

## Crossover from anisotropic to isotropic transport in $R_{2/3}A_{1/3}\text{MnO}_3$ perovskites determined by crystal symmetry

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The transport properties of  $\text{Pr}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  and  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  perovskites have been studied by means of thermoelectric power measurements in high-quality single crystals. It was observed that, whereas  $\text{Pr}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  exhibits anisotropic conducting properties,  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  does not. The former crystallizes in an orthorhombic structure, with different Mn-O-Mn bond lengths and angles in the  $ab$  plane and along the  $c$  axis, and the latter in a rhombohedral structure, with identical Mn-O-Mn bonds and angles; therefore, we relate this qualitative change of the conducting regime to the different crystal structures.

Mixed-valence manganese-based perovskites are materials of high interest from both the scientific and technological point of view, due to the peculiarities exhibited by their transport properties.<sup>1</sup> These transport properties have been found recently to be anisotropic in layered materials,<sup>2</sup> due to the decoupling of in-plane (MnO planes) and out-of-plane transport behavior. In the prototypical CMR  $R_{2/3}A_{1/3}\text{MnO}_3$  manganites ( $R$  is rare-earth;  $A$  is divalent alkali),<sup>3,4</sup> their pseudocubic perovskite structure should make it difficult to observe any anisotropy in electrical conduction. Recently, Zeng and Wong reported the observation of anisotropic transport properties of LaCaMnO thin films.<sup>5</sup> Here we will show that this anisotropic behavior is not a general property of Mn-based perovskites, but there are two conduction regimes, isotropic and anisotropic, related to the crystal structure of the considered material.

For this purpose two high-quality  $\text{Pr}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  and  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  single crystals were available. They were prepared with the same technique used in Ref. 6. In Fig. 1 the x-ray pattern for the  $\text{Pr}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  is shown. The analysis indicated high purity and almost perfect single crystal-structure, with a rocking curve full width at half maximum of  $0.04^\circ$ . Deviations from the expected orientation were found to be lower than  $0.5^\circ$ . Special care was taken in order to ensure that no mixture of phases is present in our crystals due to the synthesis route. For this reason room temperature x-ray diffraction patterns of powdered samples were recorded and adjusted by the Rietveld method.  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  is rhombohedral ( $R\bar{3}c$ , spatial group 167) whereas  $\text{Pr}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  was found to be orthorhombic ( $Pbnm$ , spatial group 62). Long-time high resolution scans were performed between the (0,0,2) and (0,0,4) peaks, showing no presence of twinned structures. Bond distances and angles are summarized in Table I. dc-magnetization measurements were done in order to estimate the Curie temperatures,  $T_c$ , where the ferromagnetic-to-paramagnetic transition takes place. Values of 286 K and 360 K were obtained for  $\text{Pr}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  and  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  respectively, in good agreement with the literature.

Seebeck effect measurements were preferred as the measuring technique, because the Seebeck coefficient,  $\alpha(T)$ , depends only on temperature and potential gradients between two measuring points.<sup>8</sup> This eliminates the dependence of the data on sample shapes. Also, Palstra *et al.*<sup>9</sup> have signaled that thermopower provides unique insight into the transport mechanisms of these materials. Measurements of  $\alpha(T)$  were performed with a homemade apparatus similar to the described by Goodenough *et al.*<sup>10</sup> A temperature difference of 1 K was applied between two parallel cuts of the sample. The sign of the temperature difference was reversed in order to check the results. The cuts were done so that they were perpendicular to the  $c$  axis, and other two perpendicular to the  $ab$  plane. Only slight deviations from the desired orientation of less than  $0.5$  degrees in PrSr and  $4^\circ$  in LaSr were observed.

First,  $\alpha(T)$  was measured along the  $c$  axis and parallel to the  $ab$  plane in  $\text{Pr}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ . The results are presented in Fig. 2(a). It is seen that the coefficient is the same in both directions below  $T_c$ . In the ferromagnetic phase the value is very small, as in similar materials.<sup>9</sup> At a temperature similar to the  $T_c$  estimated from dc-magnetization measurements, a jump is observed, as expected; but an important difference is detected:  $\alpha(T)$  along the  $ab$  plane is

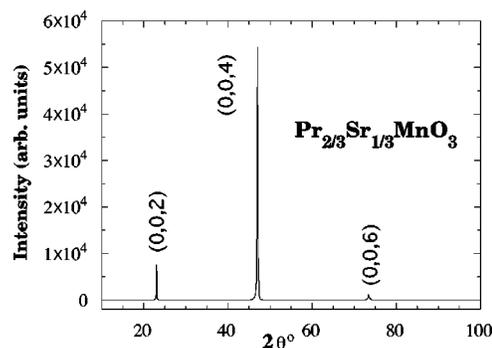


FIG. 1. X-ray diffraction pattern of the  $\text{Pr}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  single crystal. Only sharp (002), (004), and (006) peaks are observed, demonstrating the high quality of the crystal.

TABLE I. Room-temperature structural parameters refined for both phases. The site occupancies were kept at fixed values consistent with the nominal stoichiometry. For  $Pbnm$ , the atomic positions are  $\text{Pr}^{3+}/\text{Sr}^{2+}$ :  $4c(x,y,0.25)$ ;  $\text{Mn}^{3+}/\text{Mn}^{4+}$ :  $4a(0,0,0)$ ;  $\text{O}^{2-}(\text{I})$ :  $4c(x,y,0.25)$ ;  $\text{O}^{2-}(\text{II})$ :  $8d(x,y,z)$ . The hexagonal axes setting were used for the refinement of the structure belonging to the  $R-3c$  space group. The atomic positions are  $\text{La}^{3+}/\text{Sr}^{2+}$ :  $6a(x,y,0.25)$ ;  $\text{Mn}^{3+}/\text{Mn}^{4+}$ :  $6b(0,0,0)$ ;  $\text{O}^{2-}$ :  $18e(x,0,0.25)$ . Numbers in parenthesis are standard deviations.

Sample	$\text{Pr}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ $Pbnm-(O')$	$\text{La}_{2/3}(\text{Sr})_{1/3}\text{MnO}_3$ $R-3c$
Lattice parameters		
$a$	5.4570(2)	5.5017(1)
$b$	5.4896(1)	
$c$	7.7044(2)	13.3609(1)
Bond length and angles		
$d_{\text{Mn}-\text{O}(I)}$	1.957(2)	1.9510(2)
$d_{\text{Mn}-\text{O}(II)}$	2.00(1)	1.9510(2)
$d_{\text{Mn}-\text{O}(III)}$	1.90(1)	1.9510(2)
$\theta_{\text{Mn}-\text{O}(I)-\text{Mn}}$	159.3(1)	167.60(1)
$\theta_{\text{Mn}-\text{O}(II)-\text{Mn}}$	163.8(5)	167.60(1)
$\langle r_{A,Ln} \rangle$	1.222	1.247
Tolerance factor	0.924	0.933
Goodness of Fit	1.47	1.91
Rb	5.77	5.23

around 15% higher (in absolute value) than along the  $c$  axis. This result is basically similar to the one of Zeng and Wong,<sup>5</sup> who report anisotropy of the transport properties for temperatures above the region where the ferromagnetic-to-paramagnetic phase transition of their  $\text{LaCaMnO}$  thin films takes place. The situation is different for  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  [Fig. 2(b)]: below  $T_c$  the behavior is similar to the previous case,  $\alpha(T)$  is equal for both the  $c$  axis and the  $ab$  plane; nevertheless, for  $T > T_c$  the conducting regime keeps on being isotropic.

In order to analyze the results, the crystal structure of both materials must be taken into account. Both present a distorted perovskite structure, but the spatial groups are different.  $\text{Pr}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  crystallizes in the orthorhombic  $Pbnm$  structure and  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  in the rhombohedral  $R-3c$  one. The key is that for the  $Pbnm$  case the Mn-O-Mn bond lengths and angles are different. In the case of the  $R-3c$  structure all the Mn-O-Mn bonds and angles are equivalent (see Table I). Provided that the transfer integral between two Mn sites (and therefore the conductivity of such bond) is strongly dependent on the bond angle,<sup>11</sup> the conclusion is that the origin of the anisotropic behavior in the transport properties lies in the different crystal structures. The crossover from orthorhombic to rhombohedral symmetry in  $R_{2/3}A_{1/3}\text{MnO}_3$  perovskites takes place at a tolerance factor [defined as  $t = d(R-O)/\sqrt{2}d(\text{Mn}-O)$ ] value of about 0.93.<sup>12</sup> For the compounds considered here  $\text{Pr}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  has  $t = 0.924$  and  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$   $t = 0.933$ , i.e., one at each side of the boundary line at  $t \approx 0.93$ .<sup>13</sup>

In our opinion, the physical implications of such crossover have not been conveniently highlighted. In a recent in-

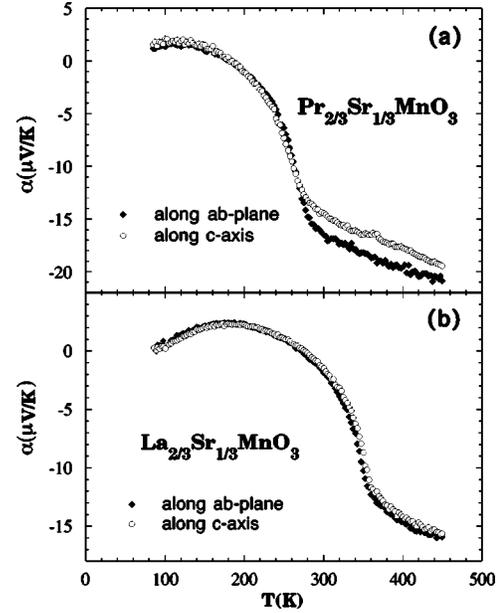


FIG. 2. (a) Temperature dependence of the thermoelectric power of a  $\text{Pr}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  single crystal, along the  $c$  axis and along the  $ab$  plane. Note the difference in  $\alpha(T)$  for  $T > T_c$  depending on the orientation of the crystal. (b) The same for a  $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$  single crystal. The behavior is now isotropic in all the studied temperature ranges.

vestigation of the ferromagnetic-to-paramagnetic phase transition in  $\text{La}_{2/3}(\text{Ca},\text{Sr})_{1/3}\text{MnO}_3$  perovskites, it was found that an increase of the Sr doping (and therefore of the tolerance factor) leads to a qualitative change of the nature of the magnetic phase transition, which goes from first- to second-order type.<sup>14</sup> The change takes place at  $t \approx 0.93$ . Such coincidence with the aforementioned boundary line makes us think that there might be a relationship between the crystal structure and the physics governing the behavior of these materials.<sup>15</sup> As orthorhombic symmetry allows a cooperative Jahn-Teller distortion and the rhombohedral one does not,<sup>16</sup> effects like the qualitative changes of the type of phase transition might be consequences of the disappearance of the cooperative JT distortion (pointed out to be important in the physics of these perovskites<sup>17</sup>).

Consequently, we think that a phase diagram, separating anisotropic from isotropic conduction regimes, can be set for all the  $R_{2/3}A_{1/3}\text{MnO}_3$  perovskites, with a phase boundary at  $t \approx 0.93$ , which is also the boundary of the orthorhombic-to-rhombohedral phases.

In summary, through thermoelectric power measurements, it has been determined that  $R_{2/3}A_{1/3}\text{MnO}_3$  perovskites can exhibit isotropic or anisotropic transport properties. It is proposed that the anisotropic regime is characteristic of orthorhombic phases and the isotropic one is characteristic of rhombohedral phases, in which isotropic Mn-O bonds and Mn-O-Mn angles are present.

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- <sup>13</sup>For each composition  $\langle r_A \rangle$  (average ionic radius of the A site) was calculated from the tabulated values of R.D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr. **A32**, 751 (1976) for atoms in ninefold coordination. The choice of an effective coordination number of 9 instead of 12 for La, Pr, and Sr is justified on the basis of the spontaneous cooperative puckering of the  $\text{MnO}_6$  octahedra as a consequence of the small size of these central cations. The room temperature, ambient-pressure tolerance factor was calculated from the sum of the empirical ionic radii given in the above-mentioned samples. Different values of  $t$  for same compounds can be found in the literature, due to the different sources taken for ionic radii data.
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