Raman Spectroscopy Of Perovskite-like Manganites

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Abstract. Some problems concerning Raman spectroscopy of perovskite-like La$_{1-x}$Ca$_x$MnO$_3$ ($0 < x < 1$) manganites are discussed. The selection rules for the Raman spectra obtained from quasicubic samples with different type of twinning are determined. A dependence of the intensity of the Raman lines on the distortions of the structure is proposed. The typical spectral features characteristic for the different states of the manganites (insulating one with or without Jahn-Teller distortions, conductive, charge- and orbitally-ordered and disordered) are commented.

The perovskites are particularly interesting class of materials because slight changes of their chemical content can lead to drastic changes of their structural, electric and magnetic properties. Ten years ago, they attracted a renewed interest due to the discovery of the so-called “colossal” negative magnetoresistance (CMR) exhibited near the temperature where metal-insulator and paramagnetic-ferromagnetic transitions occur. La$_{1-x}$Ca$_x$MnO$_3$ ($0 < x < 1$) is one of the most studied CMR systems. LaMnO$_3$ [1] and CaMnO$_3$ [2] at room temperature are paramagnetic insulators (at low temperatures antiferromagnetic insulators). The low temperature phase of the hole-doped samples La$_{3+1-x}$Ca$_x$MnO$_3$ (0.15 < x < 0.45), is a ferromagnetic metal, as the Curie temperature $T_C$ has a maximum about 240 K for $x = 0.3$ [3,4]. In very narrow range near $x = 0.5$ at low T, a formation of charge- and orbitally-ordered (COO) insulating antiferromagnetic state can be observed [5].

From a crystallographic point of view, among all above mentioned compounds, Ca$^{2+}$Mn$^{4+}$O$_3$ has a crystal structure closest to the one of a perfect crystal. As the Mn$^{4+}$ ($t_{2g}^3$) is a non-Jahn-Teller (JT) ion, the six Mn-O bonds in the MnO$_6$ octahedra are almost equal and the real structure (with space group $Pnma$) is fixed mainly by the octahedral tilts [with Glazer’s notation $(a b^c a')$], governed by the tolerance factor $t = (r_{La/Ca} + r_O)/[\sqrt{2}(r_{Mn} + r_O)]$. In LaMnO$_3$, Mn$^{3+}$ ($t_{2g}^3e_g^1$) are JT ions and this leads to deformation of the MnO$_6$ octahedra (existence of two shorter and two longer Mn-O bonds). At proper preparation conditions (slow cooling in oxygen-free atmosphere) the JT octahedral distortions are spatially coherent and the structure has the same space group $Pnma$ as CaMnO$_3$ [1]. LaMnO$_3$, however, can be prepared with disordered JT octahedral distortions. In this case the structure has averaged rhombohedral $R-3c$ space group [6]. In the high T phase of La$_{0.5}$Ca$_{0.5}$MnO$_3$ there are dynamical equilibrium between the JT distorted Mn$^{3+}$O$_6$ and the undistorted Mn$^{4+}$O$_6$ octahedra. Their lifetime is limited by the mobility of the charge carriers. Only below the critical
temperature these states are ordered and stable in the time, that leads to formation of a superstructure with low \( P2_1/m \) symmetry [5]. In opposite, at low temperatures in \( \text{La}_1-x\text{Ca}_x\text{MnO}_3 \) (0.15 < x < 0.45), the mobility of the carriers is so high that the JT distortions cannot develop around the Mn\(^{3+}\) ions. The resulting structure with metallic and ferromagnetic properties has averaged \( \text{Pnma} \) symmetry.

Raman spectroscopy is a sensitive tool for the study of both local and spatially coherent structural changes. Since there are no Raman-active lattice vibrations in the ideal cubic \( \text{Pm-3m} \) perovskite, all phonon features in the spectra of perovskite-like manganites originate from either coherent or incoherent lattice distortions. In this case, however, Raman spectroscopy meets several serious difficulties. To avoid the overheating, the laser power on the spot should be 1 mW or lower (in micro-Raman experiments) [1]. The samples are opaque and strongly absorbing. As a result the lines in the spectra have very low intensity and their number is always lower than the one predicted by the group theory. It makes the assignment of the lines observed to definite atomic vibrations difficult and ambiguous.

First step to resolve the problem is to separate the lines into groups with equal symmetry using their selection rules in the spectra. Unfortunately, even using single crystals or highly oriented thin films, they are highly twinned. The twinning depends on the crystal structure and on the type of material. \( \text{CaMnO}_3 \) samples are quasi-cubic and they consist of orthorhombic twins with \( \text{Pnma} \) symmetry and six different orientations. The calculated selection rules are given in Table 1 [2].

### TABLE 1. Calculated intensities of the Raman lines in different scattering configurations.

<table>
<thead>
<tr>
<th>Symmetry of modes</th>
<th>xx=yy</th>
<th>xy</th>
<th>x’y’=yy’</th>
<th>x’y’</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_g )</td>
<td>((a+c)^2+2b^2)/6 )</td>
<td>((a-c)^2/12 )</td>
<td>( [a'^2+(a+2b+c)^2]/4 )</td>
<td>((a-2b+c)^2/24 )</td>
</tr>
<tr>
<td>( B_{2g} )</td>
<td>( 4d^2/6 )</td>
<td>( 0 )</td>
<td>( d^2/6 )</td>
<td>( 3d^2/6 )</td>
</tr>
<tr>
<td>( B_{1g} ) and ( B_{3g} )</td>
<td>( 0 )</td>
<td>( 2e^2/6 )</td>
<td>( 2e^2/6 )</td>
<td>( 0 )</td>
</tr>
</tbody>
</table>

It is seen that the \( B_{1g} \) and \( B_{3g} \) cannot be distinguished from the available scattering configurations, but they have different intensity ratios (0:1:1:0) compared to the modes with other symmetry. \( B_{2g} \) modes can be identified by their specific intensity ratios (4:0:1:3) in the four scattering configurations. The intensity ratios of the \( A_g \) modes can be different since they depend on three independent variables. Some special cases are given in Refs. [2,5].

Another type of twinning is observed for orthorhombic \( \text{Pnma} \) \( \text{LaMnO}_3 \) single crystals. There are only two type of twins. They have parallel \( y \) axes and exchanged \( x \) and \( z \) axes (similar twinning have \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) crystals). The selection rules for \( A_g \) and \( B_{2g} \) modes in these quasi-tetragonal samples are practically the same as for untwinned crystal, but the \( B_{1g} \) and \( B_{3g} \) modes are indistinguishable [1]. The selection rules for the case of rhombohedral samples with \( R-3c \) symmetry are given in Ref. [6].
Next step in the analysis of the Raman spectra is the assignment of the lines to definite atomic vibrations. The Raman-allowed modes of the structure of La\(_{1-x}\)Ca\(_x\)MnO\(_3\) having \(Pnma\) symmetry are 24: \(7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}\). Unpolarized Raman spectra of samples from La\(_{1-x}\)Ca\(_x\)MnO\(_3\) system are given in Fig. 1. The experimental conditions for obtaining of the spectra and details for the synthesis of the samples are given in Refs. [1-3].

![Diagram showing Raman spectra of samples from the La\(_{1-x}\)Ca\(_x\)MnO\(_3\) series.](image)

**FIGURE 1.** Raman spectra of samples from the La\(_{1-x}\)Ca\(_x\)MnO\(_3\) series.

It is seen that the spectra are very different and even for one sample the changes can be large if its properties are changed (e.g. La\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\) undergoes insulator-metal transition between room T and 10 K). Qualitative explanation of the change of the intensity of the spectral lines can be done using a model describing the crystal distortions in the real \(Pnma\) structure as superposition of four basic distortions [2]. Two of them are the octahedral tilts round the [010] and [101] cubic directions, the third one is the Jahn-Teller octahedral deformation and the fourth one is the shift of the La/Ca atoms from their sites in the ideal perovskite. The comparison of the real and the simpler structures, containing only one of the distortions, is given in Fig. 2. Analyzing the Raman-allowed modes in the simpler structures, 20 of the 24 Raman-allowed modes in the real structure have counterparts in only one of the four simpler structures. This fact can be interpreted as direct dependence of the intensity of each mode on only one distortion. Based on this model it is easy to explain the disappearance of the strong \(B_{2g}\) line near 600 cm\(^{-1}\) (see Fig. 1) in the spectra of CaMnO\(_3\) and low T metallic La\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\), where the JT distortion is negligible.

The model also predicts the existence of “soft” modes (high T second-order structural transition to the ideal cubic \(Pm-3m\) structure is possible for all structures),
having the shape of the static octahedral tilts. Their frequency should depend strongly (and neglecting the other effects as mixing with other modes and the differences of the octahedral bond lengths, it should be proportional) on the octahedral tilt angle. It is seen in Fig. 1 that $A_g$ line corresponding to the [101] octahedral tilt strongly decrease in intensity and its frequency changes from 396 cm$^{-1}$ in the case of YMnO$_3$ to 184 cm$^{-1}$ for CaMnO$_3$.

<table>
<thead>
<tr>
<th>Pnma</th>
<th>Imma</th>
<th>P4/mbm</th>
<th>P4/mbm</th>
<th>Cmcm</th>
</tr>
</thead>
<tbody>
<tr>
<td>real</td>
<td>rot.[101]</td>
<td>rot.[010]</td>
<td>J-T</td>
<td>A-shift</td>
</tr>
</tbody>
</table>

![Figure 2](image)

**FIGURE 2.** The real structure of La$_{1-x}$Ca$_x$MnO$_3$ (0 < x < 1) and the four simpler structures, containing only one of the basic distortions.

The details of the assignment of the Raman lines for all cases commented above based on comparison with the results of lattice dynamical calculations using a shell model [7] are given in Refs. [1-3].

For the strongly disordered and non-coherent structures (e.g., the high T phase of La$_{0.7}$Ca$_{0.3}$MnO$_3$) the Raman spectra cannot be explained in terms of observation of Raman-allowed or forbidden normal modes, since the features in them have very large bandwidths and weak temperature and scattering configuration dependences. In this case the spectra are dominated by disorder-induced bands, reflecting the oxygen partial phonon density of states [4].

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**REFERENCES**