Raman Shift of $RMnO_3$ (R = La, Pr, Nd, Sm) Manganites

WANG Wei-Ran(王巍然)[1,2], XU Da-Peng(许大鹏)[1*], SU Wen-Hui(苏文辉)[1,3,4]

[1]*Department of Physics, Jilin University, Changchun 130023*

[2]*Northeast China Institute of Electric Power Engineering, Jilin 132012*

[3]*Centre for the Condensed-Matter Science and Technology, Harbin Institute of Technology, Harbin 150001*

[4]*International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110015*

(Received 27 October 2004)

Raman-active phonons in orthorhombic perovskite-like $RMnO_3$ were studied by measuring Raman spectra in various scattering configurations. The experimental Raman line wave numbers and the expected shapes for the phonon modes were compared to those reported for other perovskite-like compounds with the Pnma structure and to the results of lattice dynamical calculations. The observed Raman lines in the spectra of $RMnO_3$ were assigned to definite atomic motions. The remaining spectral weight can be explained by the presence of dynamic John–Teller distortions that lower the symmetry of the cubic perovskite.

PACS: 78. 30. −j, 36. 20. Ng, 87. 64. Je

The properties of $RMnO_3$ have been intensively studied since it was found that partial substitution of R by Ca, Sr, or Ba results in structural changes and the occurrence of colossal magnetoresistance near the temperatures of spin ordering of Mn ions.[1] The structural and transport properties for Al-, Fe-, and Ag-doping perovskite manganese was studied.[2,3] It is plausible to expect that structural changes and magnetic ordering will also influence the phonon spectra. Raman scattering is known to be a powerful technique to study the dynamical processes caused by phonons, charge carriers, and spins that may affect the magnetoresistance process. Although Raman spectra of other orthorhombically distorted perovskites with the *Pnma* structure, particularly in rare earth and yttrium aluminates and orthochromates,[4] have been reported, there are practically no data on the Raman scattering from orthomanganites.

$R\mathrm{MnO_3}$ compounds crystallize in the orthorhombic structure [space group *Pnma* (D_{2h}^{16}) and $Z = 4$][5,6] for R (R = La to Dy) with larger ionic radius.

Stoichiometric $R\mathrm{MnO_3}$ compounds are interesting since they present a static John–Teller distortion, with orbital ordering. The absence of Mn mixed valence determines the insulating character of these samples. Raman phonons have been studied in orthorhombic $\mathrm{LaMnO_3}$ single crystals[7,8] and in Sr doped compounds.[8,9] Illiev *et al.* have observed the Raman active phonons of orthorhombic $\mathrm{LaMnO_3}$ and $\mathrm{YMnO_3}$,[7] and hexagonal $\mathrm{YMnO_3}$,[10] and estimated their frequencies from lattice dynamical calculations. Several works reported the effect of the oxygen content and the rhombohedral structure on the Raman features. The John–Teller effect is also mainly responsible for the distortion of the cubic perovskite structure. In this Letter, we display the John–Teller effect in the spectra of optical phonons.

We have studied the Raman phonons and the Raman shift of stoichiometric $\mathrm{RMnO_3}$ (R = La, Pr, Nd and Sm) compounds, with the orthorhombic *Pnma* structure, as a function of the rare earth ion, and the effect of the rare earth ion in the Raman spectrum, with, specifically, wave number moving.

The samples $\mathrm{LaMnO_3}$, $\mathrm{PrMnO_3}$, $\mathrm{NdMnO_3}$ and $\mathrm{SmMnO_3}$ studied here present the *Pnma* orthorhombic structure (D_{2h}^{16}), with $Z = 4$). The structure of the samples was investigated by x-ray diffractometer. The x-ray diffraction (XRD) patterns were recorded using a Rigaku D-ax-r A X-ray Diffractometer (Japan) with Cu K_α radiation ($\lambda = 1.5418$ Å) operated at 20 kW. Raman spectra were obtained with a Raman spectrograph (HR800) with a CCD detector and excited with the 632.8 nm line of a He-Ne laser and output power of 20 mW. The spectra have been obtained with a ×100 objective (focus diameter larger than 1 micron), and recorded in the backscattering geometry.

At atmospheric pressure the rare-earth manganite $R\mathrm{MnO_3}$ crystallizes in an orthorhombic phase (space group *Pnma* (D_{2h}^{16}), $Z = 4$). The latter structure is typical for $R\mathrm{MnO_3}$ compounds with R of larger ionic radius (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, or Dy).[11]

The XRD patterns of the rare-earth manganites $R\mathrm{MnO_3}$ (R = La, Pr, Nd and Sm) shown that the rare-earth manganites $\mathrm{RMnO_3}$ exists in a form of orthorhombic phase (space group *Pnma* (D_{2h}^{16}), $Z = 4$), and we can calculate the unit cell parameter a, b, and c (in Table 1).

The Raman active modes of *Pnma* structure (mirror plane m is perpendicular to the long c-axis) are $7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g}$ and the non-zero components of the Raman tensors are (xx, yy, zz), (xy), (xz),

** Email: xu_dapeng@sina.com

©2005 Chinese Physical Society and IOP Publishing Ltd

Table 1. $R\mathrm{MnO_3}$ cell parameter and fractional atomic coordinates in the orthorhombic structure.

	Unit-cell parameter a	Unit-cell parameter b	Unit-cell parameter c	Unit-cell volume V	R^{3+} ionic radius r	Rare-earth atomic mass m (g/mol)	Frequency with $A_g(\omega)$
$\mathrm{LaMnO_3}$	5.532	5.722	7.699	243.7	1.06	138.9	285.412
$\mathrm{PrMnO_3}$	5.45	5.786	7.589	239.31	1.01	140.9	319.215
$\mathrm{NdMnO_3}$	5.38	5.854	7.557	238	1.00	144.2	331.695
$\mathrm{SmMnO_3}$	5.358	5.825	7.483	233.55	0.96	150.4	352.861

and (yz) for A_g, B_{1g}, B_{2g} and B_{3g} representations, respectively,[12] as shown Fig. 1.

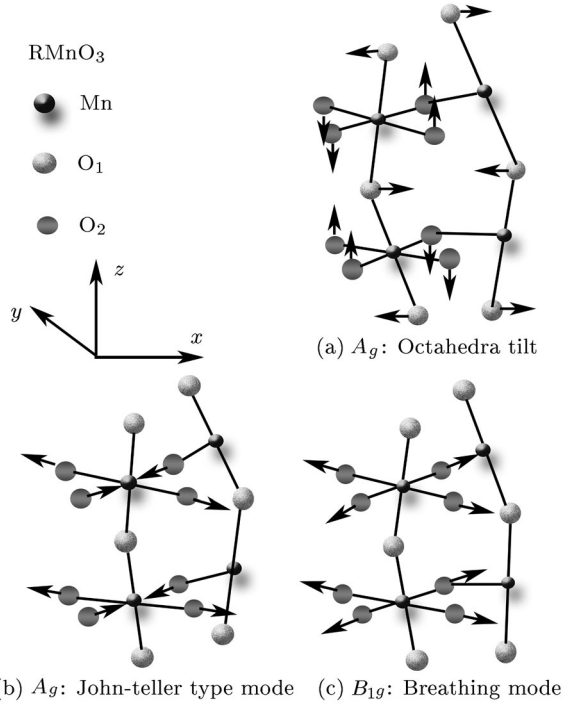


Fig. 1. (a) Octahedra tilt (A_g symmetry); (b) asymmetric stretching (A_g symmetry); (c) symmetric stretching (B_{1g} symmetry).

In Raman spectrum (Fig. 2), the three main peaks correspond to the following modes and symmetries: the symmetric stretching of the basal oxygen of the octahedra [Fig. 1(c)], around $610\,\mathrm{cm^{-1}}$ (B_{1g} symmetry); the asymmetric stretching at $480\,\mathrm{cm^{-1}}$ (A_g symmetry) associated with the John–Teller distortion [Fig. 1(b)]; and the tilt of the octahedral at $280\,\mathrm{cm^{-1}}$ (A_g symmetry) [Fig. 1(a)]. The modes at the lowest energies are those related to the rare earth movements.[13]

All the samples studied here have the orthorhombic *Pnma* structure. In Table 1, we show the variation of the unit cell parameters and cell volume with the ionic radius of the rare earth. The variation of the b parameter is very small compared to those of a and c; this is due to the tilting scheme of the $\mathrm{MnO_6}$ octahedral in *Pnma* perovskites where the distortion, driven by a reduction of the rare earth size and a aggrandizement of the rare earth mass, leaves the parameter b almost unchanged. In addition, we can observe a change in this cell parameter behaviour (Table 1). The observed decrease in the unit cell volume scales with the R^{3+} size.

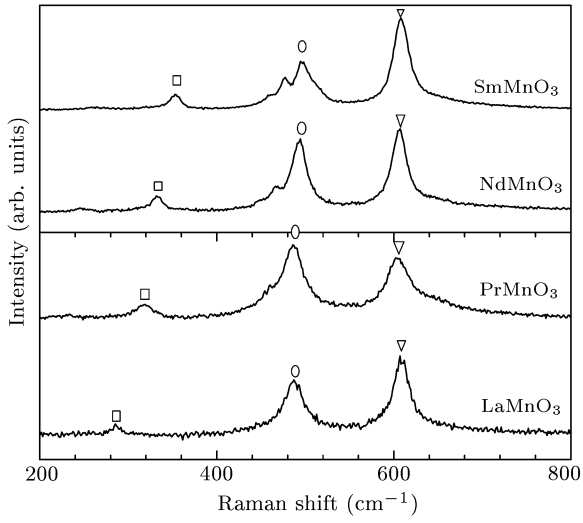


Fig. 2. Raman spectra of the $\mathrm{RMnO_3}$ sample with the orthorhombic structure for the different rare earth elements. The squares denote the tilt of the octahedron, the circles represent the asymmetric stretching, and the down-triangles denote the symmetric stretching.

In order to estimate the importance of both the terms in the observed phonon frequencies we have evaluated the expected changes in the phonon frequencies caused by the variation of the interatomic distances in the crystal. Taking into account a simple model for the interatomic force constants, $K = F_{ij}/r_{ij}$ and $\omega = (K/m)^{1/2}$, where F_{ij} are constants that depend on i and j ions, and r_{ij} are, in the present case, Mn–O distances, we can estimate the changes in the stretching modes (at $610\,\mathrm{cm^{-1}}$ and $480\,\mathrm{cm^{-1}}$) due to the changes of these distances obtained from Ref. [14]. Then, the dominant mechanism for the observed frequency shift is due to anharmonic scattering of phonons.

The observed frequency shift at $280\,\mathrm{cm^{-1}}$ is more obvious than the others (Fig. 2). The tilt of the octahedron at $280\,\mathrm{cm^{-1}}$ (A_g symmetry) [Fig. 1(a)] is due to the influence of rare earth ions. The phonon modes near $280\,\mathrm{cm^{-1}}$ of different ions are different, which depend on the atomic mass and the ionic radius of the rare earth element. We can find the shift of wave number (near $280\,\mathrm{cm^{-1}}$) in the Raman spectrum increasing with the augmentation of atomic mass of the rare earth element (see Table 1 and Fig. 2).

We have studied the Raman active phonons of stoichiometric $R\mathrm{MnO_3}$ compounds with orthorhombic structure. We have correlated the frequencies of the three most intense modes of the orthorhombic samples, with some structural parameters such as Mn–O bond distances, atomic mass of the rare earth and John–Teller distortion.

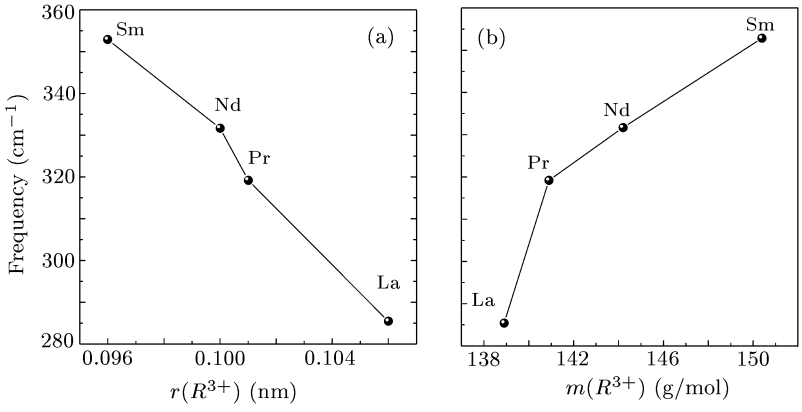


Fig. 3. (a) Dependence of the stretching mode frequency with the ionic radius of $R\mathrm{MnO_3}$. (b) Dependence of the stretching mode frequency with the atomic mass of $R\mathrm{MnO_3}$.

As the ionic radius of the rare earth decreases and the atomic mass of the rare earth increases, the frequency of the mode at 280 cm^{-1} increases dramatically, following a linear dependence with the Raman shift (Fig. 3). The stretching mode at 610 cm^{-1} behaves inversely with the mean distances of Mn-O bonds in the basal plane. We correlated the Raman peak at 480 cm^{-1} was correlated with the John–Teller distortion for compounds with large ionic radii.

References

[1] Khomskii D I and Sawatzky G A 1997 *Solid State Commun.* **102** 87
[2] Cui Y J, Jia G Q and Han Y B 2004 *Chin. Phys. Lett.* **21** 540
[3] Wu J and Zhang S Y 2004 *Chin. Phys. Lett.* **21** 382
[4] Udagawa M, Kohn K, Koshizuka N and Tsushima T 1975 *Solid State Commun.* **16** 779
[5] Yakel H L, Koehler W C, Bertaut E F and Forrat E F 1963 *Acta Crystal.* **16** 957
[6] Alonso J A, Martinez-Lope M J, Casais M T and Fernandez-Diaz M T 2000 *Inorg. Chem.* **39** 917
[7] Iliev M N, Abrashev M V, Lee H G, Popov V N, Sun Y Y, Thomsen C, Meng R L and Chu C W 1998 *Phys. Rev.* B **57** 2872
[8] Podobedov V B, Weber A, Romero D B, Rice J P and Drew H D 1998 *Phys. Rev.* B **58** 43
[9] Granado E, Moreno N O, Garcia A, Sanjurjo J A, Rettori C, Torriani I, Oseroff S B, Neumeier J J, McClellan K J, Cheong S W and Tokura Y 1998 *Phys. Rev.* B **58** 11435
[10] Iliev M N, Lee H G, Popov V N, Abrashev M N, Hamed A, Lmeng R and Chu C W 1997 *Phys. Rev.* B **56** 2488
[11] Moussa F, Hennion M, Rodriguez-Carvajal J, Moudden H, Pinsard L and Revcolevschi A 1996 *Phys. Rev.* B **54** 15149
[12] Martin-Carron L and de Andres A 2001 *J. Alloy Compounds* **323/324** 417
[13] Martin-Carron L , de Andres A, Martinez-Lope M J, Casais M T and Alonso J A 2001 *J. Alloy Compounds* **323/324** 494
[14] Rodriguez-Carvajal J, Hennion M, Moussa F, Moudden A H, Pinsard L and Revcolevschi A 1998 *Phys. Rev.* B **57** R3189