Polarized Raman scattering in single crystals of $Nd_{0.7}Sr_{0.3}MnO_3$

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Abstract. We report polarized Raman scattering in single crystals of $Nd_{0.7}Sr_{0.3}MnO_3$. The temperature dependence of the MnO_6 octahedral bending and stretching modes observed in the XX spectra points to the existence of local lattice distortions, possibly polarons. The XY spectra have been analyzed using a collision-dominated model, which allows the extraction of the carrier scattering rate.

Keywords. Raman scattering; colossal magnetoresistance; polaron; manganite.

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1. Introduction

It is now well-established that the physics of manganites exhibiting colossal magnetoresistance [1] is characterized by a strong interplay between spin and lattice degrees of freedom [2]. $Nd_{0.7}Sr_{0.3}MnO_3$ (NSMO 0.3) is one such compound, which has been the center of attention of many research groups due to its interesting magnetic and transport properties. The largest reported CMR has been observed in thin films of NSMO 0.3 (as large as $10^6\%$ at 60 K and 8 T) [3]. Magnetization and dynamical studies of the time-dependent magnetization of NSMO 0.3 have shown the presence of magnetic disorder and spin frustration below T_C [4]. Neutron scattering measurements show that the spin correlation length remains approximately 20 Å at T_C and grows to 100 Å only at about $0.95T_C$ [5]. Recent NMR measurements have shown evidence for strong carrier localization below T_C [6] resulting in a 'phase separation' into carrier-rich and carrier-poor regions. An understanding of the interplay between spin and lattice degrees of freedom as a function of temperature is essential to correlate all the above interesting experimental findings. Raman scattering is well suited for such a study since it has proved to be a powerful and simple tool for the detection of Jahn–Teller distortions and for the study of phase transitions in magnetic semiconductors such as the La-based manganites and EuB_6 [7]. In this report we present Raman scattering measurements on single crystal samples of NSMO 0.3 from 295 K to 5 K.

2. Experimental

The single crystal was grown in an infrared image furnace by the floating zone technique. Raman measurements were performed in the spectral range of 5–1100 cm^{-1} using a CCD detector with a 5145 Å Ar laser. The temperature of the sample was varied from 5–300 K using a continuous flow cryostat.

3. Results and discussion

The XX spectra at different temperatures are shown in figure 1a. The spectra consist of peaks at 65 cm^{-1}, 250 cm^{-1}, 480 cm^{-1} and 660 cm^{-1}. Recent lattice dynamical calculations for orthorhombic LaMnO$_3$ [8] indicate that the 660 cm^{-1} peak corresponds to an in-phase stretching mode of the MnO$_6$ oxygen cage where the O^{2-} ions of the xz plane vibrate along the Mn–O direction. The 480 cm^{-1} peak is associated with an out-of-phase bending mode of the oxygen cage where the O^{2-} ions vibrate perpendicular to the Mn–O line. The 480 cm^{-1} peak has been identified to couple with the e_g electron in the well studied Jahn–Teller compound LaMnO$_3$ [9]. The low frequency modes are associated with rotations of the oxygen cage and do not involve internal distortions of MnO$_6$.

The temperature dependence of the 65 cm^{-1}, 250 cm^{-1} and 480 cm^{-1} peak positions, obtained from Gaussian fits after correcting the spectra for the background and the Bose–Einstein thermal factor ($[1 + n(\omega)] = [1 - \exp(-\hbar\omega/k_B T)]^{-1}$) are shown in figures 1b, 1c and 1d. The 250 cm^{-1} peak exhibits a sudden hardening across T_C (200 K) and the 480 cm^{-1} peak exhibits a softening below T_C. The hardening of the 65 cm^{-1} and 250 cm^{-1} modes represent an ordering of the MnO$_6$ octahedra due to a reduction in the Jahn–Teller
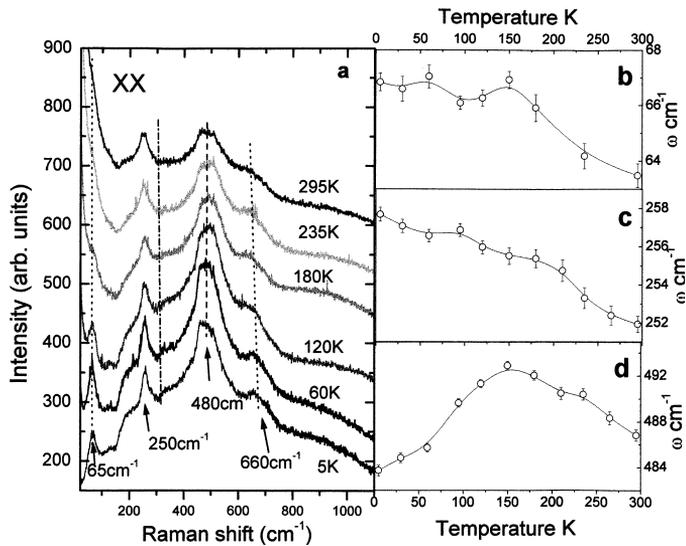

Figure 1. (**a**) XX spectra. (**b**)–(**d**) Temperature dependence of the observed modes.

distortion in agreement with earlier reports [7]. It was not possible to obtain accurate Gaussian fits for the 660 cm^{-1} mode as it appears as weak shoulder (figure 1a).

Neutron diffraction studies of NSMO 0.3 [10] at 300 K and 1.7 K show that the lattice parameters and the Mn–O bond lengths are weakly temperature dependent. This suggests that the anomalous temperature dependence of the 480 cm^{-1} peak reflects the presence of local lattice distortions (due to the Jahn–Teller effect [11]) and does not represent a structural transition. Similar temperature dependence has been observed in the corresponding phonon mode in La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ [12] across T_C indicating a strong spin-lattice coupling. However, the major difference between the present study and previous ones is that in NSMO 0.3 the 480 cm^{-1} mode softening is observed well below T_C (150 = 0.75T_C) whereas in La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$, it coincides with T_C. The softening of the 480 cm^{-1} mode represents a reduction in the spin-lattice coupling pointing to a decrease in the lattice distortions. Since the 480 cm^{-1} mode is expected to couple with the e_g electron which is mobile in NSMO 0.3, the distortions too are mobile resulting in the formation of polarons.

The anomalous softening of the 480 cm^{-1} mode corresponds to a reduction in the Jahn–Teller distortion and an increase in electron mobility. In NSMO 0.3 this occurs well below T_C unlike the La-based manganites where such effects coincide with T_C [12, 13]. Thus between 150 K and T_C the Jahn–Teller distortions are the source of the strong carrier localization observed in NMR [6] and the small spin–spin correlation length observed below T_C in neutron diffraction [5]. The existence of local lattice distortions and charge localization below T_C suggests that the dynamic Jahn–Teller effect is the likely source of the phase separation observed in NMR below T_C in NSMO 0.3.

In order to study the temperature dependence of electronic excitations we have studied the Raman response in the XY geometry (figure 2a). Previous Raman studies have shown that the low frequency response of manganites in the paramagnetic phase is 'collision-
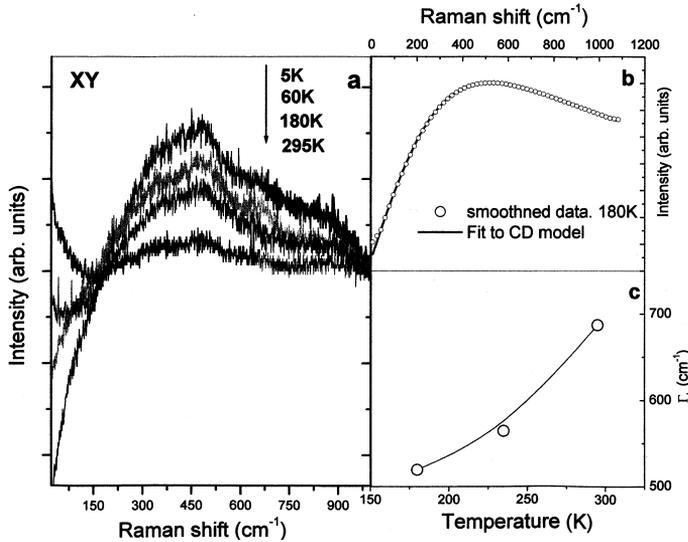

Figure 2. (**a**) XY spectra. (**b**) Typical fit to the collision-dominated model. (**c**) Temperature dependence of the carrier scattering rate.

dominated' associated with diffusive hopping of carriers. Below T_C there is a crossover to a response typical of strongly correlated metals [14]. Figure 2a shows the change in the low frequency response upon cooling across T_C, which is illustrative of this crossover. The XY spectra were analyzed using a collision-dominated model [14] in which the electronic Raman scattering intensity is given by

$$I(\omega) = [1 + n(\omega)]\frac{B_L \omega \Gamma_L}{\omega^2 + \Gamma^2}, \tag{1}$$

where B_L is the symmetry-dependent scattering amplitude and Γ_L the carrier scattering rate. A typical fit is shown for the spectrum at 180 K in figure 2b. In the La-based manganites a frequency-dependent carrier scattering rate of the form $\Gamma_L = \Gamma_O + \alpha\omega^2$, where α reflects electron correlation effects, has been used to improve the fitting quality. In the present study we found that it was not necessary to consider a frequency dependent form for Γ_L. This suggests that correlation effects are small in NSMO 0.3 probably due to the strong carrier localization discussed above. The temperature dependence of the scattering amplitude obtained from fitting eq. (1) to the XY spectra is shown in figure 2c. The values of the scattering rate obtained for NSMO 0.3 are much higher than that reported for $Pr_{0.63}Sr_{0.37}MnO_3$ (PSMO: $T_C = 300$ K) [14] pointing to the larger disorder in NSMO 0.3 due to its lower T_C. At 5 K the scattering rate for NSMO 0.3 is an order of magnitude larger than that for PSMO. The reason for such a large difference in the scattering rates at a temperature well below the T_C's of both samples is at present not clear.

Acknowledgement

References

[1] R von Helmolt, J Wecker, B Holzapfel, M Schultz and K Sanwer, *Phys. Rev. Lett.* **71**, 2331 (1993)
   A J Millis, *Nature* **392**, 147 (1998)
[2] A J Millis, R Mueller and Boris I Shraiman, *Phys. Rev.* **B54**, 5405 (1996)
[3] C Xiong, Q Li, H L Ju, S N Mao, L Senapati, X X Xi, R L Green and T Venkatesan, *Appl. Phys. Lett.* **66**, 1427 (1995)
[4] N H Nam, R Mathieu, P Nordblad, N V Khiem and N X Phuc, *Phys. Rev.* **B62**, 1027 (2000)
[5] A Fernandez-Baca, P Dai, H Y Hwang, C Kloc and S-W Cheong, *Phys. Rev. Lett.* **80**, 4012 (1998)
[6] M Pattabiraman, P Murugaraj, G Rangarajan, C Dimitropoulos, Jean-Philippe Ansermet and G Papavassiliou (to be published)
[7] S Yoon, H L Liu, G Schollerer, S L Cooper, P D Han, D A Payne, S-W Cheong and Z Fisk, *Phys. Rev.* **B58**, 2795 (1998)
[8] M N Iliev, M V Abrashev, H-G Lee, V N Povov, Y Y Sun, C Tomsen, R L Meng and C W Chu, *Phys. Rev.* **B57**, 2872 (1998)
[9] L Martin-Carrón and A de Andrés, *J. Alloys Comp.* **323-324**, 417 (2001)
[10] F Millange, V Caignaert, G Mather, E Suard and B Raveau, *J. Solid State Chem.* **127**, 131 (1996)

[11] X Xiong, B Dabrowski, O Chmaissem, Z Bukowski, S Kolesnik, R Dybzinski, C W Kimball and J D Jorgensen, *Phys. Rev.* **B60**, 10186 (1999)

[12] D B Romero, V B Podobedov, A Weber, J P Rice, J F Mitchell, R P Sharma and H D Drew, *Phys. Rev.* **B58**, R14737 (1998)

[13] E Granado, N O Moreno, A García, J A Sanjurjo, C Rettori, I Torriani, S B Oseroff, J J Neumeier, K J McClellan, S-W Cheong and Y Tokura, *Phys. Rev.* **B58**, 11435 (1998)

[14] H L Liu, S Yoon, S L Cooper, S-W Cheong, P D Han and D A Payne, *Phys. Rev.* **B58**, R10115 (1998)