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A. Paolone, P. Roy, Andrei Pimenov, Alois Loidl, O. K. Mel'nikov, A. Ya. Shapiro

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Infrared phonon spectrum of pure and doped $LaMnO_3$

A. Paolone* and P. Roy
LURE, Centre Universitaire Paris–Sud, BP 34, 91898 Orsay Cedex, France

A. Pimenov and A. Loidl
Experimentalphysik V, EKM, Universität Augsburg, D-86135 Augsburg, Germany

O. K. Mel'nikov and A. Ya. Shapiro
Institute of Crystallography, Russian Academy of Science, 117333 Moscow, Russia
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The infrared reflectance spectra of two $LaMnO_3$ crystals (pure and doped) have been measured at various temperatures between 300 and 10 K. The infrared active phonons of the two samples have been studied in detail and have been compared to recent lattice dynamics calculations. In the case of the undoped $LaMnO_3$, the number of infrared active phonons agrees with the predictions of group theory. In contrast the phonon structures of the doped sample are broader and do not allow to identify all the expected lines.

The discovery of colossal magnetoresistance in the manganese oxides[1–4] with a perovskite crystal structure, $R_{1-x}A_xMnO_3$ (R=La, Pr, Nd,… and A=Ca, Sr, Ba, Pb,…), have attracted renewed interest in these compounds. Despite the wide effort devoted to these oxides in the last decades, some of their properties have not been studied in detail yet. In the present paper we have focused our attention on one of these properties: the infrared phonon spectra of pure and doped $LaMnO_3$ crystals.

The crystal structure of $LaMnO_3$ has been investigated by means of neutron[5] and x-ray diffraction.[6] Below $T \approx 750$ K $LaMnO_3$ has an orthorhombic structure (*Pnma* space group)[5] which originates from the ideal cubic perovskite structure due to the Jahn-Teller instabilities of the Mn^{3+} ion.[7] Using the elemental cell, it is possible to calculate the number of infrared active and Raman-active phonon modes by means of group theory. Iliev *et al.*[8] predicted the existence of 60 phonons, of which 24 are Raman active ($7A_g+5B_{1g}+7B_{2g}+5B_{3g}$), 25 are infrared active ($9B_{1u}+7B_{2u}+9B_{3u}$), 8 are silent ($8A_u$), and 3 are acoustic ($B_{1u}+B_{2u}+B_{3u}$). The infrared active phonons of B_{1u}, B_{2u}, and B_{3u} symmetry correspond to oscillations of the dipole moment along the z, y, and x direction, respectively, with x, y, and z defined in Ref. 8.

The Raman spectrum of $LaMnO_3$ have been deeply investigated at room temperature by Iliev *et al.*[8] and by Podobedov *et al.*[9] and the Raman-active modes have been assigned by a comparison with the results of lattice dynamic calculations.[8] Moreover, the temperature dependence between 300 and 10 K of the Raman phonon spectrum of $LaMnO_3$ have been reported by Granado *et al.*[10] Concerning the infrared phonon spectrum of this compound, however, the earlier literature based on polycrystalline samples[11] does not allow us to determine most phonon frequencies. More recently Jung *et al.*[12] reported the room-temperature reflectance spectrum of polycrystalline $La_{1-x}Ca_xMnO_3$ samples with different x values, but as this study is mainly centered on the electronic part of the spectrum, the authors did not analyze the phonon absorptions. Calculations of the infrared phonon spectrum based on lattice dynamics and the comparison of calculations with the experimental infrared spectrum of polycrystalline $LaMnO_3$ were recently performed by Fedorov *et al.*[13] A reasonable assignment for the observed phonons was made by these authors,[13] but powders usually provide an infrared spectrum with broader features than crystals and the peak positions of phonon measured in a powder system can be shifted with respect to the real positions in crystals. Indeed, not all the expected lines were experimentally observed by these authors.[13]

We have measured the infrared reflectance spectra of two $LaMnO_3$ crystals as a function of temperature, from 300 down to 10 K, in the frequency range 25–12 000 cm^{-1} in order to obtain information about the infrared (IR) phonon spectrum of these compounds.

The two $LaMnO_3$ crystals were grown by the floating zone method with radiation heating.[14] Chemical analysis and electron paramagnetic resonance (EPR) measurements revealed that the sample LMO 1 has the nominal $LaMnO_3$ stoichiometry, while in LMO 2 there is a concentration of $8 \pm 2\%$ of Mn^{4+} ions, so that this last sample is doped. X-ray-diffraction measurements showed that the measured crystals were heavily twinned, so that reflectance measurements with polarized light, in order to determine the phonon polarization, could not be performed. Thus our reflectance spectra are a mean of the contributions coming from different crystalline axes.

Reflectance measurements in the frequency range 25–12 000 cm^{-1} were performed using a BOMEM DA 8 rapid scanning interferometer. Different sources, beam splitters, detectors, and optical windows allowed covering the whole range. Synchrotron radiation was used in the far infrared, while laboratory sources were used above 600 cm^{-1}. To obtain the absolute value of the reflectivity we gold evaporated our samples and used the gold evaporated sample spectrum as a reference to calculate the absolute reflectivity.

The real part of the optical conductivity has been obtained from the reflectance measurements by means of Kramers-Kronig transformations. In the high-frequencies region (ω

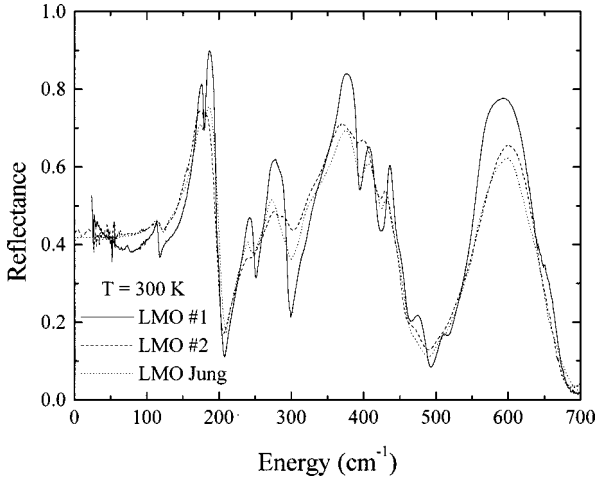

FIG. 1. The reflectance spectra at room temperature of LMO 1, LMO 2, and the $LaMnO_3$ sample of Ref. 12.

$>12\,000\ \mathrm{cm}^{-1}$), the reflectivity measured by Jung *et al.*[12] for a $LaMnO_3$ crystal sample between 12 000 and 240 000 cm^{-1} was assumed. Above 240 000 cm^{-1}, the usual ω^{-4} extrapolation was used. At low frequencies, between 0 and 25 cm^{-1} the reflectance values were fixed to a constant value, even though we verified that the present conductivity spectra are not really sensitive to the low-frequency extrapolation.

In Fig. 1 the reflectance spectra of the two $LaMnO_3$ crystals presently studied together with the reflectance spectrum of $LaMnO_3$ measured by Jung *et al.*[12] are reported in the frequency region 25–700 cm^{-1}. All these spectra have been measured at room temperature. It is clear that these three reflectance spectra present the same major features, however, in the undoped sample, LMO 1, they are much better resolved while in the doped sample, LMO 2, the phonon structures are broader and less resolved, probably due to the disorder present in this sample. The spectrum measured by Jung *et al.*[12] strictly resembles the spectrum of LMO 2, thus indicating that the sample of Ref. 12 is doped. It should be noticed that doping of manganites should be carefully controlled as it affects the physical properties of these compounds.

In Fig. 2 the reflectance spectra of LMO 1 and LMO 2 at 300 and 10 K are reported. It is noteworthy that as usual the phonon features become narrower at low T. Moreover some new phonon absorptions can be evidenced at $T=10$ K, especially for the sample LMO 1.

To quantitatively study the phonon contributions to the infrared spectrum of $LaMnO_3$ we calculated the optical conductivity, $\sigma(\omega)$, as previously described and we fitted the $\sigma(\omega)$ curves by means of the usual expression of σ obtained by the Lorentz model:

$$\sigma(\omega)=\frac{1}{60}\sum_j \frac{S_j\omega^2\gamma_j}{(\omega_j^2-\omega^2)^2+\gamma_j^2\omega^2},$$

where S_j, γ_j, and ω_j are the intensity, width, and frequency of the jth oscillator and the numerical factor is due to the fact that S_j, γ_j, and ω_j are expressed in cm^{-1} and $\sigma(\omega)$ is expressed in $\Omega^{-1}\,\mathrm{cm}^{-1}$.

In Fig. 3 the optical conductivity spectra of LMO 1 and LMO 2 at 300 and 10 K are reported together with the best-fit curves obtained using the minimum number of oscillators allowing a good fit of the experimental data. In Table I the phonon frequencies, obtained through a fit procedure, for LMO 1 and LMO 2 at 300 and 10 K are presented. It can be noticed that for the undoped sample LMO 1 at 10 K one can observe all the 25 phonon lines expected for the crystal symmetry of $LaMnO_3$. At 300 K in the spectrum of LMO 1 18 lines can be clearly identified, while for the doped sample LMO 2 18 features at 10 K and 13 at 300 K are present in the infrared spectrum. The frequency positions of corresponding phonons of the two samples agree within a few wave numbers. The correspondence with the frequency position of the phonon lines of the powder sample of $LaMnO_3$ of Ref. 13 is

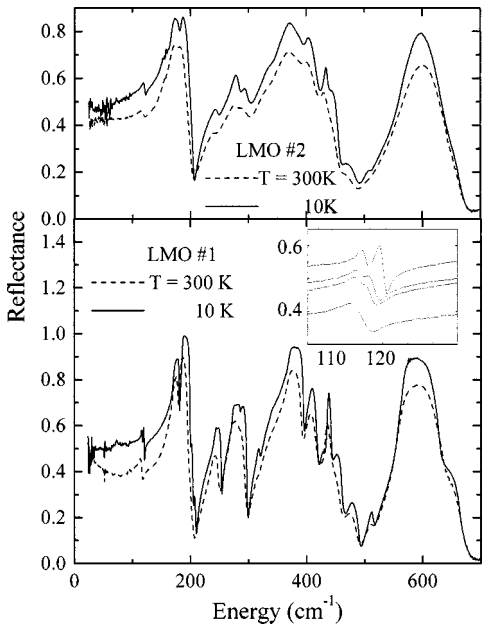

FIG. 2. The reflectance spectra of LMO 1 and LMO 2 at $T=300$ K and $T=10$ K. In the inset, the phonon centered around 115 cm^{-1} of the sample LMO 1 is reported for T = (from bottom to top) 300, 200, 150, 10 K.

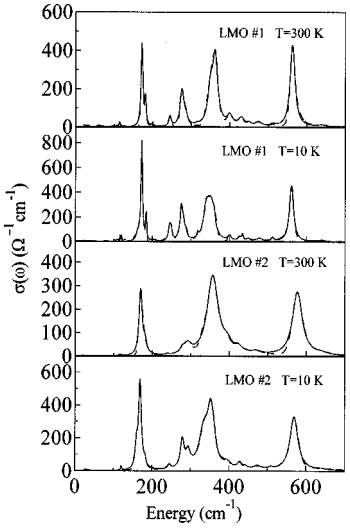

FIG. 3. The optical conductivity of LMO 1 and LMO 2 at $T=300$ K and $T=10$ K (dashed lines) and the best fit curves (solid lines).

TABLE I. The phonon frequencies (in cm^{-1}) of LMO 1 and LMO 2 at $T=300$ K and $T=10$ K compared with those of the polycrystalline sample of $LaMnO_3$ of Ref. 13.

	LMO 1 $T=10$ K	LMO 2 $T=10$ K	LMO 1 $T=300$ K	LMO 2 $T=300$ K	LMO Ref. 13
1	116	120	114	117	
2	119.5				
3	162	160			
4	172	169	172	170	
5	183.5	182	181.5	181.5	
6	201	200	199	199	194
7	207				
8	245	245	245	240	247
9	249				
10	268				
11	275		275		
12	280	279	280	279	
13	287	294	287	292	287
14	318		315		
15	340	335			344
16	352	352	350		
17	360	360	362	357	368
18	400	396	400	395	384
19	426	428	430	424	416
20	434				438
21	449	442	450		455
22	478	474	475	470	469
23	512	508	512		510
24	561	569	563	577	574
					594
25	640	640	640	640	621

not as remarkable. In the powder sample it is possible to identify only 14 phonons at 10 K and even at this temperature they appear as broad bands, typical of polycrystalline samples.

Lowering the temperature, in LMO 1 and LMO 2 more phonon peaks become visible in the infrared spectrum. Neutron-diffraction measurements[5] revealed that the crystal symmetry of $LaMnO_3$ does not change below $\approx$800 K, so that the increasing number of IR lines is only due to the narrowing of phonons which in turn allows us to better identify the different components of the spectrum. A nice example of this temperature effect is reported in the inset of Fig. 2: in the case of LMO 1, the phonon centered at 114 cm^{-1} at 300 K with a width of 3 cm^{-1} splits into two components centered at 116 and 119.5 cm^{-1} with a width of 1.2 and 1.5 cm^{-1}, respectively. In the case of LMO 2 the same phonon, which at $T=300$ K is centered at 117 cm^{-1}, does not split into its two components at 10 K, probably because the sample LMO 2 is doped and thus presents a larger amount of disorder which broadens the phonon lines. When performing reflectance measurements with a better resolution (0.07 cm^{-1}, 10 times better resolution than the data reported in the figure) we could not identify in this frequency region more than two components in the spectrum of LMO 1 at 10 K and more than one unique component for LMO 1 at 300 K and LMO 2 at every measured temperature.

TABLE II. Comparison of the best-fit frequencies (in cm^{-1}) of the phonon peaks obtained for LMO 1 for $T=10$ K with the phonon frequencies obtained by means of the lattice dynamics calculations of Ref. 13 and Ref. 15. In the case of theoretical calculations the obtained symmetry of the different phonon modes is reported.

Expt.	Ref. 13	Ref. 15
	76 (B_{1u})	76 (B_{1u})
		86 (B_{3u})
		90 (B_{2u})
116	117 (B_{3u})	121 (B_{3u})
119.5		
		135 (B_{1u})
		135 (B_{2u})
162		167 (B_{1u})
172		
183.5		186 (B_{3u})
	191 (B_{2u})	
	194 (B_{1u})	
201		202 (B_{3u})
207		207 (B_{2u})
		225 (B_{3u})
	233 (B_{2u})	
	233 (B_{3u})	
245		244 (B_{1u})
249		
268		264 (B_{1u})
275	273 (B_{1u})	
	276 (B_{3u})	
280	283 (B_{2u})	
287		
	294 (B_{3u})	
		300 (B_{2u})
		306 (B_{3u})
		308 (B_{1u})
318	318 (B_{1u})	
	332 (B_{3u})	330 (B_{2u})
	334 (B_{1u})	
340		
352		
360		367 (B_{1u})
	388 (B_{2u})	
		394 (B_{1u})
		399 (B_{3u})
400	401 (B_{3u})	
	412 (B_{2u})	
	419 (B_{1u})	
426		
434	431 (B_{1u})	
449	443 (B_{3u})	
478		
	495 (B_{1u})	
		506 (B_{3u})
512		516 (B_{2u})
	521 (B_{3u})	
561		562 (B_{2u})
	577 (B_{1u})	579 (B_{1u})
	580 (B_{2u})	582 (B_{3u})
	580 (B_{3u})	
	625 (B_{2u})	
640		

Very recently, two theoretical analyses of the $LaMnO_3$ phonon frequencies and polarization vectors at the Γ point of the Brillouin zone have been carried out by Fedorov *et al.*[13] and by Smirnova.[15] Both these analyses are based on group theory and on lattice-dynamical calculations and assume that the $LaMnO_3$ unit cell belongs to the *Pnma* space group. In Table II we report the comparison between the experimental value of the infrared-active phonon frequencies of LMO 1 at $T=10$ K and the two set of calculated phonon frequencies together with the attributed symmetry. It can be noticed that the two set of calculated frequencies are quite different among them. Moreover, the symmetry of the different phonon lines are not in agreement. The experimental values of the infrared-active phonons of $LaMnO_3$ are quite different from both sets of calculated frequencies, especially in the low-energy part of the spectrum. It should be noticed, however, that the elemental cell of $LaMnO_3$ is quite complex, making the lattice dynamics calculations extremely difficult. Moreover, the calculations of Refs. 13 and 15 are *ab initio* and do not include any optimization of their model parameters in order to match the calculated frequencies with their experimental values.

Due to the disagreement between the experimental and the calculated frequencies of the phonons of $LaMnO_3$, it is not possible to obtain information about the symmetry of these spectral lines to assign the different phonon peaks to the various contributions from different crystal axes. Further infrared spectroscopy measurements performed on single crystals are necessary to make such assignment.

In conclusion, we have measured the reflectance spectra of two $LaMnO_3$ samples as a function of temperature. One of them has the ideal stoichiometry, while the other has $8 \pm 2\%$ of Mn^{4+} ions, thus indicating that this sample is doped. Only in the case of stoichiometric $LaMnO_3$ measured at $T=10$ K the number of infrared-active phonons agrees with the prediction of group theory. In the doped samples the spectral lines are much broader and it is impossible to identify all the 25 expected vibrations.

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*Present address: INFM-Department of Physics, University of Rome ''La Sapienza,'' Piazzale. A. Moro 5, 00185 Rome, Italy.

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