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Magnetic ordering effects in the Raman spectra of $La_{1-x}Mn_{1-x}O_3$

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Temperature-dependent Raman spectra of polycrystalline $La_{1-x}Mn_{1-x}O_3$ samples, referred to as $LaMnO_{3+\delta}$ for convenience, were correlated to their structural and magnetic properties for different δ. For $\delta \leqslant 0.05$, a *softening* of the $\sim 610\ cm^{-1}$ Raman mode is observed below the magnetic ordering temperature. This *softening* is reduced as δ increases from 0.00 to 0.05. This behavior is not associated with lattice anomalies, and is interpreted in terms of a spin-phonon coupling caused by a phonon modulation of the superexchange integral. A quantitative analysis of this effect is presented. [S0163-1829(99)10737-9]

In recent years, much effort has been devoted to understanding the physics involved in the transport and magnetic phenomena of perovskite manganites. It was claimed that the early double-exchange (DE) theory[1] cannot explain quantitatively the large conductivity drop near the ferromagnetic-paramagnetic (FM-PM) transitions for doped compounds.[2] The presence of lattice polarons, possibly enhanced by the strong Jahn-Teller character of the Mn^{3+} ion, has been invoked to explain the large change in electron kinetic energy at $T \sim T_C$,[2] as well as other anomalous physical properties of these materials.[3–5] Such polarons are expected to be present when $\tau_h > \omega_\alpha^{-1}$, where τ_h is the electron transfer time and ω_α is the frequency of an optical-mode lattice vibration associated with a dynamic Jahn-Teller distortion,[6] i.e., a stretching mode. Therefore, lattice vibrations possibly play an important role in the conduction mechanism of this class of materials. Although the parent compound $LaMnO_3$ is an antiferromagnetic (AFM) insulator, the study of the lattice and magnetic properties of this material may be taken as a starting point to a consistent understanding of the more complex physical properties of the doped compounds.

Perovskites with an orthorhombic *Pnma* space group present 24 Raman active modes $(7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g})$. Lattice dynamical calculations and assignment of the Raman modes of $LaMnO_3$ were done previously by Iliev *et al.*[7] In a recent work, we reported a *softening* of the 604 cm^{-1} stretching mode below T_N for the orthorhombic $LaMnO_{3.0}$,[8] also observed by others.[9] This effect was associated with spin-phonon interactions,[9] and exchange striction effects.[8] Nevertheless, a detailed study that explains the *softening* of the 604 cm^{-1} stretching mode in $LaMnO_3$ is still missing. In this work, we present Raman and x-ray studies of the $LaMnO_{3+\delta}$ controlled oxygen content series ($\delta \leqslant 0.07$). We conclude that the observed anomalous shifts for the $\sim 610\ cm^{-1}$ mode in the samples with $\delta \leqslant 0.05$ are due to a phonon modulation of the xz-plane superexchange integral and not to the lattice anomalies observed below the magnetic transitions. From a first-neighbors contribution, we obtain the value of the second derivative of the xz-plane superexchange integral with respect to the stretching oxygen displacements in the Mn-O(xz) direction.

In this paper, for simplicity, the nomenclature $LaMnO_{3+\delta}$ is used. However, we should mention that the O^{2-} ions cannot be accomodated interstitially in the lattice. Thus, from a crystallographic point of view, the correct formula for this series is $La_{1-x}Mn_{1-x}O_3$ with $x \sim \delta/3$.[10] General properties of cation-deficient samples with the $La_{1-x}Mn_{1-y}O_3$ formula have been systematically studied in the literature.[10–14]

The $LaMnO_{3+\delta}$ samples studied in this work were grown by different methods. Samples with $\delta = 0.00$, 0.03, 0.05, and 0.07 were prepared following the nitrate decomposition method using Mn and La_2O_3 as starting materials.[15] The sample referred to as $LaMnO_3$: Ar annealed was prepared by standard ceramic methods, heating stoichiometric mixtures of the corresponding oxides.[16] The structure and phase purity of the samples were checked by x-ray powder diffraction. Well resolved x-ray patterns were obtained with Cu $K\alpha$ radiation of a Rigaku conventional source and a high-resolution diffractometer with low-temperature attachment. Lattice parameters were obtained using a Rietveld refinement program.[17] Magnetization (dc/ac) measurements have been taken in a Quantum Design PPMS magnetometer. Details of the Raman experimental setup are given elsewhere.[8] Except for the x-ray experiments, all the measurements as a function of T were done with increasing temperature.

A summary of the structural and magnetic properties of the studied samples is given in Table I. The Ar annealed sample and those with $\delta = 0.00$ and 0.03 are mainly AFM with a FM component that increases with δ. For simplicity, we will refer to all these samples as AFM. The sample with $\delta = 0.07$ is FM. Finally, the sample with $\delta = 0.05$ presents a complex magnetic behavior that can be ascribed to frustrated FM or mixed FM/AFM phases.[15] All the samples studied in this work present orthorhombic $Pnma$ crystal structure between 15 and 300 K.

TABLE I. Magnetic and structural data for the samples studied in this work.

Sample	Magnetic properties: Magnetic ordering	Magnetic properties: Critical temperature	Structural properties $T=300$ K: **a** (Å)	**b** (Å)	**c** (Å)	**V**/f.u. (Å^3)
$LaMnO_3$ [a]	AFM	$T_N=141$ K	5.724(1)	7.696(1)	5.534(1)	60.95(3)
$LaMnO_{3.00}$	AFM	$T_N=138$ K	5.702(1)	7.702(1)	5.538(1)	60.80(3)
$LaMnO_{3.03}$	AFM	$T_N=124$ K	5.645(1)	7.721(1)	5.540(1)	60.37(3)
$LaMnO_{3.05}$	Complex	$T_C=115$ K	5.595(1)	7.746(1)	5.538(1)	60.00(3)
$LaMnO_{3.07}$	FM	$T_C=162$ K	5.533(1)	7.789(1)	5.538(1)	59.67(3)

[a] Ar annealed.

The Raman spectra at $T=10$ K of the Ar annealed and $\delta=0.00$ samples are similar to that reported by us for $LaMnO_{3.0}$.[8] As δ increases we observe (i) a broadening of all the Raman modes and (ii) a systematic shift of the 292 and 604 cm^{-1} modes in the Ar annealed sample to 270 and 616 cm^{-1}, respectively, in the $\delta=0.07$ sample. These effects are somewhat similar to those observed in the $La_{1-x}Sr_xMnO_3$ system for increasing x.[9]

The T dependence of the frequency of the ~ 610 cm^{-1} Raman mode is shown in Fig. 1 for all studied samples. This mode was associated to an in-phase stretching vibration of $O^{2-}(xz)$ ions against Mn^{3+} ions.[7] For $\delta \leqslant 0.05$, an anomalous *softening* of this mode is observed near and below the magnetic ordering temperature. This *softening* is reduced as δ increases. For the FM $\delta=0.07$ sample, no change in the behavior of the ~ 610 cm^{-1} mode is observed below T_C, within our experimental resolution.

Figure 2 shows the T dependence of the $Pnma$ lattice parameters **a**, **b**/$\sqrt{2}$, and **c** and the unit cell volume **V** for the $\delta=0.00$ and 0.07 samples. Although the T variation of lattice parameters of samples with similar values of δ has been previously reported,[11] our samples present different behavior of the **a** and **c** ($Pnma$) parameters as compared to the **b** and **a** ($Pbnm$) published parameters.[11] Despite these differences, some common features in the T dependence of the lattice parameters for the samples studied in both works can be found. Small anomalies are observed in the lattice parameters for the AFM $\delta=0.00$ sample below T_N, which may be associated with exchange strictive effects near T_N. For the FM $\delta=0.07$ sample, large lattice parameter anomalies are found around T_C that may be due to charge ordering effects.[11] Despite the lattice parameter changes found for our samples, within our experimental resolution, no anomaly has been observed on the unit cell volume near the magnetic ordering.

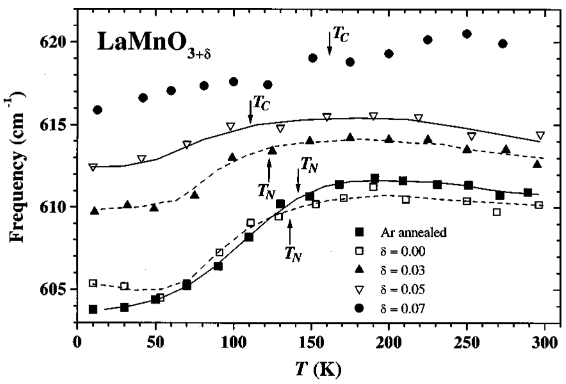

FIG. 1. Temperature dependence of the frequency for the ~ 610 cm^{-1} stretching mode, for the Ar annealed and $\delta=0.00$, 0.03, 0.05, and 0.07 samples. Dashed and continuous lines are guides to the eyes.

In magnetic materials, the frequency change of a phonon α with T can be written as

$$\omega_\alpha(T)-\omega_\alpha(T_0)\equiv\Delta\omega_\alpha(T)=(\Delta\omega_\alpha)_{latt}+(\Delta\omega_\alpha)_{anh}+(\Delta\omega_\alpha)_{ren}+(\Delta\omega_\alpha)_{s\text{-}ph}. \tag{1}$$

The first term on the right-hand side is the contribution to the phonon frequency of the change of the ionic binding energies due to the lattice expansion/contraction. It is usually approximated by the Grüneisen law:

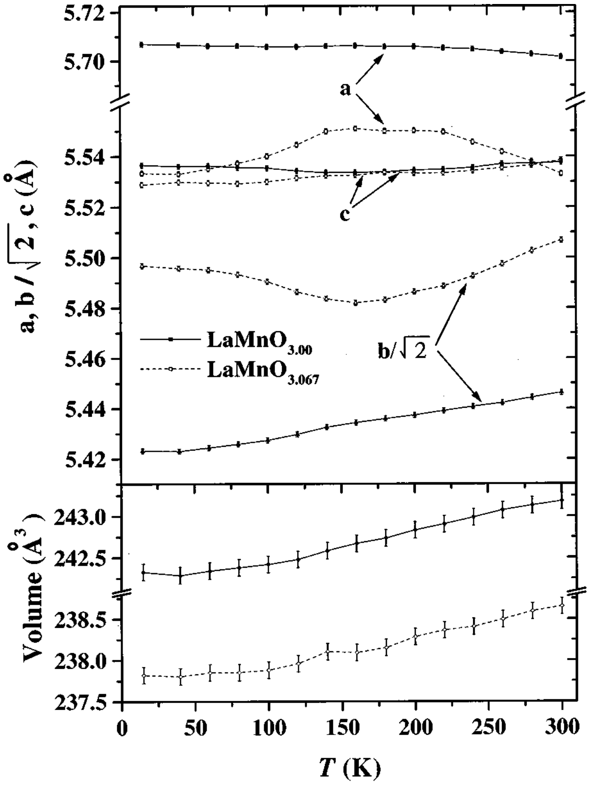

FIG. 2. Temperature dependence of the lattice parameters **a**, **b**/$\sqrt{2}$, and **c** and of the *Pnma* unit cell volume **V** for the $LaMnO_{3.00}$ (continuous lines) and $LaMnO_{3.07}$ (dashed lines) samples.

$$\left(\frac{\Delta\omega_\alpha}{\omega_\alpha}\right)_{latt} = -\gamma_\alpha\left(\frac{\Delta \mathbf{V}}{\mathbf{V}}\right), \tag{2}$$

where γ_α is the Grüneisen parameter for the normal mode α. Equation (2) is applicable for cubic crystals or for isotropically expanded lattices. However, for the system studied here this is not applicable (see Fig. 2), and one should also consider the possibility of phonon frequency shift due to lattice anomalies, even in the absence of a lattice unit cell volume change. The lattice expansion/contraction due to anharmonicity and/or magnetostriction effects are all included in $(\Delta\omega_\alpha)_{latt}$. The second term in Eq. (1), $(\Delta\omega_\alpha)_{anh}$, is the intrinsic anharmonic contribution, i.e., the anharmonic frequency shift at constant volume. The term $(\Delta\omega_\alpha)_{ren}$ accounts for the effect in the phonon α of a renormalization of the electronic states that may occur near the spin ordering temperature.[18,19] Finally, $(\Delta\omega_\alpha)_{s\text{-}ph}$, the spin-phonon contribution, is caused by the modulation of the exchange integral by lattice vibrations. This contribution was considered formally by Baltensperger and Helman for the europium oxide structure.[20] Below we adapt their formalism to the case of undoped perovskite manganites ($\delta\sim 0$).

In a nearest-neighbors approximation, the spin-averaged exchange energy for LaMnO$_3$ can be written as

$$H_{spin} \approx -\sum_{i,j>i} J_{ij}\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle, \tag{3}$$

where J_{ij} is the superexchange integral, $\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle$ is the scalar spin correlation function and the summation in j is over three nearest neighbors of the ith Mn ion such that each pair is not considered twice. Notice that the DE coupling energy is ignored in this treatment ($\delta\sim 0$), as well as the Dzyaloshinsky-Moriya and magnetocrystalline anisotropy energies. The change of J_{ij} due to the αth Raman active normal mode of vibration, ΔJ_{ij}^α, can be obtained by a second-order Taylor expansion on the O^{2-} displacements associated to that mode:

$$\Delta J_{ij}^\alpha(\mathbf{u}_k^\alpha(t)) = [\mathbf{u}_k^\alpha(t)\cdot\boldsymbol{\nabla}_k]J_{ij} + \tfrac{1}{2}[\mathbf{u}_k^\alpha(t)\cdot\boldsymbol{\nabla}_k]^2 J_{ij}, \tag{4}$$

where $\mathbf{u}_k^\alpha(t)$ is the displacement vector from the equilibrium positions of the kth O^{2-} ion, placed between the ith and jth Mn^{3+} ions, for the αth normal mode of vibration. Notice that we have assumed first neighbors interactions only. Inserting Eq. (4) into Eq. (3) and considering the Hamiltonian $H = H_{latt} + H_{spin}$, the total potential energy of a Raman-active normal mode α is separated into ''lattice'' and ''spin'' contributions, where the ''spin'' term may be written in the form

$$U_{spin}^\alpha = \frac{1}{2}\sum_k \mathbf{u}_k^\alpha(t)\mathbf{D}_{spin}\mathbf{u}_k^\alpha(t). \tag{5}$$

The angular frequency shift of the phonon due to magnetic ordering is then given by

$$(\Delta\omega_\alpha)_{s\text{-}ph} = \frac{1}{2\mu_\alpha\omega_\alpha}\sum_k \hat{\mathbf{u}}_k^\alpha\mathbf{D}_{spin}\hat{\mathbf{u}}_k^\alpha, \tag{6}$$

where μ_α is the reduced mass and $\hat{\mathbf{u}}_k^\alpha = \mathbf{u}_k^\alpha/|\mathbf{u}_k^\alpha|$.

Undoped LaMnO$_3$ presents *Pnma* crystal structure, and in this case we can write

$$(\Delta\omega_\alpha)_{s\text{-}ph} = -\frac{N}{2\mu_\alpha\omega_\alpha}\{2\langle\mathbf{S}_i\cdot\mathbf{S}_j\rangle_{xz}[\hat{\mathbf{u}}_{\mathrm{O}1}^\alpha(t)\cdot\boldsymbol{\nabla}_{\mathrm{O}1}]^2 J_{xz} + \langle\mathbf{S}_i\cdot\mathbf{S}_j\rangle_y[\hat{\mathbf{u}}_{\mathrm{O}2}^\alpha(t)\cdot\boldsymbol{\nabla}_{\mathrm{O}2}]^2 J_y\}, \tag{7}$$

where N is the number of Mn^{3+} ions and O1 and O2 refer to an xz-plane and a y-direction O^{2-} ion, respectively. Notice that for undoped LaMnO$_3$ the magnetic coupling is FM in the xz plane and AFM in the y direction.[21] Thus, in a molecular field approximation, we have $\langle\mathbf{S}_0\cdot\mathbf{S}_1\rangle_{xz} \approx 4[M_{sublatt}(T)/4\mu_B]^2$, where $M_{sublatt}(T)$ is the FM sublattice magnetization per Mn^{3+} ion. Taking into consideration xz-plane stretching vibrations, Eq. (7) reduces to

$$(\Delta\omega_{stret})_{s\text{-}ph} \approx -\frac{2}{m\omega_\alpha}\frac{\partial^2 J_{xz}}{\partial u_{stret}^2}\left(\frac{M_{sublatt}(T)}{4\mu_B}\right)^2, \tag{8}$$

where m is the oxygen mass.

To analyze the origin of the observed *softening* for the 604 cm^{-1} stretching mode of the AFM samples, we first consider the lattice contribution $(\Delta\omega_\alpha)_{latt}$ in Eq. (1). Assuming that the energy of an **ac**-plane O(xz) stretching mode is mainly determined by the binding between Mn and O(xz) ions, a *softening* of this mode below T_N would be consistent with (i) an increase of the Mn-O(xz) bond lengths and/or (ii) a decrease of the Mn-O(xz)-Mn bonding angle. The T dependence of the D_{2h}^{16} (*Pnma*) lattice parameters **a**, **b**$/\sqrt{2}$, and **c**, of the $\delta = 0.00$ sample (see Fig. 2) shows a small increase of 0.005 Å of the **c** parameter, while the **a** parameter remains nearly constant below $T_N = 138$ K. This behavior is not consistent with either (i) or (ii). Actually, it may be associated with a decrease of the angle between the **ac** plane and the plane defined by the Mn^{3+} and the four surrounding O(xz) ions, due to exchange strictive effects, and therefore to an increase of the Mn-O(xz)-Mn bonding angle. Another indication that the lattice contribution is not important is the fact that the $\sim$610 cm^{-1} Raman mode is quite insensitive to lattice parameter variations. Notice that, within our experimental resolution, the stretching mode frequency of the sample with $\delta = 0.07$, with strong lattice anomalies below $T_C = 162$ K (see Fig. 2), does not show any anomaly below

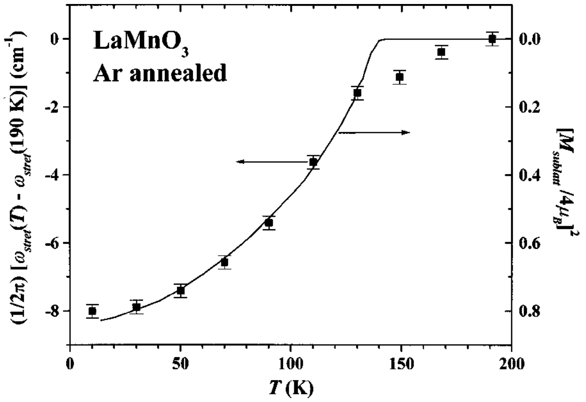

FIG. 3. Squares: Temperature dependence of the shift of the frequency of the 604 cm^{-1} mode with respect to its value at $T = 190$ K, $\frac{1}{2\pi}[\omega(T) - \omega(190\ \mathrm{K})]$, for the LaMnO$_3$: Ar annealed sample. Line: $[M_{sublatt}(T)/4\mu_B]^2$ for an AFM LaMnO$_3$ sample with $T_N = 140$ K (taken from Ref. 12).

this temperature (see Fig. 1). Also, the frequency of this mode for the sample with $\delta = 0.00$ is nearly constant for $150 < T < 300$ K, where the lattice changes are of the same order of those observed below 150 K. Therefore, the lattice term in Eq. (1), $(\Delta\omega_\alpha)_{latt}$, cannot explain the observed shift of the ~ 610 cm^{-1} stretching mode below T_N for the AFM $LaMnO_{3+\delta}$ samples. Besides, the observed anomalous *softening* cannot be explained by the pure anharmonic term in Eq. (1), $(\Delta\omega_\alpha)_{anh}$, since no anomaly is observed in the linewidth of the ~ 610 cm^{-1} peak, within our experimental resolution.[8] Finally, the well-known insulating character of near-stoichiometric $LaMnO_3$ for all temperatures[11] indicates that our AFM samples do not present any effect of renormalization of electronic states near T_N. Therefore, we suggest that the magnetic term in Eq. (1), $(\Delta\omega_\alpha)_{s\text{-}ph}$, is responsible for the anomalous behavior of the stretching mode in the AFM $LaMnO_{3+\delta}$ samples.

Figure 3 shows the frequency shift of the stretching ~ 610 cm^{-1} mode relative to its value at $T = 190$ K, $\frac{1}{2\pi}[\omega(T) - \omega(190\text{ K})]$, for the Ar annealed sample. This sample proved to be our most homogeneous sample, i.e., the sample which presented the smallest frequency change of the ~ 610 cm^{-1} Raman mode for light focused in different regions of the sample. The shift was scaled to the normalized square of the sublattice magnetization, $[M_{sublatt}(T)/4\mu_B]^2$, taken from Ref. 12 for a similar $LaMnO_3$ sample with $T_N = 140$ K. The scaling is remarkably good, and consistent with Eq. (8). This proves that the anomalous shift of the frequency of the stretching Raman mode is actually due to spin-phonon interactions. From the data of Fig. 3 and Eq. (8), we obtain $(\partial^2 J_{xz}/\partial u_{stret}^2) = +16$ mRy/Å^2.

The actual magnetic moments alignment in the ground state of $LaMnO_3$ has been the subject of current research.[22–24] It was suggested that J_{xz} and J_y are rather sensitive to the strength of the Jahn-Teller distortion, quantified by the ratio between the long and short Mn-O bonds.[22] In-plane stretching vibrations modulate this ratio, therefore the $(\partial^2 J_{xz}/\partial u_{stret}^2)$ value obtained for the stoichiometric sample may become an important parameter to be taken into consideration when modeling the magnetic structure of this compound. The reduction of the *softening* of the ~ 610 cm^{-1} mode as δ increases indicates that $(\partial^2 J_{xz}/\partial u_{stret}^2)$ decreases as the cooperative Jahn-Teller distortion is reduced (see Table I).

In summary, the Raman spectra of $LaMnO_{3+\delta}$ were analyzed in terms of their structural and magnetic properties. The anomalous *softening* of the ~ 610 cm^{-1} stretching mode observed below the magnetic ordering for the orthorhombic samples with $\delta \leqslant 0.05$ was ascribed to a phonon modulation of the nearest-neighbors exchange integral. From our data, we found that $(\partial^2 J_{xz}/\partial u_{stret}^2) = +16$ mRy/Å^2 for the Ar annealed sample. The value of this constant may help the modeling of the magnetic structure in this material.

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