Abstract

This thesis is divided into two parts; the first part presents results on the effect of the flow of fluids and electrochemical bias on single walled carbon nanotubes (SWNT). Issues pertaining to the entry of water into the cylindrical pores of the SWNT and its freezing dynamics have also been addressed in the first part of the thesis. The second part of the thesis deals with Raman scattering studies of iron perovskite namely $CaFeO_3$ and $La_{0.33}Sr_{0.67}FeO_3$ across their charge-disproportionation transition temperatures.

PART 1

Chapter 1: Introduction

This chapter presents an overview of the systems studied in this thesis, i.e., (i) SWNT and (ii) iron perovskite's containing iron in $Fe^{4+}(d^4)$ state, namely $CaFeO_3$ and $La_{0.33}Sr_{0.67}FeO_3$. It also contains an introduction to the two spectroscopic techniques used in the present thesis, namely Raman scattering and Nuclear Magnetic Resonance. A quantum mechanical picture of Raman scattering, in general, and resonance Raman scattering in particular along with a brief introduction to the apparatus used both for the micro-Raman and the low-temperature experiments is presented in this chapter. A general introduction to Nuclear Magnetic Resonance (NMR) is also given with an emphasis on various interactions leading to the broadening of the NMR absorption linewidths.

Chapter 2: Carbon nanotube liquid flow sensors

This chapter presents experimental results and theoretical understandings of the generation of electrical signals by flowing polar/ionic liquids over a mat of SWNT. We first

present experimental findings that the flow of a variety of liquids on SWNT bundles induces an electrical signal (voltage/current) in the sample along the direction of the flow. The electrical response is found to be a logarithmic function of the flow speed over a wide range. The magnitude of the signal generated depends sensitively on the ionic conductivity and the polar nature of the liquid and weakly on the viscosity of the liquid. Furthermore its direction can be controlled by electrochemical biasing of the nanotubes. The ratio of the open circuit voltage to the short circuit current is found to be governed by the nanotube resistance. These experimental findings are inconsistent with the conventional idea of a streaming potential as the possible cause. Our measurements suggest that the dominant mechanism responsible for this highly sub-linear response should involve a direct forcing of the free charge carriers in the nanotubes by the fluctuating Coulombic field of the liquid flowing past it.

Two alternative understandings of the experimental findings are also presented in this chapter. The first mechanism invokes the idea of a “pulsating ratchet” whereby the charge carriers in the nanotubes experience an asymmetric spatial bias because of the shear-induced deformation of the ion-plus-polar atmosphere at the liquid-solid interface temporally modulated by the liquid flow. In addition, we also propose that experimental findings can be understood qualitatively in terms of three inter-related ideas: (a) *Induced friction*: The fluctuating charge density of the ions close to the nanotube couples coulombically to the charge carriers in the nanotube and, therefore, offers a friction to the motion of these charge carriers (in addition to the Ohmic friction intrinsic to the carbon nanotubes); (b) *Flow-induced drag*: In virtue of the above frictional coupling, an imposed liquid flow drags the charge carriers along through the nanotube; (c) *Reduction of induced friction at high flow speeds*: The space-time correlated Coulombic fluctuations, inherent to the liquid electrolyte, are *advected* by the liquid flow, and thus get Galilean boosted (Doppler shifted) as seen in the mean rest frame of the drifting carriers in the nanotube. This would cause a reduction of the frictional grip to the motion of the charge carriers in the nanotube with increasing flow speed resulting in a sublinear dependence of the charge drift-velocity (electrical response) on the liquid flow speed. With the above in mind, a quantitative derivation of these frictional effects, first from a heuristic argument, and then analytically from a Langevin-equation treatment have been presented.

Chapter 3: Direct generation of voltage and current by gas flow over carbon nanotubes and semiconductors

Having obtained experimental evidence of the generation of liquid flow induced electrical signals over single-walled carbon nanotubes, it was only natural to look for the same effect by flowing gases over nanotubes. We show here a direct generation of measurable voltages and currents when gas flows at modest speeds of a few meters per second over single-walled carbon nanotubes . Interestingly, unlike the previous effect (generation of voltages by flow of liquids over single-walled carbon nanotubes), this effect is not specific to single-walled carbon nanotubes and occurs for a wide variety of solids, including single and multi-walled carbon nanotubes, doped semiconductors and metals. Moreover, the gas flow induced signals depend quadratically on the gas flow velocities. This is in sharp contrast to the results obtained by flowing liquids over single-walled carbon nanotubes where the liquid flow generated signal was found to be logarithmically dependent on the flow velocities. In this chapter we provide evidence that the underlying mechanism for the gas flow generated electrical signal is an interplay of Bernoulli's principle and the Seebeck effect: Pressure difference along streamlines gives rise to temperature difference across the sample which, in turn, produces the measured voltage.

Chapter 4: Water at nanoscale confined in single walled carbon nanotubes studied by NMR

In this chapter, we seek experimental evidence of the occupancy of water in the cylindrical pores of the nanotubes. Proton NMR studies have been carried out as a function of temperature from 210 K to 300 K of water confined within SWNT. The NMR lineshape at and below the freezing point of bulk water is asymmetric which can be decomposed into a sum of two Lorentzians. The intensities of both the components decrease with lowering of temperature below 273 K, one component L_1 vanishing below 242 K and the other component L_2 below 217 K. Following the simulations of Koga *et al.* (*Nature*, **412**, 802, 2001) showing that the radial density profile of confined water in SWNT has a distribution peak at the center which disappears below the freezing temperature, the L_1 component is associated with the protons of the water molecules at the center and the L_2 component is associated with protons of water molecules associated at a distance ~ 3 away from the walls of the nanotubes. In this scenario the complete freezing of the water at $\sim 212\ \mathrm{K}$ is preceded by the withdrawal of the water molecules from the center of the nanotubes.

Chapter 5: Electrochemical tuning of band structure of single walled carbon nanotubes probed by in-situ resonance Raman scattering

The work presented in this chapter is motivated by the experimental observation that SWNT have excellent actuating properties, i.e, porous sheets of carbon nanotubes were shown to suffer length changes when subjected to electrochemical bias, with action observed up to 1 KHz. The fast response of the nanotube actuator rules out any mechanism related to the intercalation of ions as is applicable to the case of the polymer actuators. This chapter presents results of in-situ resonance Raman scattering of SWNT investigated under electrochemical biasing. The experimental results show that the intensity of the radial breathing mode varies significantly in a non-monotonic manner as a function of the cathodic bias voltage, but does not change appreciably under anodic bias. The tangential mode is, however, not affected. These results can be quantitatively understood in terms of the changes in the energy gaps between the one-dimensional van Hove singularities in the electron density of states arising possibly due to the alterations in the overlap integral of π-bonds between the p-orbitals of adjacent carbon atoms. This chapter also contains results from *ab-initio* restricted Hartree Fock calculations in a simplistic geometry where a nanotube is surrounded by two concentric rings of ions. The *ab-initio* calculation results suggest that the dominant contribution to the strain developed in the nanotubes originates from the electrostatic interactions between the ions and the delocalized π electrons as compared to the doping effects.

PART 2

Chapter 6: Raman scattering in $CaFeO_3$ and $La_{0.33}Sr_{0.67}FeO_3$ across the charge disproportionation phase transition

Temperature dependent micro-Raman studies of orthorhombic $CaFeO_3$ and rhombohedral $La_{0.33}Sr_{0.67}FeO_3$ were carried out with an aim to study the role of phonons in the formation of the charge disproportioned state ($Fe^{4+} \rightarrow Fe^{5+} + Fe^{3+}$) below the transition temperature (T_{co}) of 290 K and 200 K, respectively. Shell model lattice dynamics calculations were performed for $CaFeO_3$ to assign the Raman modes and determine their vibrational pattern. Temperature dependence of the peak positions and peak widths of various modes for both the systems show distinct changes across their respective transition temperatures. In $CaFeO_3$ the symmetric stretching mode at 707 cm^{-1} splits into two modes, 707 cm^{-1} and 684 cm^{-1}. Interestingly, the 707 (684) cm^{-1} mode appears only in HH(HV) polarization. In comparison, the Raman band at 704 cm^{-1} in $La_{0.33}Sr_{0.67}FeO_3$ which has been assigned to the Raman forbidden symmetric stretching mode, disappears below T_{co}. In addition, two modes at 307 cm^{-1} and 380 cm^{-1} of $La_{0.33}Sr_{0.67}FeO_3$ approach each other at T_{co}. Our experiments show that for both the systems, $CaFeO_3$ and $La_{0.33}Sr_{0.67}FeO_3$, the lattice distortion changes across T_{co}.

Chapter 7: Summary and future outlook

The last chapter summarizes our main findings reported in the thesis. It also contains possible future studies which are worth pursuing to add further insights in the issues addressed.