PREFACE

The exotic phenomenon of superconductivity was discovered way back in 1911 by Kamerlingh Onnes of Leiden as a consequence of the liquefaction of helium in 1908. The saga of high temperature superconductivity started with the discovery of La-Ba-Cu-O system with T_c = 35K by Bednorz and Muller. Later, Chu et al showed that the T_c of La-Sr-Cu-O could be raised from 35K to 50K by applying pressure. Subsequently, Y-Ba-Cu-O system was reported with a T_c of 90K, well above 77K, the boiling point of liquid nitrogen, which represented one of the greatest triumphs of scientific endeavour. In a systematic study, different rare earths were substituted for yttrium and in most of these cases single phase oxides which superconduct in the 90K range were found. The structures containing Cu and O in the same plane are found to be responsible for metallic conduction in both La-Ba-Cu-O and Y-Ba-Cu-O systems.

It is generally believed that all that is needed to signpost the way to the development of materials with high critical temperatures even to room temperature and above, is the formulation of a proper theoretical understanding of superconductivity in these materials. Although many

theories based on Resonant Valence Bond, excitons, polarons, magnons, and fermions have appeared to explore the mystery of pairing mechanism in superconductivity, still it remains unclear. In conventional superconductors, the role of phonons is well established. However, in high T_c superconductors, the role played by phonons is controversial. Even if they do not mediate the pairing mechanism, they are likely to play an important subsidiary role , hence the ongoing interest in the phonon structure of these materials. In this work, an attempt has been made to determine the phonon frequencies of different rare-earth substituted 123 systems using normal-coordinate analysis and lattice dynamical studies.

This thesis presents four chapters. Chapter 1 deals with the theoretical aspects of high T_c superconductivity, recent developments, applications and future prospects.

At present, the mechanism of high T_c superconductivity is a challenging problem and much work has to be done in both theoretical and experimental fields. Hence, the study on the compositional and structural dependence of superconductivity is important to substantiate this mechanism in Cu containing oxides and to prepare new high T_c

materials.

Chapter 2 includes the details regarding the fabrication methods of the superconducting samples and the experimental techniques involved in their preparation. The samples are prepared by solid state reaction method. Resistivity measurements are made using standard four-probe technique to establish the efficiency of the superconductor and to confirm if the fabricated sample shows perfect conductivity at a particular transition temperature. The pressure shift of T_c and a.c susceptibility measurements for the compounds are also studied. Superconducting properties of $HoBa_2Cu_3O_7$ are studied and the following observations are made:

1. All resistance versus temperature curves have slight shoulder in the transition temperature range.

2. The pressure shift of T_{co} and T_{cf} is small.

3. The superconducting transition terminates at 93K at atmospheric pressure.

4. dR/dT changes with increasing pressure.

The assignment of spectral features to specific lattice vibrations is an important step to understand their role in

superconductivity. Raman and far-infrared studies have contributed significantly for the explication of the high T_c superconducting mechanism. Although, many reports of superconductivity for rare earth atoms have appeared, systematic investigations for the whole rare earth family are scarce. Cardona et al have studied the infrared and Raman spectra of the superconducting cuprate perovskites and reported the origin of phonon softening and the systematic variation of phonon frequencies with ionic radius. Normal coordinate calculations have been extensively used for various metal oxides to study their vibrational analysis. In this method, non-central forces such as those involved in angle bending can be readily treated. These calculations using infrared and Raman details have allowed a detailed assignment of the vibrational features of the superconducting systems.

In Chapter 3, a clear picture of the normal coordinate analysis of the spectral frequencies and the form of zero wave vector vibrations of the high temperature superconductors $HoBa_2Cu_3O_7$, $DyBa_2Cu_3O_7$ and $SmBa_2Cu_3O_7$ are presented. These systems crystallize in the orthorhombic structure with the space group $P_{mmm}(D_{2h})$. According to factor group analysis, the 13 atoms of the unit cell yield a

total of 36 non-zero vibrational frequency modes at q=0, which is represented as

$$\Gamma = 5A_g + 5B_{2g} + 5B_{3g} + 7B_{1u} + 7B_{2u} + 7B_{3u}$$

where A_g, B_{2g} and B_{3g} are Raman active modes while B_{1u}, B_{2u} and B_{3u} are infrared active modes. The normal coordinate calculation is performed using Wilson's FG matrix method by utilising the programs GMAT and FPERT after suitable modifications. A simple valence force field is used. The structural parameters employed to carry out these calculations are tabulated. The calculated vibrational frequencies and the potential energy distributions are also given. To check whether the chosen set of vibrational frequencies contributes maximum to the potential energy associated with the normal-coordinate of the superconducting material, the potential energy distribution is calculated using the relation

$$P.E.D = F_{ii}L^2_{ik}/\lambda_k$$

The evaluated frequencies agree close to the available observed infrared and Raman frequencies giving further support to the present assignment. The results and discussion are given in detail in the respective subsections of chapter 3.

Chapter 4 describes the lattice dynamics of lithium halides and high temperature superconductors. There has been considerable theoretical and experimental interest in the study of the lattice dynamics of alkali halides, which form a relatively simple class of ionic solids. For the basic understanding of the physical properties such as thermal, elastic,dielectric, infrared, etc.,it is indispensable to have a knowledge of the phonon frequency spectrum which can be achieved by means of theoretical models of lattice dynamics.

The lattice dynamics of LiF,LiCl,LiBr,LiI,LiD and LiH has been investigated using three body force shell model. A substantial concentration of electrons along the bonding directions is required to counter balance the self-repulsion of a structure. This distribution of electron gives rise to the three body forces. In the present work, a shell model is developed by reformulating the original TSM which takes care of the effect of many body interactions in the lattice potential. Here, the various interactions between the ions are treated in a more general way without making them numerically equal. In order to investigate the consequences of the modification included in TSM, this model has been applied to describe the lattice dynamics of lithium halides and hydrides with a modified valence of z=0.88 instead of

z=1.0. The phonon dispersion relation along the three principle symmetry directions (q,0,0), (0,0,q) and (0,q,0) obtained from this model have been compared with the available neutron data and found to give better agreement. The calculated model parameters, phonon frequencies and the phonon dispersion curves are presented in this chapter.

This model has been extended to study the lattice dynamics of the high T_c oxides $HoBa_2Cu_3O_7$, $DyBa_2Cu_3O_7$ and $SmBa_2Cu_3O_7$ where the calculations are based on interionic potentials instead of force constants. A group theoretical analysis based on the orthorhombic structure predicts 15 Raman active modes and 21 infrared active modes. The phonon frequencies at the zone centre of the Brillouin zone , which are of interest for the interpretation of the infrared and Raman spectrum are presented and the vibrational assignments are discussed. The calculations yield not only the phonon frequencies at the zone centre but also throughout the Brillouin zone.

The phonons so indentified can be used for the characterisation of the superconducting materials,for example, to determine in a non-destructive way, the oxygen content of YBCO and related systems. The results thus pave

the way to ascertain the role of phonons in the superconducting mechanism and serves as a guide for further experimental studies on the vibrational properties of these systems.

A part of the material presented in this thesis has been published / communicated in the form of papers in various journals as follows:

1. Normal coordinate analysis of the zero wave vector vibrations of $SmBa_2Cu_3O_7$, Indian J.Pure and Appl.Phys. 29, 803, 1991

2. Normal coordinate analysis of the zero wave vector vibrations of $DyBa_2Cu_3O_7$, Pramana - J. Phys. 37, 327, 1991

3. Preparation and characterization of the superconductor $HoBa_2Cu_3O_7$, Proc. Indian Natn. Sci. Acad. 58A, 371, 1992

4. Normal coordinate analysis of the zero wave vector vibrations of $HoBa_2Cu_3O_7$, Vibl. Spectrosc. 3, 79, 1992

5. Lattice dynamics of LiD and LiH, Indian J. Phys. 67A, 29, 1993

6. Lattice dynamics of some lithium halides, Indian J. Pure and Appl.Phys. 31, 57, 1993.

7. Lattice dynamics of $HoBa_2Cu_3O_7$, Intl. J. Mod. Phys. (Communicated)

8. Lattice dynamics of the high T_c superconductor $DyBa_2Cu_3O_7$, Arabian J.Sci. and Engg. (Communicated)

9. Three body force shell model of $SmBa_2Cu_3O_7$, Australian J.Phys. (Communicated)