Volume and Anisotropic Spontaneous Striction in Layered Manganites: Role of Charge Localization and Magnetic Interactions

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Thermal expansion measurements have been performed on single crystals of $R_{2-2x}Sr_{1+2x}Mn_2O_7$ (R = Pr, Nd, and Dy) over a wide temperature range (4–900 K). Our analysis allows us to give a general explanation for the large lattice anomalies observed in the layered manganites. Localization of the carriers gives rise to volume and anisotropic anomalies in the paramagnetic regime. The anisotropic distortion is enhanced with the establishment of long-range antiferromagnetism, whereas it is quenched by long-range ferromagnetic order.

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Layered manganites with the general formula $(R/Sr)_{n+1}Mn_nO_{3n+1}$ $(n = 1, 2, \ldots)$ are parent compounds of the perovskite manganites ($n = \infty$). Recently, a great deal of attention has been focused on these materials, due to the observation of colossal magnetoresistance in these systems [1]. Their tetragonal layered crystallographic structure provides a very anisotropic and low-dimensionality character. Both effects interplay with the magnetotransport and can give rise to interesting phenomena in some compositions, such as the existence of low-field tunneling magnetoresistance in bulk single crystals [2]. Because of the strong coupling between the lattice and the orbital degrees of freedom that occurs in these manganite systems, a complete understanding of the magnetotransport properties requires a comprehensive knowledge of the lattice effects. Neutron diffraction [3–6] and dilatometry [7] experiments have provided evidence for the existence of a huge spontaneous anomalous thermal expansion (TE). In $Nd_{2-2x}Sr_{1+2x}Mn_2O_7$ ($x = 0.5, 0.45$) the gradual change in the lattice parameters seen close to the antiferromagnetic (AF) ordering temperature, has been attributed to an exchange striction effect [3]. In the La-Sr series, abrupt changes in lattice parameters have been reported to take place at the onset of ferromagnetism (FM) [4–7]. These anomalies, which are related to coherent lattice distortions, undergo a sign reversal at the $x = 0.36$ doping level [6,7], whereas the jump observed in the incoherent lattice effect is unaffected [6]. The application of a magnetic field in the La-Sr compounds leads to gigantic magnetoelastic effects near T_C [6,7]. In addition, for La-Sr $x = 0.4$, unusual TE effects have also been detected below $T \approx 300$ K [4].

There is still controversy concerning the possible mechanisms that give rise to the observed lattice effects. A better understanding requires answers to several questions, such as, is there any link between the sharp anomalies seen in the lattice parameters at T_C in La-Sr $x = 0.4$ with the anomaly observed at higher T? Is this anomaly also present in other layered manganite compounds? Is it simply a coincidence that the low-T anomalies in La-Sr and Nd-Sr are both observed close to the long-range magnetic ordering temperature? Finally, we should also reflect on whether the well-established mechanisms explaining the TE anomalies in 3D perovskites [8] are applicable in these more complicated systems. This paper is an attempt to find a more general explanation for the observed lattice behavior in these systems. With this aim we have performed a dilatometric study over a very wide temperature range (4–900 K) along the main symmetry directions of several single crystals of the layered manganites. Measuring up to temperatures where the behavior of the materials can be modeled using conventional theory allows us to make plain the magnitude of any anomalous contributions. This is essential in order to answer a fundamental question: whether the observed anisotropic anomalies also involve any *volume change*. This point, which has surprisingly been overlooked in previous studies of these systems, is a very important condition that has to be considered when building any reliable model of these materials.

We have selected for our study four compounds (that we will refer to as R-327), which are representative of the series from the point of view of their different low-T magnetic and transport properties. The compound $La_{1.2}Sr_{1.8}Mn_2O_7$ is a metallic FM ($T_C = 120$ K) [4], $Nd_{1.5}Sr_{1.5}Mn_2O_7$ is AF ($T_N = 190$ K), with metalliclike conduction and a spin-glass-like transition at $T_F = 50$ K [9], $PrSr_2Mn_2O_7$ is an insulating AF ($T_N = 130$ K, $T_F = 25$ K), and $DySr_2Mn_2O_7$ is an insulating paramagnet (PM) with $T_F = 30$ K [10]. The results for the TE of La-327 were obtained from the neutron diffraction data given in the work of Mitchell *et al.* [4]. Note that these compounds also possess different tetragonal deformations and preferential occupation of the R/Sr perovskite sites, as a consequence of their different doping level and size of the rare earth, which will reinforce the generality of our conclusions. The single crystals of R-327 with R = Pr, Nd, and Dy were grown in air in an IR image furnace

(NEC, SC-N35HD) using the floating-zone technique. The growth rate used was 7–8 mm h^{-1} with the feed and seed rods counterrotating at 30 rpm. The single crystals were oriented and cut along the symmetry directions in order to perform the TE characterization in the range $4 \leq T \leq 900$ K. A strain-gauge technique was used in the range $T \leq 300$ K. A commercial quartz push rod with a linear transducer setup was used for the TE measurements in the high-T range. Our TE measurements are in good agreement with neutron diffraction results, as has been observed by comparing the in-plane TE of a $NdSr_2Mn_2O_7$ single crystal and the data published for the magnetically ordered phase of a sample of the same nominal composition in Ref. [3].

X-ray powder diffraction confirmed that all of the compounds have a tetragonal structure (space group $I/4mmm$). The TE was observed to be isotropic within the ab plane. Thus, uniaxial (cylindrical) symmetry is a good approach. In the following we will consider $(\Delta l/l)_{ab}$ as the TE measured along any direction within the ab plane and $(\Delta l/l)_c$ as the TE along c. In Fig. 1 we show $(\Delta l/l)_c$ (a) and $(\Delta l/l)_{ab}$ (b) for some compounds of the series. A large anisotropy in the TE is observed, as expected for a tetragonal structure. We observe that, for high enough T, all the curves display a linear behavior. The anharmonic phonon contribution to the TE has been calculated using the Grüneisen-Debye (GD) model. We have assumed $\theta_D = 500$ K, which is a typical value for the manganites (see [8] and references therein) and fitted to the slope of the experimental curves in the high-T range (dashed lines). A smooth divergence from the GD law appears with cooling below a certain value, T^*, of about 800 K in Dy-327 and 550 K in the other samples. This unusual behavior, which becomes very marked at low T, is characterized by a contraction of the in-plane distances which is smaller than expected from the GD law (in some cases an expansion is even observed) and stronger along c. Note that the anomalous TE reaches values as large as $(\Delta l/l)_c = -0.33\%$ in Pr-327. By subtracting the calculated phonon contribution, we isolate the anomalous TE contribution. We have performed the analysis in terms of the normal strain modes of the cell assuming uniaxial symmetry. Combining the measurements along the main symmetry directions, the anomalous deformation is separated into the isotropic volume change ω [see schema in Fig. 2(a), upper panel] and the anisotropic deformation λ, which describes the change in the c/a ratio and is volume independent [Fig. 2(a), lower panel]. These strain modes, ω and λ, can be shown to be proportional to $2(\Delta l/l)_{ab} + (\Delta l/l)_c$ and $(\Delta l/l)_c - (\Delta l/l)_{ab}$, respectively [11]. A large anomalous volume striction ω of positive sign is observed in all the compounds studied (Fig. 2, upper panels). By linking it, we observe a negative anisotropic anomalous TE (Fig. 2, lower panels). This means that these systems undergo a smooth change of shape into a less elongated unit cell. In La-327, ω and λ were obtained by analyzing the data from Ref. [4]. The high-T anomaly had been reported to take place only along the a direction. Nevertheless, our quantitative GD analysis reveals that the anomaly affects both the a (b) and c directions, giving rise to the volume and shape anomalies displayed in Fig. 2(a).

A trend of increasing values of ω and T^* is observed on moving from left to right in the upper panels in Fig. 2, i.e., with decreasing R radius. We see very clearly that the gigantic anisotropic striction effects reported at the

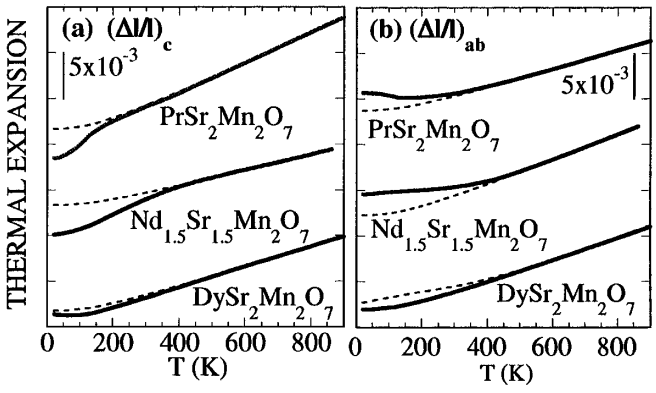

FIG. 1. TE vs temperature measured along the c direction (a) and along a direction lying on the ab plane (b) for different compounds of the series (solid lines). The phonon contribution calculated using a Grüneisen-Debye model with $\theta_D = 500$ K is also displayed (dashed lines).

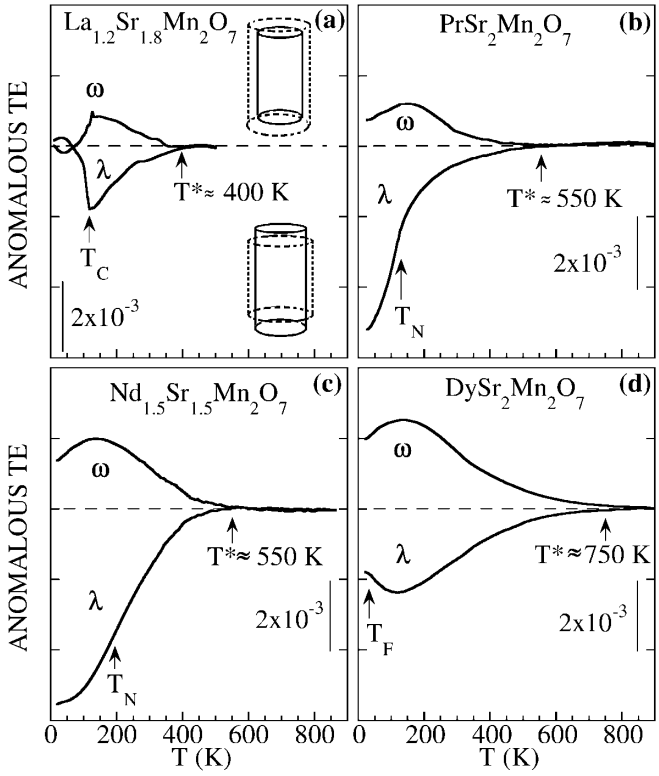

FIG. 2. Anomalous volume (ω) and anisotropic (λ) contributions to the thermal expansion in the indicated compounds.

FM transition in La-327 also involve a very sharp change in volume, which is *suppressed* at $T \leq T_C$. The compounds without long-range FM ordering display qualitatively similar volume anomalies, with a smooth maximum in $\omega(T)$ within the range 100–200 K. For Dy-327, where the anomalous effect extends to very high T, we do not rule out the possibility that ω is slightly underestimated.

The anomalous anisotropic deformation displays a more complex behavior than that described above for the anomalous volume deformation, with very different contributions depending on the compound (Fig. 2, lower panels). While in La-327, λ collapses at the FM transition together with ω, it reaches especially large values in Nd- and Pr-327, approximately double than in Dy-327. In the La-Sr compounds the unusual distortion is quenched in the metallic regime established below T_C. This behavior is similar to that observed in the cubic manganites [8]. An interesting point is the close resemblance between the observed T dependence of λ in La-327, and the T dependence of the distortion of its MnO_6 octahedra as given in Ref. [6]. By extending this result to the rest of compounds, this implies that the anisotropic deformation in layered manganites must be dominated by the distortion of the MnO_6 octahedra.

A clear qualitative difference is observed in the anomalous TE of Dy- and La-327 vs Nd- and Pr-327. In the former compounds, λ and ω show a strikingly symmetric behavior with respect to the horizontal axis, with a maximum in both ω and the absolute value of λ. In contrast, the pattern becomes very asymmetric in Nd- and Pr-327 at low T, with a large monotonous decrease of λ. This points to the existence of *two possible contributions to the anisotropic TE* λ. One of them (λ_{PM}) shows the same T dependence as ω and scales with T, $\lambda_{PM}(T) \propto -\omega(T)$. The other, λ_{AF}, appears only in those compounds which exhibit long-range AF ordering, and shows no correlation with the volume change. In Fig. 3 we have represented these separate contributions. Following our discussion, $\lambda_{PM}(T)$ has been determined by scaling $-\omega(T)$ to coincide with the total contribution λ in the high-T PM range. Taking the difference of these two quantities we obtain the anisotropic low-T contribution $\lambda_{AF} = \lambda - \lambda_{PM}$. Note that the magnitude of λ_{PM} increases sharply at T_N for Pr-327. This is also reflected in the increase of the in-plane distances seen for this compound in Fig. 1(b). We have observed similar in-plane TE anomalies for $Pr_{1.2}Sr_{1.8}Mn_2O_7$ and $NdSr_2Mn_2O_7$, close to their AF ordering temperatures (210 and 140 K, respectively [10]). The change in λ_{AF}, at the onset of AF order in Nd-327, is not as sharp as in Pr-327, but this contribution also becomes extraordinarily large near T_N. The existence of long-range AF ordering must undoubtedly be connected with the observed low-T enhancement in λ. This conclusion is reinforced by the behavior of Dy-327: PM over most of the temperature range studied, it does not show any additional enhancement of λ at low T [see Fig. 3(d)]. The spin-freezing transition at 30 K has no detectable effect on the TE.

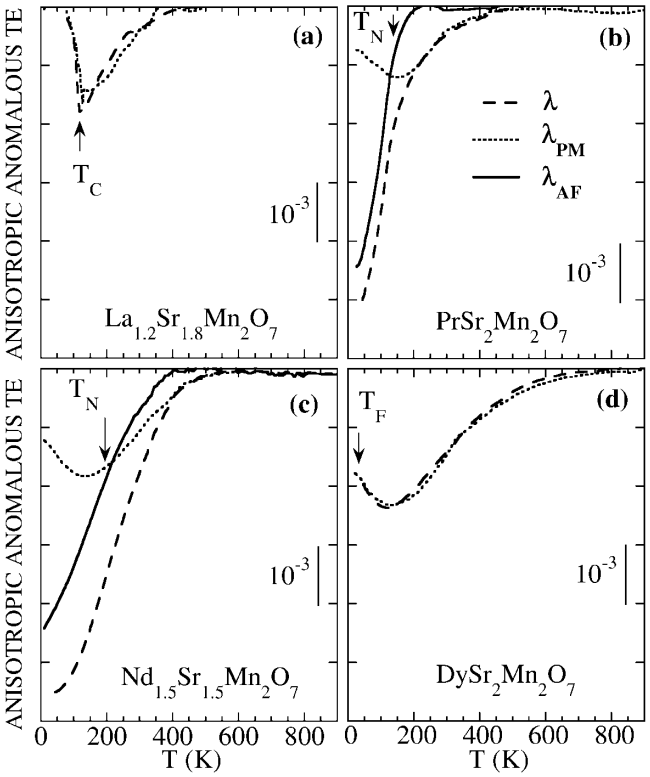

FIG. 3. Estimated components of the anisotropic TE contribution λ (see text): λ_{PM} anisotropic component linked to localization, λ_{PM} component linked to long-range AF order.

Let us now discuss the possible mechanisms producing the different contributions to the anomalous TE. The observed correlation between ω and λ_{PM} suggests a common origin for these two quantities. The behavior of incoherent lattice distortions at T_C observed in the La-Sr series points to the existence above T_C of a fully distorted $Mn^{3+}O_6$ (and undistorted $Mn^{4+}O_6$) octahedra [6]. This is a consequence of the removal of the degeneracy of the orbital degrees of freedom by the tetragonal crystal field, and is allowed due to the adiabatic behavior of the carriers in this temperature range. A Fermi level energetically lower than this energy splitting would lead to a preferential occupation of one of the orbital states. This can explain the anisotropic component, λ_{PM}, in the PM regime. We propose that the localized Mn^{3+}/Mn^{4+} regime in the layered manganites starts below T^*. As in the case of the cubic manganites, the anomalous volume of the octahedra increases as a consequence of the carrier localization. This isotropic increase of the relative distances disappears abruptly when the potential energy is transformed into the kinetic energy gain of the carriers at T_C. The fact that no collapse of the volume anomaly is observed at the insulator-metal-like transition in Nd-327 can be understood by taking into account the large resistivity value of this compound within the whole T range [9]. This apparent incoherence between the transport and

lattice behavior can be understood by assuming the existence of electronic phase segregation. In fact, experimental evidence for the existence of metallic and charge localized phases has been recently given for $LaSr_2Mn_2O_7$ [12].

Within the above described framework we can also explain how λ_{PM} can change sign and become positive in the metallic La-Sr compounds at low doping levels [6,7] (the total anisotropic deformation λ is in these compounds, given by the only contribution λ_{PM}). The existence of a volume anomaly can be clearly inferred in all the cases, even for the critical composition $x = 0.36$, where no anisotropic lattice effects have been observed [6,7]. The localization mechanism is thus present throughout the series. The different sign displayed by λ_{PM} is consistent with the fact that uniaxial and planar Mn anisotropies entail corresponding axial and planar lattice distortions, due to the preferential occupation of one of the two possible orbital states, namely, $3d_{z^2-r^2}$ and $3d_{x^2-y^2}$ [7]. La-Sr $x = 0.3$ belongs to the first case, with $\lambda_{PM} > 0$, whereas La-Sr $x = 0.4$ and all of the other compounds studied here display (spontaneous) planar Mn anisotropy [3,9,13,14] and $\lambda < 0$.

The explanation of the lower T enhancement of the anisotropic deformation (λ_{AF} contribution) must take into account the observed correlation with the establishment of long-range AF ordering. This suggests the possibility of a role for an exchange-striction mechanism [3]. However, this argument does not seem very plausible from a quantitative point of view, as the transverse fluctuations of the magnetization at the magnetic ordering temperatures usually produce very small TE effects. Exceptions occur in those systems in which longitudinal fluctuations of the magnetization give way to localized moments, as in the case of Invar systems or when there is a structural transition at the ordering temperature. This does not appear to be the case in the layered manganites [3,4]. The lack of an additional effect accompanying the rare-earth ordering taking place at lower T, as well as the lack of a correlated volume anomaly, is also against an exchange-striction mechanism. The possibility that λ_{AF} is due to a charge-orbital ordering transition is very unlikely. Its existence would imply an additional contribution to the volume anomaly, which is not observed.

We will argue a possible explanation for λ_{AF} in the following discussion. It can be expected that the localization of the carriers below T^* is associated with AF correlations which inhibit the hopping of charge carriers. Evidence for the existence of AF in-plane correlations in the PM range of La-327 has been, in fact, reported [15]. The T dependence found for λ ($= \lambda_{PM}$) is very similar to the intensity of these AF correlations. This connection would confirm that the local symmetry reduction following the AF short-range order should imply a local orbital order with the consequent lattice distortion [15]. The enhancement of λ with long-range AF order (giving rise to λ_{AF}) can then be explained as a reinforcement of the same effect, whereas ω and λ become negligible in the presence of long-range FM ordering. The effects observed with the application of a magnetic field on the TE are compatible with this explanation. In La-Sr, the magnetic field induces a collapse of the anomalous TE near to T_C, giving rise to large magnetostriction in the paramagnetic phase [7]. Application of magnetic field in the AF compounds does not lead to an abrupt collapse but to an enhancement of the lattice anomaly [16]. There is still controversy about the existence, order of magnitude, and type of AF ordering in the La-Sr compounds [17–19]. The existence of AF correlations above T_N also needs to be studied in the relevant T range [20].

In summary, the large anomalous contribution to the TE observed in single crystals of layered manganites has two important components. The first appears at high T, and involves both volume (ω) and anisotropic (λ_{PM}) lattice changes. We propose that the gradual localization of carriers well above room temperature, which is probably linked to AF correlations, is responsible for this contribution and has an anisotropic character due to a preferential occupancy of the orbital states. A substantial additional anisotropic contribution (λ_{AF}) is found in the AF compounds close to T_N. The lattice anomalies are quenched in the FM compounds below T_C, as a consequence of the carrier delocalization.

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