Optical study in the charge-ordered phase of $(Nd_{1-x}Sr_x)MnO_3$

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Abstract

We report the Sr-concentration dependence of Raman spectra in $(Nd_{1-x}Sr_x)MnO_3$ ($x \sim 1/2$). In the charge-ordered phase of the $x = 0.50$ and 0.49 samples, several new Raman peaks appear. In the $x = 0$ .48 sample, no new Raman peak is observed, indicating that the charge-ordered phase transition does not occur. We propose that the symmetry of the lattice in the charge-ordered phase is $Pnmm$.

Key words: charge and orbital orders; manganite; Raman scattering; Jahn-Teller effect

1. Introduction

RMnO$_3$ systems, where R is rare-earth and/or alkaline-earth elements, the double exchange interaction between Mn ions shows various electronic and magnetic properties. Especially, the charge-ordered (CO) phase transition in these systems has attracted much attention. In this phase transition, the electron-phonon coupling plays an important role.

In our previous report, [1] we measured Raman scattering in $(Nd_{0.50}Sr_{0.50})MnO_3$ to study the CO phase transition at T_{CO} (= 158 K when $x = 0.50$),[2] and demonstrated that the Raman scattering is one of the useful tools to study this phase transition. Above T_{CO}, a weak and broad Raman peak was observed around 200 cm^{-1}, indicating that the lattice symmetry was $Ibmm$ with a small orthorhombic lattice distortion. Below T_{CO}, we observed several new Raman peaks, indicating that the lattice symmetry was lowered.

The CO phase was observed in a narrow region of $x - T$ phase diagram.[3] The jump of the resistivity due to the CO phase transition disappeared when x = 0.48. In this work, we report the x dependence of Raman spectra and discuss the lattice symmetry of the CO phase in $(Nd_{1-x}Sr_x)MnO_3$ ($x \sim 1/2$).

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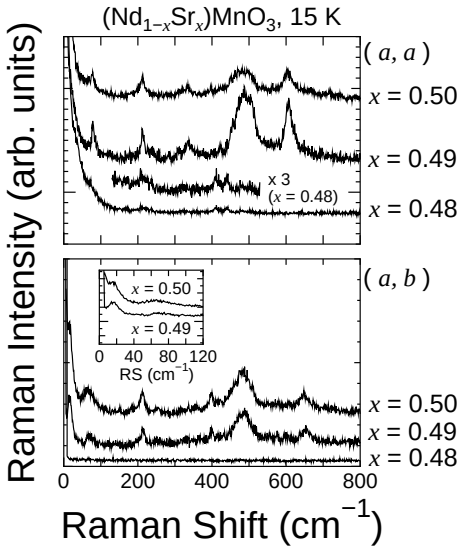

Fig. 1. The (a, a) (upper panel) and (a, b) (lower panel) Raman spectra in $Nd_{1-x}Sr_xMnO_3$ (x = 0.48, 0.49, and 0.50) at 15 K. The low-frequency (a, b) spectra in the x = 0.50 and 0.49 samples are plotted in the inset.

2. Experiments and Results

The Sr concentration $x = 0.50$, 0.49, and 0.48 single crystals were prepared by the floating-zone method.

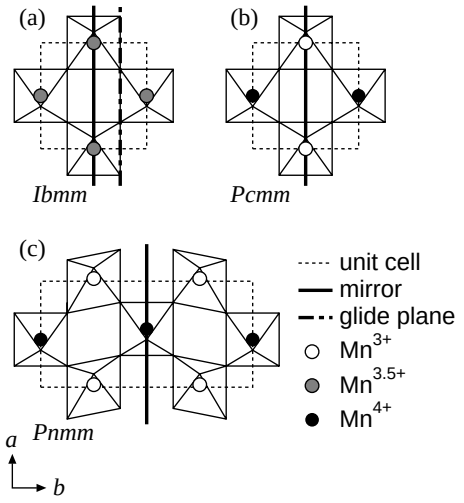

Fig. 2. Schematic crystal structures in $Nd_{1-x}Sr_xMnO_3$ (x = 0.50) at RT (a) and in the CO phase without (b) and with (c) Jhan-Teller effects CO (c) phases. The typical mirrors and glide plane in the ac plane are shown. For simplification, only the MnO_6 octahedra are shown.

The crystal axes and Sr concentrations were checked carefully by X-ray diffraction and resistivity measurements, respectively. The polarized Raman spectra are excited with the 514.5-nm line of Ar^+-ion laser. A_g and B_{1g} phonons are detected with the (a, a) and (a, b) geometries, respectively. The details of the sample preparations and measurements are written in Ref. 1.

Figure 1 shows the polarized Raman spectra at 15 K in the $x = 0.50$, 0.49 and 0.48 samples. When $x = 0.50$ and 0.49, the Raman spectra are similar to each other. Above T_{CO} of the $x = 0.49$ sample, only a broad and weak Raman peak around 200 cm^{-1} was observed, as well as the $x = 0.50$ sample.[1] When x= 0.48, three Raman peaks at 210, 413, and 440 cm^{-1} were observed in the (a, a) spectrum, but not in the (a, b) one.

We observed a magnetic excitation at 16 cm^{-1} in the (a, b) spectra when $x = 0.50$ and 0.49, as shown in the inset of Fig. 1. In the present work, we could not distinguish this peak in the (a, a) geometry from the tail of the laser line, which was reported in the previous work,[1] because of the surface condition. The peak frequency softened with increasing temperatures. Our analysis, however, showed that the excitation energy was almost temperature independent and the softning is owing to the overdamping.[1]

3. Discussion

When $x = 0.48$, we observed three A_g phonons at 15 K, which is consistent with the group theoretical analysis based on the $Ibmm$ symmetry.[1] The CO phase transition does not occur in this sample. When x = 0.49 and 0.50, new Raman peaks are observed, indicating that the system is in the CO phase at 15 K.

Next, we discuss the symmetry in the CO phase of the $x = 0.50$ and 0.49 samples. Our polarized Raman spectra in the CO phase, including the number of Raman peaks, are similar to those in the CO phase of $(La_{0.5}Sr_{0.5})MnO_3$ measured by Abrashev *et al.*[4] They introduced the effective lattice structure with $Pbmm$ symmetry, which is a minimal isomorphic supergroup of $P2_1/m$.[5] The lattice structure in the CO phase of $(Nd_{0.5}Sr_{0.5})MnO_3$ should be reduced to this effective one.

Because the $Ibmm$ symmetry does not have a maximal subgroup which has $a \times 2b \times c$ superlattice, we consider the following two step phase transition. Because the CO phase transition is the first-order one, two or more symmetry operations can be broaken at T_{CO}. Above T_{CO}, as shown in Fig. 2(a), there are two equivallent $Mn^{3.5+}$ sites, two b-mirrors, and two n-glide planes in the ac plane for a unit cell. In the CO phase, Mn^{3+} and Mn^{4+} sites become unequivalent. If we consider only the charge ordering, as shown in Fig 2 (b), the lattice symmetry belongs to $Pcmm$ which contradicts to the formation of superlattice observed by neutron diffraction.[6] When the Jahn-Teller distortion in the $Mn^{3+}O_6$ octahedron is considered, as shown in Fig. 2(c), the lattice symmetry becomes $Pnmm$, which is consistent with the result of Ref. 6. If the small rotation of the oxigen ions are negligible, the structure in Fig. 2(c) is reduced to the effective structure of $(La_{0.5}Sr_{0.5})MnO_3$. The $Pnmm$ symmetry in the CO phase can explain the results in the Raman scattering and the neutron diffraction. We, therefore, conclude that the lattice symmetry in the CO phase is $Pnmm$.

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