Chapter 7

Summary

Manganites being complex systems are interesting from underlying physics point of view in addition to their promising technological applications. The present thesis reports the results on the investigation of vibrational properties of manganites under far from equilibrium conditions and an attempt is made to complement these properties of lanthanum manganites to understand the CMR physics. In these systems, an important issue is the influence of phononic and electronic degrees of freedom on phenomenon like CMR. High pressure and temperature tunes the interplay between lattice and electronic degrees of freedom in manganites. Internal pressure induced by increasing \(<r_A>\) (i.e. average ionic radius of A-site ion) also brings a delicate balance in a similar fashion. The double exchange mechanism introduced to understand ferromagnetism in manganites, is not sufficient alone to account for their magnetotransport properties (chapters 1 and 3). Some features exhibited by doped manganites are difficult to understand without taking into account the Jahn-Teller coupling between the electrons and phonons. This view is further supported by the close relationship between the structural and electronic phase diagram (chapter 1).

As a matter of fact, LaMnO₃, which undergoes phase transition at high temperature, is considered in its cubic and rhombohedral phase. It is also considered to study the effect Sr-doping at A-site. In addition, to understand the effect of pressure and temperature, 30 % Sr-doped LaMnO₃ i.e. La₀.₇Sr₀.₃MnO₃ (LSMO) is considered at different applied pressure and temperature. Due to decreased symmetry of rhombohedral LaMnO₃ and more number of atoms in rhombohedral unit cell as compared to cubic LaMnO₃, the number of phonon modes at zone centre of rhombohedral LaMnO₃ is more. The difference in structural symmetry of cubic and rhombohedral manganites is manifested in their phonon spectra and density of states. Structure phase transition from orthorhombic-rhombohedral-cubic gradually removes buckling of MnO₆ octahedral and leads to reduction in electron-phonon interaction accompanied by achieving higher symmetry. Besides structural symmetry, A-site ion radius, doping, temperature and pressure also cause the modification in phonon dispersion curves, phonon density of states and phonon branches, splitting the phonon modes into a pair of non-degenerate (A) and doubly degenerate (E) modes with broadening and overlapping. Doping by Sr atoms at La-site changes A-site ionic radius \(<r_A>\) which untilts octahedral framework and the far away oxygen atoms in first co-ordination shell start to feel an attractive interaction as they come closer to A-site. This increased attractive interaction is
transmitted to Mn-O network as an effective internal pressure, which is accompanied by the decrease in Jahn-Teller distortion resulting into the increase in $T_c$ and apparently metallicity of manganites increases (ferromagnetism). In vibrational spectra, this is complemented with the softening of $A_{1g}$ phonon modes originating due to MnO$_6$ rotation and high frequency stretching mode (chapter 3). In insulating orthorhombic phase of parent LaMnO$_3$, this mode is higher than that in the Sr-doped rhombohedral LaMnO$_3$. The correlation of the frequency of $A_{1g}$ mode with angle $\alpha$ of the rhombohedral distortion indicates that the doping at A-site of undoped LaMnO$_3$ reduces the Jahn-Teller distortion and manifested in softening of the $A_{1g}$ mode following the linear relation. Substitution of Sr atoms at A-site regularizes the crystal structure maintaining the tilting of the octahedra. The application of internal pressure introducing a divalent atom at A-site thereby reduces the electron-phonon coupling and system achieves character that is more metallic. In addition, calculation of the thermodynamic parameters exhibit that the cubic LaMnO$_3$ with the highest symmetry has the lowest specific heat and Debye temperature among undoped cubic LaMnO$_3$ and rhombohedral LaMnO$_3$, and rhombohedral Sr-doped LaMnO$_3$. The doping at La-site by Sr atom softens the lattice at high temperatures (above 100 K), which is reflected in softening of $A_{1g}$ phonon modes in rhombohedral structure.

The use of temperature and pressure as thermodynamic variables provides with a simple but powerful means by which interaction within the system can be modified without changing the doping level. Sr-doped LaMnO$_3$ in rhombohedral phase for $x' = 0.3$ is considered to see the effects of temperature and pressure on phonon properties. Softening of the stretching mode in the phonon dispersion curve of La$_{0.7}$Sr$_{0.3}$MnO$_3$ at specific temperature reflects the instability of phonon modes causing Jahn Teller lattice distortion (chapter 4). The $A_{1g}$ phonon mode corresponding to the rotations of MnO$_6$ octahedra also undergoes softening while the stretching mode of MnO$_6$ octahedra, which is a JT phonon mode with Mn-O bond character contributing to the highest frequency region, hardens upon reduction in temperature. The lattice softening as a result of temperature variation is manifested in decrease in Debye temperature ($\theta_D$) at 300 K. The temperature dependence of the atomic displacement is correlated with the anharmonic lattice distortion via the effective Grüneisen parameter $\gamma_{eff}$ for rhombohedral La$_{0.7}$Sr$_{0.3}$MnO$_3$ systems. The presence of anharmonic lattice modes is also indicated by anomalously high value of Grüneisen parameter.

The application of external pressure always increases the Curie temperature ($T_c$) widening the Mn-O-Mn bond angle and compressing Mn-O and A-O bond lengths. It also reduces the local distortion of the MnO$_6$ octahedra and structure of systems becomes more cubic with reduction in electron-phonon coupling through the modification of the frequency of the octahedral bending and stretching modes. The $A_{1g}$ mode is the most sensitive to pressure variation, which seems to be related with the changes in JT distortion. Phonon dispersion curves reveal that both the (IR and Raman) frequencies of modes involving the vibrations of La atom which actually do not depend on the octahedral distortion, are almost pressure independent while the stretching and rotational modes ($E_g$ and $A_{2u}$) involving oxygen atom vibrations (high frequency) and related to the
MnO$_6$ octahedra show linear pressure induced hardening (chapter 5). The pressure behaviour of stretching and rotational modes ($A_{2u}$ and $E_g$) also suggests that the Mn-O-Mn angle is close to the ideal 180° value of the cubic structure and therefore the system would be of more metallic character. The rotational frequency of MnO$_6$ octahedra is not changing fast which indicates that the octahedra are not severely distorted by the application of pressure. Therefore, it can be concluded that the hardening of phonon frequencies is consistent with the increase in $T_C$ with pressure. The phonon peaks in the higher energy side of the phonon density of states show decrease in peak width with the increase of pressure and hence there appears reduction in electron-phonon interaction and lattice disorder responsible for the JT distortion. The effective mode Grüneisen parameter depicts that pressure induces the reduction of JT distortion, which is signature of the rhombohedral structure.

The phonon properties investigated for the NaCoO$_2$ compound in its two different geometry positions are significantly different for the sodium atoms. The in-plane mode is found to occur at lower frequency and is insensitive to Na positions, while the out-of-plane mode is sensitive to the sodium position, and gives rise to the higher frequency modes with Na(2) position and lower with Na(1) positions. A temperature dependent investigations of phonons can lead to some understanding of insulator-Metal transition and charger ordering, which is not performed in the present study.