

## Phonon Raman scattering in $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ ( $x = 0, 0.2, 0.3, 0.4,$ and $1.0$ )

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The Raman-active phonons in perovskite-like  $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$  ( $x = 0, 0.2, 0.3, 0.4,$  and  $1.0$ ) were studied by measuring Raman spectra at temperatures of 295 and 5 K. The changes in the spectra with Co doping are correlated with the decrease of orthorhombic distortions. Surprisingly more phonon lines than allowed for the rhombohedral  $\text{LaCoO}_3$  structure were observed.

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The manganese perovskites of the type  $\text{R}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{R} = \text{rare earth}, \text{A} = \text{Ca}, \text{Sr}, \text{Ba}, \text{or Pb}$ ) have been subject of scientific investigations for many decades. Recently, this interest has been renewed due to the observation of a colossal magnetoresistance [1,2], charge, spin, and orbital ordering effects as a function of  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio [3–5]. Another system, Mn-site-doped, with the composition  $\text{LaMn}_{1-x}\text{D}_x\text{O}_3$  ( $\text{D} = \text{Cr}, \text{Fe}, \text{Co}, \text{or Ni}$ ) was intensively studied in the 60's, but colossal magnetoresistance was not mentioned in them until the 90's [6]. While Raman spectra of La-site-doped compounds have been reported in numerous of publications [7–13], surprisingly nothing was done on Mn-site-doped compounds. In this work we report the results of an optical phonon study in the perovskite oxides  $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$  ( $x = 0, 0.2, 0.3, 0.4,$  and  $1.0$ ). The end member of this system, namely  $\text{LaCoO}_3$  has been the subject of continuing interest since the 50's due to unusual magnetic properties and two spin-state transitions [14,15].

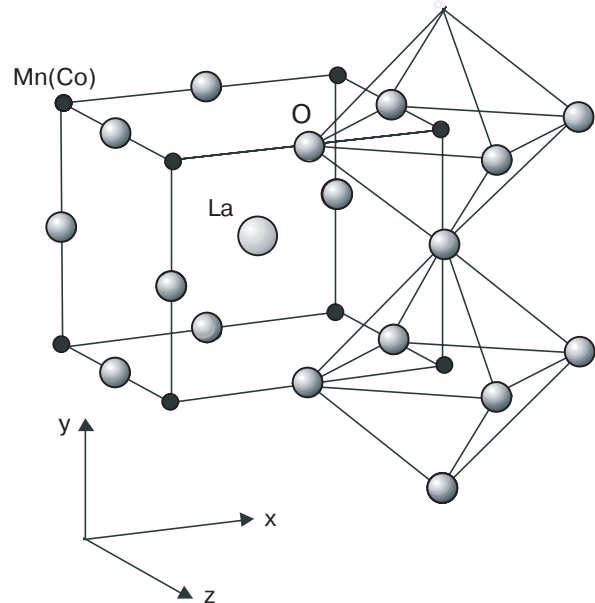


Fig. 1. Unit cell of the simple perovskite structure.

Factor group analysis and selection rules for the zone-center vibrational modes of orthorhombic LaMnO<sub>3</sub> and rhombohedral LaCoO<sub>3</sub>

Sample and space group	Atom	Number of equivalent positions (Wyckoff notation)	Site symmetry	Irreducible representation of modes	Activity and selection rules
LaMnO <sub>3</sub> <i>Pnma</i> ( <i>D</i> <sub>2h</sub> <sup>16</sup> ) <i>Z</i> = 4	La	4(c)	<i>C</i> <sub>s</sub>	$2A_g + B_{1g} + 2B_{2g} + B_{3g} + A_u + 2B_{1u} + B_{2u} + 2B_{3u}$	$\Gamma_{\text{Raman}} = 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$
	Mn	4(b)	<i>C</i> <sub>i</sub>	$3A_u + 3B_{1u} + 3B_{2u} + 3B_{3u}$	$\Gamma_{IR} = 9B_{1u} + 7B_{2u} + 9B_{3u}$
	O <sub>1</sub>	4(c)	<i>C</i> <sub>s</sub>	$2A_g + B_{1g} + 2B_{2g} + B_{3g} + A_u + 2B_{1u} + B_{2u} + 2B_{3u}$	$\Gamma_{\text{acoustic}} = B_{1u} + B_{2u} + B_{3u}$ $\Gamma_{\text{silent}} = 8A_u$
	O <sub>2</sub>	8(d)	<i>C</i> <sub>1</sub>	$3A_g + 3B_{1g} + 3B_{2g} + 3B_{3g} + 3A_u + 3B_{1u} + 3B_{2u} + 3B_{3u}$	$A_g$ : $a_{xx}, a_{yy}, a_{zz}$ $B_{1g}$ : $a_{xy}$ ; $B_{2g}$ : $a_{xz}$ ; $B_{3g}$ : $a_{yz}$
LaCoO <sub>3</sub> <i>R</i> $\bar{3}c$ ( <i>D</i> <sub>3d</sub> <sup>6</sup> ) <i>Z</i> = 2	La	2(b)	<i>C</i> <sub>3i</sub>	$A_{1u} + 2A_{2u} + B_{2u} + 2E_u$	$\Gamma_{\text{Raman}} = A_{1g} + 4E_g$
	Co	2(a)	<i>D</i> <sub>3</sub>	$A_{2g} + A_{2u} + E_g + E_u$	$\Gamma_{IR} = 3A_{2u} + 5E_u$
	O	6(e)	<i>C</i> <sub>2</sub>	$A_{1g} + 2A_{2g} + 3B_g + 3E_g + A_{1u} + 2A_{2u} + 3E_u$	$\Gamma_{\text{acoustic}} = A_{2u} + E_u$ $\Gamma_{\text{silent}} = 3A_{2g} + 2A_{1u}$ $A_{1g}$ : $a_{xx} + a_{yy}, a_{zz}$ $E_g$ : $(a_{xx} - a_{yy}, a_{xy}), (a_{xz}, a_{yz})$

Raman scattering measurements were carried out in quasi-backscattering geometry using 514.5 nm argon laser line. The incident laser beam of 10 mW power was focused onto a 0.1 mm spot of the mirror-like chemically etched as grown crystal surface. The sample was mounted on the holder of a He-gas-flow cryostat using silver glue. The scattering light was analyzed with a DILOR XY triple spectrometer combined with a nitrogen-cooled CCD detector. The measurements were done in the  $xx(zz)$  scattering configuration, where  $x$  and  $z$  are the [100] and [001] quasicubic directions, respectively.

The structural properties of LaMn<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> were characterized in several publications [15–19]. The crystal structures of the end members, LaMnO<sub>3</sub> and LaCoO<sub>3</sub> were found to be orthorhombic (space group *Pnma*, *Z* = 4) [16] and rhombohedral (space group *R* $\bar{3}c$ , *Z* = 2) [17], respectively. The compounds with 0.15 <  $x$  < 0.50 have been found to be orthorhombic [18,19]. When  $x$  > 0.50 and near to 1.0, the compounds have a rhombohedral structure [19]. Around 0.5 doping level, the compounds show a mixture of two structural phases, the orthorhombic and rhombohedral [19]. The

idealized cubic perovskite structure of the LaMn(Co)O<sub>3</sub> crystal is shown in Fig. 1. The orthorhombic *Pnma* structure can be obtained by two consequent rotations of the Mn(Co)O<sub>6</sub> octahedra around the [010] and [101] directions of cubic perovskite. The rhombohedral *R* $\bar{3}c$  structure is generated by the rotation of the same octahedral about the cubic [111] direction.

Results of group-theoretical analysis for zone-center vibrations are presented in Table for orthorhombic LaMnO<sub>3</sub> and rhombohedral LaCoO<sub>3</sub>. Of the total 30  $\Gamma$ -point phonon modes, only 5 ( $A_{1g} + 4E_g$ ) are Raman active for rhombohedral LaCoO<sub>3</sub> structure and of 60  $\Gamma$ -point phonon modes, 24 ( $7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$ ) are Raman-active for orthorhombic LaMnO<sub>3</sub> structure. The increase in the phonon modes from 5 to 24 on going from rhombohedral to orthorhombic structure is due to (i) lowering of crystal symmetry which splits the doubly degenerate  $E_g$  modes into nondegenerate  $B_{2g} + B_{3g}$ , (ii) displacement of oxygen atoms into the lower symmetry site of the La-plane which introduces new Raman-active vibrations, (iii) doubling of the unit cell which folds the zone-boundary modes of the rhom-

bohedral structure into zone-center modes of the orthorhombic structure.

Raman spectra of  $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$  compounds at 295 K are shown in Fig. 2. Room temperature measurements, lattice dynamical calculations, and an assignment of the Raman modes of undoped  $\text{LaMnO}_3$  were done previously by Iliev et al. [20]. Our spectra of  $\text{LaMnO}_3$  are consistent with spectra at 300 K reported earlier [9,20]. Three broad bands centered near 280, 490, and 610  $\text{cm}^{-1}$  are observed. The line near 280  $\text{cm}^{-1}$  was assigned to a rotation-like mode [20]. The other two bands near 490 and 610  $\text{cm}^{-1}$  are related to Jahn-Teller octahedral distortions [20]. Given that the Jahn-Teller distortions are static and ordered in orthorhombic  $\text{LaMnO}_3$ , these bands are Raman-allowed modes of bending- and stretching-type character, respectively. The fourths peak in the spectrum at  $\sim 310 \text{ cm}^{-1}$  is associated with vibrations of the apex oxygen ( $\text{O}_1$ ) atoms along the  $x$  direction. The spectra of the  $x = 0.2, 0.3,$  and  $0.4$  samples look quite similar to the  $x = 0$  sample, except for the width and position of the bands in the region of 500 and 600  $\text{cm}^{-1}$ . At room temperature the spectra of the  $\text{LaCoO}_3$  sample exhibit peaks centered near 130, 160, 480, 555, 610, and 780  $\text{cm}^{-1}$ , and four broad bands at 70, 270, 340, and 400  $\text{cm}^{-1}$ .

Lowering the temperature, more phonon peaks become visible in the Raman spectra of  $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ . In Fig. 3 we present spectra measured at 5 K.

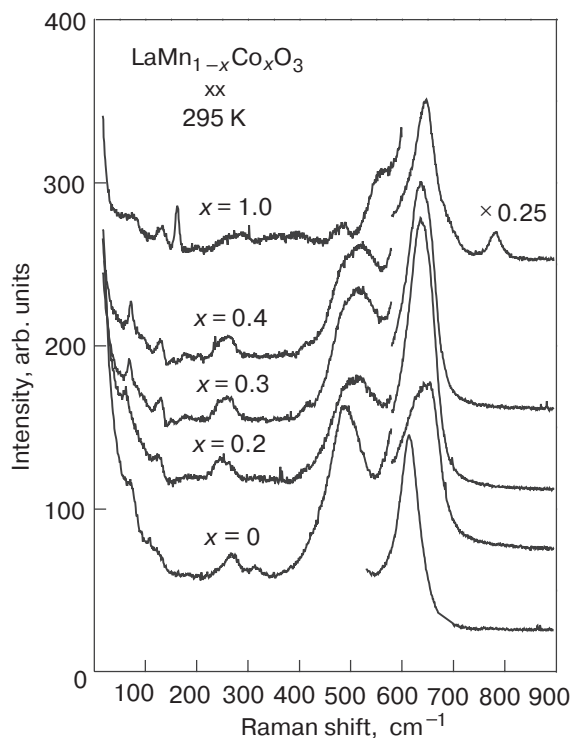


Fig. 2. Raman spectra of single crystals of  $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$  at 295 K. Spectra are shifted for clarity. The right part of the spectra are multiplied by a factor indicated there.

**$\text{LaMnO}_3$ :** The spectra on the  $\text{LaMnO}_3$  sample show 10 resolved peaks at 80, 110, 130, 154, 184, 257, 280, 314, 496, and 610  $\text{cm}^{-1}$ . The strong high frequency lines in the studied sample are broader than the corresponding lines in the spectra of measured earlier [9,20]. The reason for this broadening is the presence of a small amount of excess oxygen in our sample. Using x-ray diffraction, magnetic susceptibility, and chemical analysis, the oxygen content was estimated to be 3.071.

**$\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$  ( $x = 0.2, 0.3, 0.4$ ):** It is well known that Raman spectroscopy is a sensitive tool for the study of both local and spatially coherent structural changes. Spectra of the samples with  $x > 0$  differ from the one of pure  $\text{LaMnO}_3$  and in the following we will concentrate on the effect of Mn substitution by Co on the rotation-, bending-, and stretching-like vibrations of the  $\text{MnO}_6$  octahedra. The rotational mode at 280  $\text{cm}^{-1}$  in  $\text{LaMnO}_3$  shifts to lower energy ( $\sim 270 \text{ cm}^{-1}$ ) in the samples with  $x = 0.2, 0.3,$  and  $0.4$ . The frequency of this mode is a measure of the degree of the rotational distortions (the averaged angle of octahedral tilts). For example, comparing the spectra of more distorted  $\text{YMnO}_3$  and less distorted  $\text{LaMnO}_3$  a large shift from 396 to 284  $\text{cm}^{-1}$  was observed [20]. Therefore, the softening of the rotation-like mode with Co doping is the indication of an decreasing orthorhombic distortion.

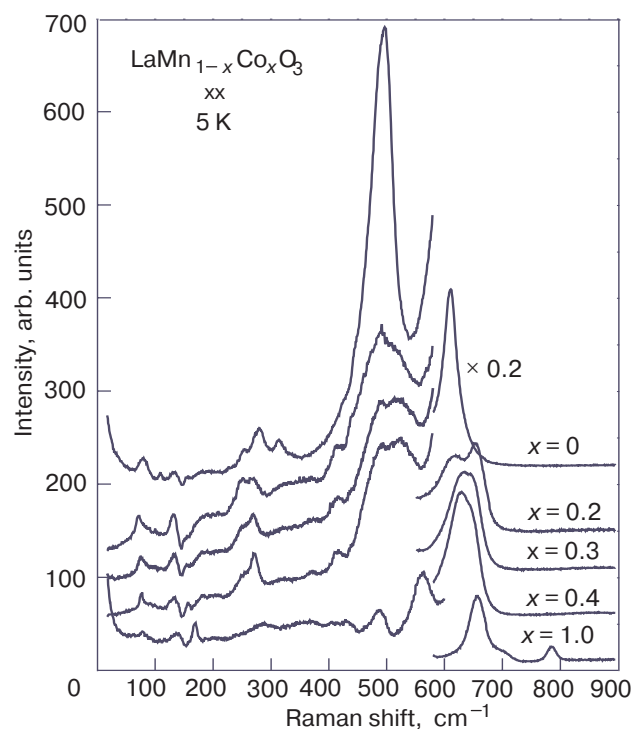


Fig. 3. Raman spectra of single crystals of  $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$  at 5 K. Spectra are shifted for clarity. The right part of the spectra are multiplied by a factor indicated there.

The scattering intensity of the phonon modes at 496 and 610  $\text{cm}^{-1}$  decreases in the Co-doped samples. The decreasing of intensity of these modes reasonably be related with the reduction of the Jahn-Teller distortions in the averaged structure, introduced by the presence of Co. Moreover, each of these modes splits into two components. This splitting can be attributed to the coexistence of two types of octahedra, namely  $\text{MnO}_6$  and  $\text{CoO}_6$  in the composition. The frequency positions of some high-frequency lines are plotted in Fig. 4.

**LaCoO<sub>3</sub>:** The spectra of  $\text{LaCoO}_3$  are, however, somewhat surprising since (i) they are not similar to the spectra of isostructural rhombohedral  $\text{LaMnO}_{3+\delta}$  [9,10,21,22],  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  [9,10], and  $\text{LaAlO}_3$  [22], (ii) due to the neutron-diffraction data the sample should have a rhombohedral symmetry  $D_{3d}^6$  and only 5 Raman-active phonon modes are expected. The main peaks in the spectra are at 75, 135, 169, 486, 560, 656, and 785  $\text{cm}^{-1}$ . Note that high-frequency lines, with large intensity in  $\text{LaCoO}_3$  even at room temperature, are not observed in the spectra of isostructural compounds. Moreover, wide bands centered approximately at 198, 281, 366, 407  $\text{cm}^{-1}$  and a shoulder at 702  $\text{cm}^{-1}$  are present in the spectrum. Probably a part of the features observed in these spectra are a contribution of second-order Raman processes, but it is more reasonable to assume that the  $\text{LaCoO}_3$  crystal has a lower symmetry than a rhombohedral one. Precise measurements of polarized Raman spectra could provide valuable information about the structure of this compound.

In conclusion, we have performed a phonon Raman study on the  $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$  ( $x = 0, 0.2, 0.3, 0.4,$  and  $1.0$ ) system at temperatures of 295 and 5 K. Characteristic changes have been observed in the phonon spectra with Co concentration and are assigned to the reduction of octahe-

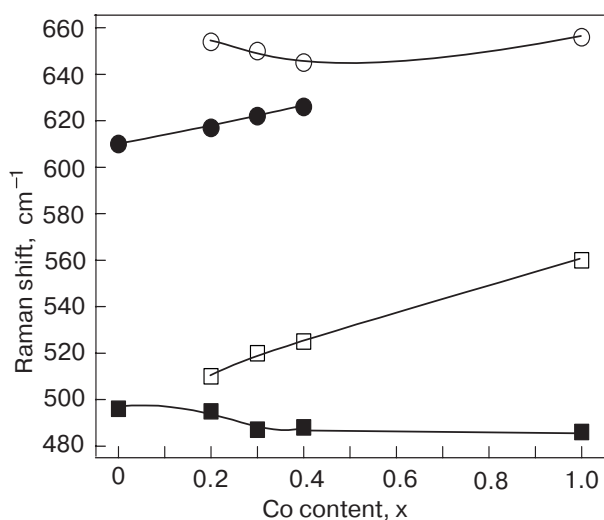


Fig. 4. Raman shift of some high-frequency phonon modes versus  $x$  in  $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$  single crystals. The lines are guides to the eyes.

dral distortions. The spectra of pure  $\text{LaCoO}_3$  exhibit a larger number of peaks than allowed for the rhombohedral ( $D_{3d}^6$ ) symmetry and a more accurate definition of the crystal structure of this compound is necessary.

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