Electronic Raman scattering and photoluminescence from 
La$_{0.7}$Sr$_{0.3}$MnO$_3$ exhibiting giant magnetoresistance

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Abstract

Raman and Photoluminescence (PL) experiments on correlated metallic 
La$_{0.7}$Sr$_{0.3}$MnO$_3$ have been carried out using different excitation wavelengths 
as a function of temperature from 15 K to 300 K. Our data suggest a Raman 
mode centered at 1800 cm$^{-1}$ and a PL band at 2.2 eV. The intensities of the 
two peaks decrease with increasing temperature. The Raman mode can be 
attributed to a plasmon excitation whose frequency and linewidths are con-
sistent with the measured resistivities. The PL involves intersite electronic 
transitions of the manganese ions.

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The recent observations of colossal magnetoresistance has stimulated a renewed interest in the electronic properties of doped $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (A = Sr, Ba, Ca, Pb and vacancies) and other transition metal oxides having strong electron correlations. The rich phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ shows a variety of phases like paramagnetic insulator, ferromagnetic metal, paramagnetic metal, spin canted insulator and ferromagnetic insulator as a function of doping $x$ and temperature. For $0 < x < 0.2$, the materials are insulating at all temperatures and are antiferromagnetic or ferrimagnetic at low temperatures. In the range $0.2 < x < 0.5$ the system shows a temperature induced transition at $T_c(x)$ from the ferromagnetic metal (at $T < T_c$) to a paramagnetic insulator. The end member ($x = 0$) is a charge transfer antiferromagnetic insulator having gap corresponding to the charge transfer excitation from oxygen 2p to manganese 3d state. Out of the $(4-x)$ manganese d electrons, three electrons occupy the tightly bound $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbitals with very little hybridization with the oxygen 2p states and can be considered as a local spin $S_c$ of 3/2. The remaining $(1-x)$ electrons occupy the $e_g$ state made of the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals and are strongly hybridised. There is a strong exchange interaction $J_H$ (Hund’s coupling) between the 3d $t_{2g}$ local spin and the 3d $e_g$ conduction electron. The $e_g$ level is further split into $e_{g}^{1\uparrow}$ and $e_{g}^{2\uparrow}$ due to the Jahn-Teller (JT) effect. The $t_{2g}^{1\uparrow} - e_{g}^{2\uparrow}$ and $e_{g}^{1\uparrow} - e_{g}^{1\downarrow}$ separation is about 2 eV as calculated by Satpathy et al using the local spin density approximation. The estimates of JT split $e_g$ band namely $e_{g}^{1\uparrow} - e_{g}^{2\uparrow} = 4E_o$ using the oxygen bond stretching frequencies to be 560 cm$^{-1}$ is 2.4 eV. It can, however, range from 0.4 eV to 4 eV as argued by Millis.

The metal – insulator transition in the intermediate doping range is qualitatively understood using the Zener’s ”Double Exchange” (DEX) model, in which the $e_g$ electron hopping from site i to j must go with its spin parallel to $S^i_c$ to its spin parallel to $S^j_c$. Millis et al have shown that DEX alone cannot explain many aspects like the low transition temperature $T_c$ and the large resistivity of $T > T_c$ phase or the sudden drop in resistivity below $T_c$. They have proposed that in addition to DEX, there is a strong electron phonon coupling such that the slowly fluctuating local Jahn-Teller distortions localise the conduction band electrons as polarons. As temperature is lowered the effective hopping matrix element $t_{eff}$...
characterising the electron itineracy increases and the ratio of JT self trapping energy $E_{JT}$ to $t_{eff}$ decreases. The JT distortion has to be dynamic because a static JT effect would cause a substantial distortion of the structure and the material would be antiferromagnetic. Coey et al. have argued from the experimental magnetoresistance data that for $T < T_c$, the $e_g$ electrons are delocalised on an atomic scale but the spatial fluctuations in the Coulomb and spin dependent potentials tend to localise the $e_g$ electrons in wave packets larger than the Mn – Mn distance. It has also been noted that doped manganites are unusual metals having resistivities greater than the maximum Mott resistivity (1 to 10 mohm cm) and a very low density of states at the Fermi level.

Optical conductivity measurements on La$_{0.825}$Sr$_{0.175}$MnO$_3$ as a function of temperature by Tokura et al. in the range of 0 – 10 eV show a band at $\sim$ 1.5 eV and spectral weight is transferred from this band to low energies with decreasing temperature. This band at $\sim$ 1.5 eV has been interpreted due to the interband transitions between the exchange split spin polarized $e_g$ bands. At $T < T_c$, the conductivity spectrum is dominated by intraband transitions in the $e_g$ band. A similar feature at $\sim$ 1 eV has been observed in Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ which shifts to lower energies with decreasing temperature which is argued to be consistent by taking into account the dynamic JT effect. There is no reported work on Raman scattering in these systems. Millis has suggested that the transition between the $e_g$ levels split by the JT interaction can be Raman active. The electronic Raman scattering can be observed from the single particle and collective plasmon excitations. The crystal structure with space group $R\bar{3}c$ ($D_{3d}^6$) with two formulas in the unit cell has $A_{1g}$ and $4E_g$ Raman active modes. Our objective was to study vibrational and electronic Raman scattering in doped manganites as a function of temperature. In this paper we report the Raman scattering from doped La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.3$) from 15 K to 300 K attributed to a plasmon mode and a photoluminescence band at $\sim$ 2.2 eV.

Polycrystalline pellets of La$_{0.7}$Sr$_{0.3}$MnO$_3$ prepared by citrate – gel route and sintered at 1473 K with an average grain size of $\sim$ 3.5 $\mu$m were used. The samples on which detailed studies were done have a resistivity of 0.4 mΩ cm at 15 K and 3.5 mΩ cm at 300 K. It shows a
phase transition from a ferromagnetic metal to a paramagnetic insulator at $T_c \sim 380$ K. The Raman measurements were carried out in the spectral range of 200 cm$^{-1}$ to 6000 cm$^{-1}$, at different temperatures from 15 K to 300 K. The spectra were recorded in the back scattering geometry using Spex Ramalog with photon counting detector (photomultiplier tube RCA C 31034 with GaAs cathode) using 514.5 nm, 488 nm and 457.9 nm lines of an Argon ion laser (power density of $\sim 1500$ watts cm$^{-2}$ at the sample). The pellet of thickness $\sim 2$ mm were mounted on the copper cold finger of the closed cycle helium refrigerator (RMC model 22C CRYODYNE) using thermally cycled GE (M/s. General Electric, USA) varnish. The temperature of the cold finger was measured using a Platinum 100 sensor coupled to a homemade temperature controller. The temperatures quoted are those of the cold finger and were measured to within a accuracy of $\sim 2$ K. The experiments were done on three differently prepared pellets of La$_{0.7}$Sr$_{0.3}$MnO$_3$ and the results were similar to the ones reported here.

Fig. 1 shows the recorded spectra at 15 K for the three different excitation wavelengths $\lambda_L$ of 514.5, 488 and 457.9 nm. Fig. 2, 3 and 4 show the spectra at different temperatures for various excitation wavelengths used. It is clear from the spectrum recorded using 514.5 nm as shown in Fig. 1, that the observed lineshape has two contributions. The spectra were, therefore, least square fitted to a sum of two Lorentzians shown by the thick solid line along with the data (open circles). The individual components are shown by thin solid lines. The intensities of the two peaks decrease with the increase in temperature. Since the spectra are rather weak and broad, the fitted parameters of the Lorentzian function (intensity and linewidths) have large error bars and hence their quantitative temperature dependence has not been possible to determine.

We have not been able to observe Raman scattering from the phonons. This can perhaps be due to the fact that the deviations from the cubic structure (for which there are no Raman active modes) are rather small. In collision dominated regime, the Raman scattering line shape from the single particle electronic excitations is given by $I(\omega) \propto (n(\omega, T) + 1)\omega \gamma B / (\omega^2 + \gamma^2)$, where $(n(\omega, T) + 1)$ is the usual Bose Einstein factor, $B$ is the strength of scattering and $\gamma$ is the relaxation rate. This Raman scattering has been observed in La$_{1-x}$Sr$_x$TiO$_3$. 


We have not been able to resolve the contribution of the electronic Raman scattering from the Rayleigh wing, presumably due to the poor surface quality of our sintered pellets.

The spectra shown in Figs 1 and 2 recorded with $\lambda_L = 514.5$ nm are a sum of two Lorentzians centered at $\sim 950$ cm$^{-1}$ and $\sim 1800$ cm$^{-1}$. The spectra recorded with three different excitation wavelengths are consistent with the interpretation that the observed lineshape is a sum of Raman mode centered at $\omega \sim 1800$ cm$^{-1}$ and a PL band centred at photon energy of 2.2 eV. The latter will appear as an apparent Raman shift which varies with different excitation wavelengths. The likely candidate for the Raman mode at 1800 cm$^{-1}$ can be a collective electronic excitation namely the plasmon. Taking the excitation to be a plasmon with frequency $\omega_p = 1800$ cm$^{-1}$, the number density of charge carriers of effective mass $m^*m_e$ can be obtained using the expression

$$\omega_p^2 = \frac{4\pi n_p e^2}{(\epsilon_\infty m^*m_e)},$$

where $\epsilon_\infty$ is the high frequency dielectric constant. Taking $\epsilon_\infty$ to be same as that of LaMnO$_3$, $\epsilon_\infty = 4.9$ we get $n_p/m^* = 1.8 \times 10^{20}$ cm$^{-3}$. The number density calculated from the doping of 0.3 carriers per unit cell of cell volume 64 Å$^3$ is $n_d = 5 \times 10^{21}$ cm$^{-3}$. Taking the effective mass of the carriers to be $m^* = 1$, it is seen that $n_p = 0.04$ $n_d$ i.e the actual number of carriers is less than $(1-x)$ per manganese site. This can be related to the model of Coey et al wherein the $e_g$ electrons though delocalised on atomic scale, are in magnetically localised wavepackets spread over the Mn – Mn separation. If the localisation energy of some carriers is less than $h\omega_p$, they will not participate in the collective plasmon excitation. The localisation need not be as magnetic polarons but may involve lattice polarons as envisaged by Millis. The reduced number of carriers is consistent with the Hall measurements of Hundley as referred by Roder et al. The observed low density of states at Fermi energy also corroborates the less number of carriers deduced from $\omega_p$. Perhaps $m^*$ can be greater than 1 which will reduce the difference between the $n_p$ and $n_d$. The least square fit with the Lorentzians yields the full width at half maximum $\Gamma$ of the Raman mode to be $\sim 1400$ cm$^{-1}$.
The DC resistivity in the free electron model is \( \rho = \frac{m}{n_e} e^2 \tau \); where \( \tau \) is the relaxation time of the carriers. Putting \( \tau^{-1} = \Gamma \), \( \rho \) can be expressed in terms of \( \omega_p^2 \) and \( \Gamma \) as \( \rho = 4\pi \Gamma/(\epsilon_\infty \omega_p^2) \). Taking \( \Gamma = 1400 \text{ cm}^{-1} \) and \( \omega_p = 1800 \text{ cm}^{-1} \), we get \( \rho = 5.3 \text{ mohm cm} \), which is remarkably close to the measured values and therefore gives confidence in our assignment of the Raman mode to be due to the plasmon. The \( \rho(T) \) and hence \( \Gamma \) increases with temperature and can therefore result in substantial reduction of Raman intensities, as seen in our experiments. The observed Raman frequency is much smaller than the estimated \( 4\epsilon_0 \) and hence is not likely to be associated with the transition between the JT split \( e_g \) bands.

Another interesting aspect of the data shown in Figs 2 – 4 is that the PL peak is also seen only in the low temperature metallic phase. The photoluminescence band is therefore linked with the excitations involving \( e_g \) states at different manganese sites. The possible transitions could be between the \( \epsilon_{2g}^1 - \epsilon_{g}^{2\uparrow} \), \( \epsilon_{g}^{1\uparrow} - \epsilon_{g}^{1\downarrow} \) or \( \epsilon_{g}^{1\uparrow} - \epsilon_{g}^{2\uparrow} \) states. It may be noted that the on-site transitions involving the above states are not optically dipole allowed as per the selection rules but these can be allowed for the states on different manganese sites. Since there is a strong temperature dependence, we rule out the possibility that the PL is due to transitions from the oxygen 2p states to the \( e_g \) states. It is possible to have a transition from \( \epsilon_{g}^{1\uparrow} (\text{Mn}^{3+}) \) to the unsplit \( e_g \) level (\( \text{Mn}^{4+} \)) level on an adjacent site. In contrast to Tokura’s interpretation, the peak in the optical conductivity at \( \sim 1 \text{ eV} \) in La\(_{0.825}\)Sr\(_{0.175}\)MnO\(_3\) and Nd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) has been attributed by Millis et al\(^3\) to the transition from \( \epsilon_{g}^{1\uparrow} \) of Mn\(^{3+}\) site to the unsplit \( e_g \) level of adjacent Mn\(^{4+}\) site. If this assignment is correct, then the observed PL band at \( 2.2 \text{ eV} \) in our experiments cannot be due to the above transition as the energy gap is too small (\( \sim 1 \text{ eV} \)). As the temperature is increased the electrons tend to get localised\(^4\) and thus making it difficult to have intersite transitions. The energy separations of the transitions mentioned before have not been determined so far. We can get rough estimates of these from the available band structure calculations, with the caution that the one electron band theory is not the correct picture for the strongly correlated electron systems and the local spin density approximation calculations underestimate the gaps.

Further experiments on these materials especially on single crystals can provide more
clues as to nature and symmetry of these excitations. The Raman mode attributed to the plasmon should occur only in polarized scattering configuration and single particle excitation contributions can be unambiguously distinguished from the Rayleigh wing.

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FIGURES

FIG. 1. Raman Spectra recorded with different excitation wavelengths 514.5nm, 488 nm and 457.9 nm at 15 K. The solid lines shows the fitted function (a sum of two Lorentzians) to the data shown by open circles. The individual components are shown by thin solid lines. The Raman and PL component are labeled as R and L, respectively.

FIG. 2. Raman Spectra in the temperature range 15 K to 300 K using 514.5 nm excitation wavelength. Fitted function of two Lorentzians is shown by the solid line for each spectrum. The intensities of the two modes decrease as temperature increases.

FIG. 3. Same as Fig. 2, but with different excitation wavelength of 488 nm.

FIG. 4. Same as Fig. 2, but with different excitation wavelength of 457.9 nm.