Chapter 1

Introduction

At the beginning of the 21st century, some issues have attracted significant interest and achieved global dimension, such as energy shortage and global warming. It had been pointed out by geophysicists that the oil source will be insufficient within five decades, resulting in an unexampled energy crisis. The way we use our limited energy sources still has lots of rooms to improve. Although there are many ways to generate electric power, a lot of energy is released in type of heat during energy transformation. On the one hand, it is a waste of energy; while on the other hand, it causes the thermal pollution to our environment. The need for more efficient use of electricity is dependent on improved thermoelectrical materials and designs.

Thermoelectric material, it is able to not only converse the temperature difference directly into electricity, but also create a heat difference from an electric voltage. The former calls Seebeck effect (or thermoelectric effect), was first discovered, accidentally, by the German-Estonian physicist Thomas Johann Seebeck in 1821. This is also the principle at work behind thermal diodes and thermoelectric generators (such as radioisotope thermoelectric generators or RTGs). The later is named Peltier effect which is often used for thermoelectric cooling, was observed by Jean Peltier, 13 years after Seebeck's initial discovery.

In 1997, I. Terasaki *et al.* observed that the Seebeck coefficient of $NaCo_2O_4$ single crystal is 100 μVK^{-1} (about ten times larger than typical metal), while it has low resistivity (200 $\mu\Omega cm$) at room temperature.[1] Hence, Na_xCoO_2 is potential technological applications as a thermoelectric material.

In 2002, K. Takada *et al*. found that Na_xCoO_2 can become a superconductor with T_c ~ 5 K when it is in hydrated cobaltate $Na_{0.33}CoO_2 \cdot 1.3H_2O$.[2] The superconductivity in $Na_xCoO_2 \cdot yH_2O$ is derived from the insertion of H_2O into the lattice of $Na_{0.7}CoO_2$ with *H*2 phase. The $Na_xCoO_2 \cdot yH_2O$ systems are interesting for the following reasons:

1. It is the first Co-based oxide superconductor.
2. The superconductivity is derived from the intercalation of H_2O into the cobalt-based oxide, which itself is not a superconductor. The system could be considered as an electron-doped Mott insulator through sodium doping.
3. The structure of $Na_xCoO_2 \cdot yH_2O$ is similar to those of high-T_c superconductors, except that the Co atoms form hexagonal orientation rather than a square orientation in each layer.[1,3] There may be new properties of superconductivity and probability to reach higher T_c.[4-6]

Moreover, Na_xCoO_2 system exhibits extraordinary physical properties that correlate with Na concentration in their layered lattice. The phase diagram is shown in Figure 1 - 1, revealing the different structural phases are associated with the Na positions and ordering.[7] As Na content increasing from $x = 0.3$, the electron ground state changes from a paramagnetic metal to a charge-ordered insulator for $x = 0.5$, and to a spin ordered phase for $x > 0.75$. The $Na_xCoO_2 \cdot yH_2O$ system represents a highly correlated electron system that exhibits a wide range of interesting physically properties, such as charge ordering, orbital ordering, magnetic ordering, thermoelectricity, and superconductivity.

For the Na_xCoO_2 system of particular interest here, the spin entropy has been found to play an essential role[3] in the dramatically enhanced thermopower[1] for large sodium content ($x \sim 0.7$), and magnetic order and spin fluctuations have been observed in this regime.[8-12] Moreover, it is noted that the layered Na_xCoO_2 materials actually have a rich variety of structural features, such as structure modulation from Na ordering. Raman-scattering spectroscopy measurement is an efficient way for understanding the local atomic arrangement change induced by oxygen shifts and Na ion ordering. Moreover, Up to the present, there were many infrared results of Na_xCoO_2 single crystals but the investigation of Na_xCoO_2 thin film was very rare. It is known that for further application, it is necessary to understand the characteristic of thin film. In order to gain additional insight into the novel properties of Na_xCoO_2 systems, we present the results of the Raman-scattering experiments and optical reflectance investigations of Na_xCoO_2 samples with $x = 0.68$, 0.75 thin films, and 0.84 single crystal. Moreover, we also present Raman mapping experiment coupled with the ratioimage method to study the morphology on the surface of Na_xCoO_2, which has never been reported.

The rest of this paper is organized as follows. Chapter 2 is the fundamental properties and a review of the important previous work of Na_xCoO_2 systems. Chapter 3 describes the Raman-scattering and infrared techniques and experimental apparatus used in this study. Chapter 4 shows the characteristic of our samples. Chapter 5 shows our experimental results and discussion. Finally, a summary will be given in Chapter 6.

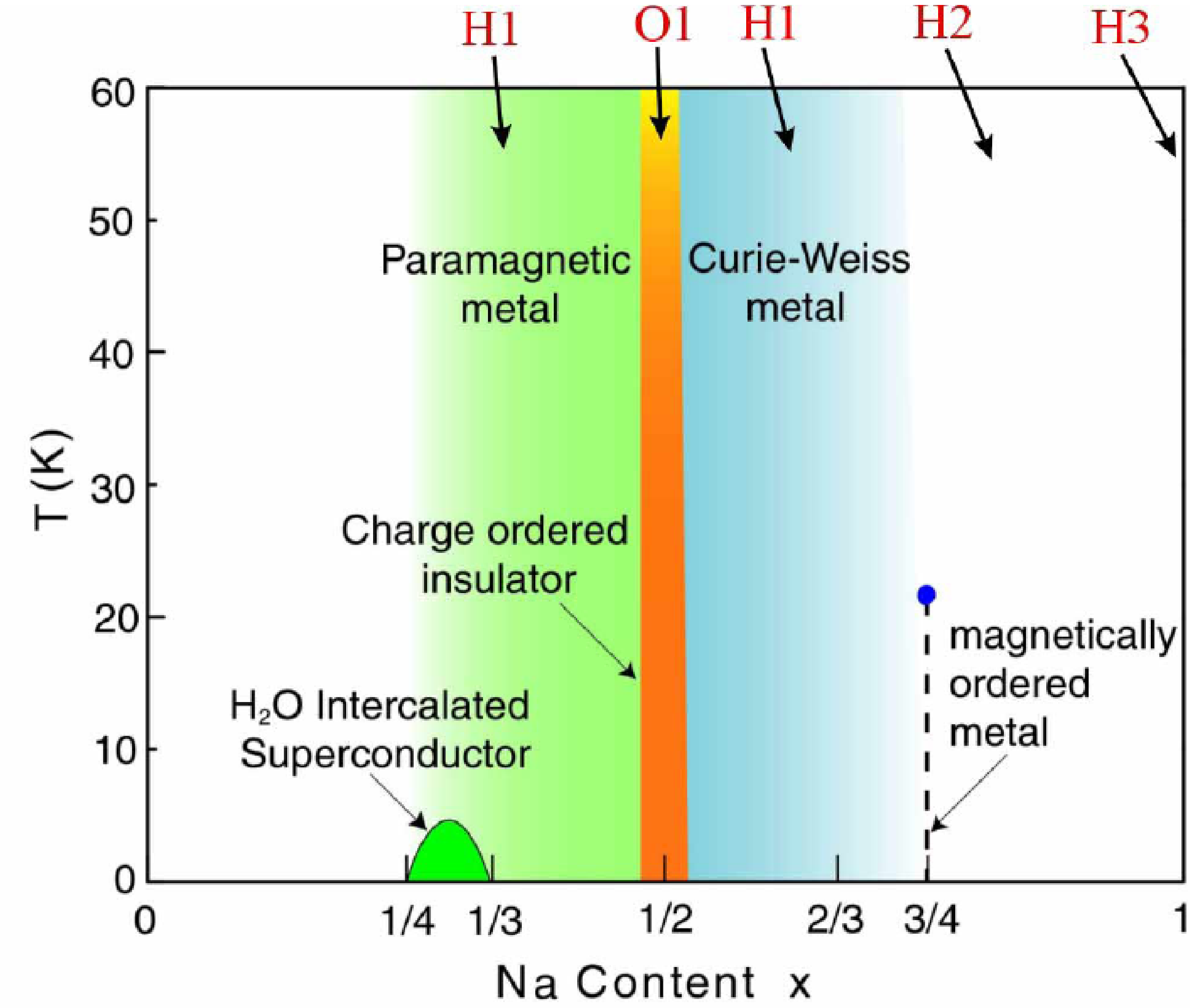

Fig. 1 - 1. Phase diagram for Na_xCoO_2 indicating the different structural phases associated with the sodium positions and ordering.[7]