 239.
- Zener, C. (1951). *Phys. Rev.* **82**, 403.
- Zhao, G. M., Keller, H., Shengelaya, A., and Mueller, K. A. (1997). *Solid State Commun.* **104**, 57.