Effect of pressure on the electrical transport and structural properties of YbNiO3

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Physics Department

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<td>TMO</td>
<td>Transition metal oxide</td>
</tr>
<tr>
<td>W</td>
<td>Band width</td>
</tr>
<tr>
<td>Δ</td>
<td>Charge transfer energy</td>
</tr>
<tr>
<td>U</td>
<td>Coulomb repulsion</td>
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<tr>
<td>R</td>
<td>Rare earth element</td>
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<tr>
<td>$T_{MI}$</td>
<td>Metal insulator transition temperature</td>
</tr>
<tr>
<td>MI</td>
<td>Metal insulator transition</td>
</tr>
<tr>
<td>$T_N$</td>
<td>Neel temperature</td>
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<tr>
<td>DAC</td>
<td>Diamond anvil cell</td>
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<tr>
<td>P</td>
<td>Pressure</td>
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<tr>
<td>F</td>
<td>Force</td>
</tr>
<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wave length</td>
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<tr>
<td>$E_g$</td>
<td>Energy gap</td>
</tr>
<tr>
<td>Z</td>
<td>Number of nearest neighbor atoms</td>
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<tr>
<td>$t_{dd}$</td>
<td>Hopping matrix element from (d-d) (transfer element)</td>
</tr>
<tr>
<td>$t_{pd}$</td>
<td>Hopping matrix element from (p-d)</td>
</tr>
<tr>
<td>$t$</td>
<td>Tolerance factor</td>
</tr>
<tr>
<td>$d_{A,X}$</td>
<td>Bond length between (A) and (X)</td>
</tr>
<tr>
<td>CF</td>
<td>Crystal field</td>
</tr>
<tr>
<td>$\Delta_{CF}$</td>
<td>Crystal field splitting</td>
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<tr>
<td>$e_g$-level</td>
<td>Energy level that contain the high energy electrons in TMO</td>
</tr>
<tr>
<td>$t_{2g}$-level</td>
<td>Energy level that contain the low energy electrons in TMO</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Distortion factor</td>
</tr>
<tr>
<td>B</td>
<td>Bulk modulus</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive x-ray</td>
</tr>
<tr>
<td>n</td>
<td>Order of diffraction</td>
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<tr>
<td>d</td>
<td>Grating space</td>
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<tr>
<td>EOS</td>
<td>Equation of state</td>
</tr>
<tr>
<td>SR</td>
<td>Synchrotron radiation</td>
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<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
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Abstract

The high pressure solid state physics has become one of the most important physics branches now a days as it study the effect of the pressure on the material physical properties and what does the material do to get rid of this effect.

One of the long-standing issues associated with strongly correlated 3d transition metal oxides (e.g. RMO$_3$) is the microscopic origin of the metal insulator (MI) transition and the nature of the ground state. As in this type of materials the MI transition is driven by strong correlation effects associated with the electron-electron interaction and the interplay between charges, orbital and spin degrees of freedom.

Here we use the change in the external pressure as a tool to tune electronic and magnetic properties of these systems by increasing the external pressure we change the bond length between the Metal and the Oxygen (d$_{M-O}$) which will modify the effective band width, also it will affect on the bond angle between the Metal and the Oxygen ($\theta_{M-O-M}$).

For applying the external pressure we use 2 diamonds crystals in a setup called the Diamond Anvil cell (DAC) which has been developed over the year’s since the first half of the 20th century till now. We prepare the cell with certain manner to allow the measurement of the resistivity of the sample and the structure properties using the x-ray diffraction method.

For measuring the resistivity of the YbNiO$_3$ under different pressures and temperatures we use a cryostat to control the temperature and reach a very low temperature, and we use the nanovoltmeter, melliammeter, and a current source to measure the electrical variables on the YbNiO$_3$.

For determining the crystal structure of the YbNiO$_3$ and the effect of the pressure on it we use a high energy x-ray beam from the synchrotron and focus it on the sample then analyze the spectra to get the structure properties of the YbNiO$_3$.

When analyzing the data for the resistivity we found that the sample behave as insulator below certain pressure and as the pressure increase some metallic properties start to appear, so the sample is said to undergo an insulator metallic transition.

When we investigate the crystal structure of the sample to see the cause of this transition and it’s relation to the crystal structure of the sample we found that the structure phase transition take place at higher pressure value as for MI transition, which indicate that the insulator metal transition isn’t accompanied by structure phase transition.
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**Tab. 4.1** represents the data of the ionic radius, tolerance factor, and the transition temperatures in RNiO$_3$ compounds.
Chapter 1

Introduction

Systems containing transition metal atoms represent a class of materials that exhibit a wide variety of interesting electronic and magnetic properties. Transition metal oxide (TMO) compounds may be good insulators, semiconductors, or metal. Many of them display a metal insulator transition by varying carrier concentration, temperature, magnetic field, and internal or external pressure. This is related to the fact that the nature of the ground state of these systems is determined by a complex balance of various parameters, including the bandwidth (W), the charge-transfer energy (\(\Delta\)), and the Coulomb repulsion energy (U). Depending on the relative magnitudes of these parameters, the system can be a metal or an insulator. Most of these systems have partially filled 3d bands and exhibit in general an antiferromagnetically ordered ground state. Here, the application of external pressure generated well-defined changes in both W and U or \(\Delta\) in such systems and thereby results in a modification of their transport and magnetic properties without disturbing the electronic identity, as it happens for example by chemical doping. Also structural phase transitions can be expected.

Among these classes of systems, TMO compounds of the RMO₃ perovskite type structure (R: rare earth ion, M: transition metal) are considered as exemplary systems in which structural instability is intimately connected with electronic and magnetic phase transitions. In this respect, the rare earth (R) nickelates (RNiO₃ perovskites) are of a special interest as being stoichiometric Mott-insulators, in which a MI transition can be induced as a function of temperature while the transition temperature (\(T_{\text{MI}}\)) increases with reducing the size of the R³⁺ ions (\(T_{\text{MI}} = 130\) K (Pr),..., 600 K (Lu) [1][2]. The temperature-induced MI transition in RNiO₃ series has been ascribed to
the opening of a small charge transfer gap at $T < T_{MI}$ that is intimately connected with an orthorhombic (Pbnm) to monoclinic (P21/n) structural transition ($R = \text{Pr}, \ldots, \text{Lu}$) \footnote{3}. The transition to a monoclinic symmetry on crossing $T_{MI}$ to the insulating state implies two independent Ni-sites and the presence of a charge ordering ($2\text{Ni}^{3+} \rightarrow \text{Ni}^{3+} + \text{Ni}^{3-}$) \footnote{5[4]}. 

In addition, the transition to a magnetically ordered state is also related to the size of the $R^{3+}$ ion, i.e. for large $R^{3+}$ ions ($R = \text{Pr, Nd}$) the MI transition is accompanied by an antiferromagnetic (AF) ordering of the (Ni) sub lattice (i.e. $T_N \approx T_{MI}$), whereas for smaller $R^{3+}$ ($R = \text{Sm} \rightarrow \text{Lu}$) $T_N$ is much smaller than $T_{MI}$ (e.g. for EuNiO$_3$, $T_N = 220$ K and $T_{MI} = 463$ K). According to the magnetic phase diagram RNiO$_3$ exhibit a crossover from antiferromagnetic insulator ($R \neq \text{La}$) to nonmagnetic metal ($R = \text{La}$) \footnote{6}. External pressure is expected to close the small charge transfer gap in RNiO$_3$ and thereby induces a pressure-induced insulator to metal (IM) transition. Indeed, recent high pressure studies on several RNiO$_3$ compound show the occurrence of a pressure-induced insulator metal transition, e.g. EuNiO$_3$ \footnote{7} and LuNiO$_3$ \footnote{8}. Such studies provide valuable information on the driving mechanism of the MI transition, in particular, the interplay between charge ordering and local structure as well as the crossover from the antiferromagnetic insulating state to the metallic nonmagnetic state.

In the frame work of this thesis, the effect of pressure on the transport, magnetic and structural properties of YbNiO$_3$ has been investigated, using electrical resistivity and x-ray diffraction. The results are discussed and compared with recent high pressure results on related RNiO$_3$ compounds.
Chapter 2

The Diamond Anvil Cell (DAC)

2.1 The development of the DAC

Until roughly two decades ago, the only alternative to nuclear tests for measuring the properties of materials at ultrahigh pressures and temperatures was shock experiments. Shock waves were driven through the material of interest while changes in the material properties during passage of the shock front were measured. However, because shock techniques are dynamic, precise material properties are difficult to measure directly. Instead, the diagnostics were focused on measurements that could be captured in such brief durations; then, using large-scale numerical simulations that incorporated data from the experiments, researchers inferred the properties of interest.

Percy Williams Bridgman, the great pioneer of high-pressure research during the first half of the 20th century, developed an opposed anvil device with small flat areas that were pressed one against the other with a lever-arm (see fig 3.1). The anvils were made
of a tungsten-carbon alloy (WC). This device could achieve pressure of a few gigapascals, and was used in electrical resistance and compressibility measurements. For his big efforts in that matter, P.W. Bridgman was honored with the Nobel Prize in 1946.

The revolution in the field of high pressures came with the development of the diamond anvil cell in the late 1950s in the National Bureau of Standards (NBS) by Weir, Lippincott, Van Valkenburg, and Bunting. The principles of the DAC are similar to the Bridgman anvils but in order to achieve the highest possible pressures without breaking the anvils, they were made of the hardest known material: a single crystal diamond. The first prototypes were limited in their pressure range and there was not a reliable way to calibrate the pressure. During the following decades DACs have been successively refined, the most important innovations being the use of gaskets and the ruby pressure calibration. The DAC evolved to be the most powerful lab device for generating static high pressure [9]. The range of static pressure attainable today extends to the estimated pressures at the Earth’s center (~360 GPa).

The development of diamond anvil cell technology has resulted in tremendous gains in knowledge of the physical world through scientific investigation of the behavior of matter under a wide range of pressures. In Earth and planetary sciences, laboratory experiments utilizing high pressure and temperature offer the only means to examine directly the conditions of deep planetary interiors. Fundamental questions about phase transformations, crystal structure and the nature of atomic bonding can be answered using high-pressure techniques. Finally, the use of high pressure to synthesize new materials, to study the behavior of existing materials and to tune material physical properties provides tremendous potential for advances in applied materials research.
The DAC consists of two opposing diamonds with a sample compressed between the culets. Pressure may be monitored using a reference material whose behavior under pressure is known. Common pressure standards include ruby[10] fluorescence, and various structurally simple metals, such as copper or platinum.[11] The uniaxial pressure supplied by the DAC may be transformed into uniform hydrostatic pressure using a pressure transmitting medium, such as argon, xenon, hydrogen, helium, paraffin oil or a mixture of methanol and ethanol[12] The pressure-transmitting medium is enclosed by a gasket and the two diamond anvils. Magnetic and microwave field can be applied externally to the cell allowing nuclear magnetic resonance, electron paramagnetic resonance and other magnetic measurements[13] Attaching electrodes to the sample allows electrical and magneto electrical measurements as well as heating up the sample to a few thousand degrees. Much higher temperatures (up to 7000 K) [14] can be achieved with laser-induced heating [15], and cooling down to millikelvins has been demonstrated [12].

Diamond, in addition of being recognized as the hardest and least compressible material, has the important property of being transparent to most of the spectrum of electromagnetic radiation, including g-ray, X-ray, portions of ultraviolet, visible, and most of the infrared region. The DAC is based upon the opposed-diamond configuration, in which a sample is placed between the polished culets of two diamonds and is contained on the sides by a metal gasket. In this configuration, very little force is required to create extremely large pressures in the sample chamber, and, because of the transparency of diamond, the sample may be examined in situ (while at elevated pressure) by optical microscope, spectroscopy (Raman, infrared, Brillouin), and diffraction techniques.

In the beginning of this century [Reinhard Boehler and Koen De Hantsetters] made a new diamond anvils with conical support Compared to conventional anvils the new design offers superior alignment stability, larger aperture, and reduced cost owing to
significantly smaller anvil diameters. Except for table and culet, all surfaces are precision ground on a lathe, which lowers cost compared to faceted anvils. The conical design allows for steel supports, which are significantly easier and cheaper to manufacture than tungsten carbide supports. Conical support also prevents seat damage upon diamond failure. An additional new feature of the anvils is the roughened outer portion of the culet, which increases friction between the anvils and the gasket. This increases the height to diameter ratio of the pressure cell and prevents bonding between gasket and diamond, which causes ring cracks during pressure release. This technique replaces complicated diamond coating procedures. The anvils have been extensively tested for culets ranging from 0.1 to 1 mm diameter up to megabar pressures. A new anvil shape with cup-shaped culets to further increase the cell volume and gasket stability is also introduced. [16]

Fig. 2.3 cross section of a ‘standard’ anvil (left) and an anvil with very large X-ray aperture

Fig. 2.4 New anvil design with a cup-shaped recess in the culet. During compression a portion of the gasket flows towards the center. This design yields higher gasket stability and increased cell height.
2.2 **Principle of work:**

The diamond anvils are skillfully cut from natural, gem quality stones to have 16 pavilion facets, a 70% table, and a working surface (culet). The anvils are cut to correct crystallographic orientation [table and culet parallel to the (100) diamond plane] and care is taken to insure parallelism of the table and culet.

The culet of the diamond anvil is typically 0.6 mm in diameter. This size insures that pressures up to 20 GPa (1GPa = 10 kbar = 10,000 bar = 9,870 atm) can be achieved (depending upon the choice of DAC). To perform studies to higher pressures, diamonds cut with smaller beveled culets are recommended.

The operation of the diamond anvil cell relies on a simple principle:

\[ P = \frac{F}{A} \]

where P is the pressure, F the applied force, and A the area.

Therefore high pressure can be achieved by applying a moderate force on a sample with a small area, rather than applying a large force on a large area. In order to minimize deformation and failure of the anvils that apply the force, they must be made from a very hard and virtually incompressible material, such as diamond.

diamond anvil cell (DAC) which is schematically illustrated in Figure 3.3 is One of the most powerful high pressure cells nowadays [17][18][19][20][21]. The DAC’s used in this thesis are modified high pressure cells following the example of Merrill-Bassett [22]. They work on basis of the Bridgman-principle [23]. The reason why taking diamonds as anvils is simple: Diamonds are the hardest material on earth which make them fit perfectly for the use under high pressure conditions. Also The sample can be viewed through the diamonds and illuminated by X-rays and visible light. In this way, X-ray diffraction and fluorescence; optical absorption and photoluminescence; Mossbauer effect, Raman and Brillouin scattering; positron annihilation and other signals can be measured from materials under high pressure.
Fig. 2.5: Simple schematic sketch of a Diamond Anvil Cell (DAC) used for the high pressure experiments. Due to their small sizes (22 mm in diameter and ≈ 14 mm in height) the DAC is suitable for most measuring apparatus.

There are many different DAC designs according to the maximum pressure of the DAC and the property we want to measure but all have four main components:

1- The force-generating device — relies on the operation of either a lever arm, tightening screws, or pneumatic or hydraulic pressure applied to a membrane. In all cases the force is uniaxial and is applied to the tables (bases) of the two anvils

2- Two opposing diamond anvils — made of high gem quality, flawless diamonds, usually with 16 facets. They typically weigh 25 to 70 mg. The culet (tip) is ground and polished to a hexadecagonal surface parallel to the table. The culets of the two diamonds face one another, and must be perfectly parallel in order to produce uniform pressure and to prevent dangerous strains. Specially selected anvils are required for specific measurements—for example, low diamond absorption and luminescence is required in corresponding experiments.

3- Gasket — a foil of ~0.2 mm thickness (before compression) that separates the two culets. It has an important role: to contain the sample with a hydrostatic fluid in a cavity between the diamonds, and to prevent anvil failure by supporting the diamond tips, thus reducing stresses at the edges of the culet. Standard gasket materials are hard metals and their alloys, such as stainless steel, Inconel, rhenium, iridium or tungsten carbide. They are not transparent to X-rays, and thus if X-ray illumination through the gasket is required then lighter materials, such as beryllium, boron nitride,[24] boron[25] or diamond [26a] are used as a gasket.

4- Pressure-transmitting medium — homogenizes the pressure. Methanol: ethanol 4:1 mixture is rather popular because of ease of handling. However, above ~20 GPa it turns into a glass and thus the pressure becomes non hydrostatic.[12] Xenon, argon, hydrogen and helium are usable up to the highest pressures, and ingenious techniques have been developed to seal them in the cell.[12]
A diamond anvil cell (DAC) is a hand-top device used in scientific experiments. It allows compressing a small (sub-millimeter sized) piece of material to extreme pressures, which can exceed 3,000,000 atmospheres (300 gigapascals).[27]

The device has been used to recreate the pressure existing deep inside planets, creating materials and phases not observed under normal conditions. Notable examples include the non-molecular ice X [28], polymeric nitrogen[29] and MgSiO$_3$ perovskite, thought to be the major component of the Earth's mantle.

Prior to the invention of the diamond anvil cell, static high-pressure apparatus required large hydraulic presses which weighed several tons and required large specialized laboratories. The simplicity and compactness of the DAC meant that it could be accommodated in a wide variety of experiments. Some contemporary DACs can easily fit into a cryostat for low-temperature measurements, and for use with a superconducting electromagnet. For the transparency of the DAC it is a perfect device for spectroscopic experiments and for crystallographic studies using hard X-rays.

The diagnostic x rays used to record these data in our DAC experiments at ultrahigh pressures are not like to those from medical or conventional laboratory x-ray units, which are too weak to yield data in a reasonable time and cannot be collimated sufficiently to collect accurate data. Rather, we use the very bright, highly coherent x-rays from a synchrotron source and collimate them to 5 to 10 µm in diameter. A combination of high beam intensity and excellent collimation is essential to reduce the time required for data collection (10 to 30 minutes at each pressure, rather than tens of days) as well as to reduce the effects that the pressure gradient across the sample has on the data.

The x-ray beam from the synchrotron source passes though the diamonds, diffracts from the sample, and passes through the pinhole collector. It then enters the detector, which records the energy diffraction pattern from the sample, data essential to identify the changing crystal structure.

The optical multichannel analyzer in the lower part of the apparatus determines the pressure at which the crystal changes take place by measuring the laser induced fluorescent light from the ruby chip pressure marker. Thus, the changing volume and density of the sample are measured as a function of pressure.

The phase transformations are thought of as those from a solid to a liquid to a gas. However, there are transformations from one solid to another, and these are the structural transformations generally studied using the DAC. In solid-to-solid structural changes, the atoms of an element rearrange themselves in response to changing pressure, changing temperature, or both to new configurations. The shape of the atomic structural “cages” changes by the rearrangement of the atoms. Structural changes can be accompanied by a sudden volume change. However, the volume change can be small enough not to be recognized or to be able to be accounted for by a normal margin of experimental error. It
can also be smooth and gradual and not exhibit the spikes associated with large, sudden changes. Whether subtle or sharply first and second order phase transitions defined, these are the structural transformations of interest in DAC experiments.

The development of diamond anvil cell technology has resulted in tremendous gains in knowledge of the physical world through scientific investigation of the behavior of matter under a wide range of pressures. In Earth and planetary sciences, laboratory experiments utilizing high pressure and temperature offer the only means to examine directly the conditions of deep planetary interiors. Fundamental questions about phase transformations, crystal structure and the nature of atomic bonding can be answered using high-pressure techniques.

Finally, the DAC has enabled us to obtain phase stability information that dynamic techniques such as shockwave methods could not supply and to incorporate that information into our theoretical models. Our scientists constantly endeavor to improve DAC experimental techniques in order to obtain better data and to obtain further information about the physical properties of any material. With the addition of a laser or a resistance heater or with cryogenic cooling, we can also use the DAC to explore the pressure-volume-temperature relationship and the resulting structural changes of any material-its equation of state and phase diagram. Higher pressure and increased temperature may force further structural changes, until the material loses its crystal structure entirely that is, it melts.

An area of new technology for obtaining high pressure and temperature data is the electrical transport experiments such as ohmic heating based on resistance to the current. Special preparation of the sample, anvils, and cell is required, and electrical connections fail easily under the high stresses present in the diamond anvil cell.
2.3 **DAC preparation**

2.3.1 **For resistivity measurement**

As shown in Figure 2.5, this design is suitable for spectroscopic measurements like x-ray diffraction or Mössbauer spectroscopy under high pressure. In order to perform electric resistivity measurements under high pressures, the preparation of the cell has to be modified. Electrical conductors - at least 12 μm tiny gold wires - have to be inserted into the sample chamber and contact with the sample. Before, the metallic gasket has to be insulated in order to protect the sample against short-circuit. For this purpose, the imprint of the diamonds in the gasket will be covered by a small piece of capton foil (Capton is a very special kind of insulating foil made of Polyimid and used in space technology e.g. for satellites for more than 30 years. It is electrical, chemical and mechanical stable also under extreme conditions). The glue for this consists of a mixture of epoxy (Uhu Endfest 300) and Al₂O₃ and serves as pressure medium to provide quasi-hydrostatic conditions. Afterwards, a small hole (Ø 100 – 250 μm) will be drilled in the center of the capton which defines the sample chamber. Then, five flattened gold wires will be taped on the facet side of the lower diamond. Their sharpened end will be kinked on the culet, so that their top reach in the center of the sample chamber. Finally, the other end of these wires will be soldered to five 100 μm Cu wires, which conduct the signals to the measuring apparatus. The last step is to fill the powder sample into the sample chamber, together with some ruby chips for the pressure determination, then the cell can be closed and looks like in Figure 2.6.

![Diagram](image.png)

*Fig. 2.6: Schematic view of the preparation of the DAC for high pressure electrical resistance measurements.*
One final comment for the reason why taking five wires instead of four, since we are doing a four-point measurement: Due to the mechanical strain on the delicate wires, during closing the cell and applying pressure, it unfortunately belongs to the business that sometimes gold wires remove from their initial position and contact other wires which leads to a short-circuit. Also very unpleasant circumstances after closing the cell breakages of the wires due to the sharp edge of the culet. Thus, we use the fifth wire just for safety reasons.

The detailed steps for preparation are:

- **Preparing the high pressure cell for resistivity**
  
  - **Paralyzing the cell**
    1. Close the cell without tightening the screws hardly
    2. Focus the microscope on the culets
    3. Get rid of those fringes
    4. Write the values in your notebook

  - **Preparing the gasket:**
    1. Put the gasket between the 2 diamonds and press them slowly till you reach the desired thickness of the gasket
    2. Re open the cell
    3. Get the gasket out and clean it
    4. Drill a hole in the center of the trace made be the diamond

  - **Isolating the gasket:**
    1. Prepare the epoxy (100 : 28) and mix them well
    2. Put the (Al₂O₃) with ratio (epoxy : Al₂O₃ = 2:3)
    3. Mix them perfectly till you get white cream
    4. Put a thin layer on the lower side of the gasket
    5. Preharden the gasket at 100°C for some (5) minutes, check if it is becoming solid or still liquid. Go on with hardening in steps of 1 min until it is STARTS to get hard

  - **Putting the gasket in the cell:**
    1. Put gasket in the cell and tighten it carefully.
    2. Harden everything for 1h at 100°C
    3. Open cell, drill hole in the center of the hole.

  - **wiring the cell:**
    1. Put the copper wire surrounding the cell and make 5 terminals
    2. Fix the copper wires using the tape until you finish the fixation of all of them then use the UHO glue for final fixation
Preparing the gold wires:
1- Take a small piece of the wire and flatten it.
2- Try to cut the gold wires using a sharp Scalpel and make a fine tip for the wire.
3- Take a small tape and put it on the gold wire.

Wiring the sample chamber:
1- Fix the 5 gold wires on the facet of the diamond.
2- Fix the wire on the facet.
3- Rip the gold wire around the terminal of the copper wire and use the silver paint to connect them.
4- Bond the tip of the gold wire on the culet of the diamond.
5- After fixing 3 wires put 2 pieces of ruby on the culet.
6- Put the last wires.

Fill the cell with the sample:
1- Fill the hole of the gasket completely by the sample.
2- Start paralyzing the cell by reaching the paralyzation values you measured before.
3- Increase the pressure slowly using the screws.

2.3.2 For x-ray measurement

For the x-ray measurement we don’t need the wires inside the cell and we don’t need the epoxy insulation, also we need to put the liquid nitrogen as a pressure medium to produce a hydrostatic pressure in the cell so we prepare the cell as follow:

Preparing the high pressure cell for x-ray

Paralyzing the cell
1- Close the cell without tightening the screws hardly.
2- Focus the microscope on the culets.
3- Get rid of those fringes.
4- Write the values in your note book.

Preparing the gasket:
1- Put the gasket between the 2 diamonds and press them slowly till you reach the desired thickness of the gasket.
2- Re open the cell.
3- Get the gasket out and clean it.
4- Drill a hole in the center of the trace made be the diamond.
○ **Fill the cell with the sample:**
  1- fill the hole of the gasket completely by the sample
  2- Start paralyzing the cell by reaching the paralyzation values you measured before
  3- Close the cell without tighten the screws hardly

○ **Filling the liquid nitrogen:**
  1- Make a liquid nitrogen bath
  2- Put the cell inside it and release the screws to allow the liquid nitrogen to flow in the cell
  3- Close the cell in the liquid nitrogen bath
  4- Measure the pressure inside the cell to make sure that the liquid nitrogen is trapped in the chamber.
  5- If it is not so you have to clean the gasket and fill the sample and the liquid nitrogen again.
  6- Leave the cell to relax over night and measure the pressure of the cell again

### 2.4 Precautions

1- You need to clean the culet perfectly using clean tissue and some acetone
2- When you increase the pressure with the screws don’t tighten them with more than 5µm per cycle
3- Don’t allow the cell to hit the ground when it is under pressure
4- Make sure that the epoxy and the sample fills the holes completely
5- Make sure that the holes are at the centers of the culets
6- Make sure that sample chamber diameter less than 50% of the culet diameter and sample chamber height is 10% of the culet diameter.

![Fig. 2.7: different views of the DAC used in our technique for high pressure electrical resistance measurements.](image)
Chapter 3

The Experimental Setup

There are many ways to perform the high pressure experiment. In each way there is different setup for the experiment and different uses for the devices in order to fit in the setup.

In this chapter we are going to discuss in detail of our experimental set up for high pressure resistivity measurements at variable temperatures which was very recently built up at the Physics Department and is being used now for the first time.

All temperature dependent electrical resistivity measurements have been performed in closed cycle cryostat. In this cryostat it is possible to measure temperatures between 7.5 and 300 K. For the temperature dependent measurements of the electrical resistivity R(T) a high pressure cell was mounted into the massive Cu pot at the bottom of a cold finger. This insert has been inserted into the Helium chamber of the cryostat.

A couple of small wires wiped around the cold finger and the heat shield of the Helium cryostat to a wiring box to provide the cell with the current and measure the potential difference. On the outer side of this box another cable conducts all the signals to an interface and then to the PC.
So the experimental setup consists of 4 main accessories: the cooling system, the resistivity system, measuring pressure system, and the X-ray system. Next we will start discussing each briefly.

3.5 **The cooling system:**

It is the system used to control the temperature of heating and cooling process and it consists of:

a) **The water cooler:**
   It is used to cool the compressor and it uses the cold water in this process. It has a thermostat to adjust the temperature of the water that comes out from it and inter the compressor. It uses a closed water cycle which means that the cold water that inter the compressor comes out again from another terminal as a hot water and inter the cooler again to be cooled.

b) **The gas compressor:**
   The gas compressor is a compact, axially symmetrical, small cooling power closed cycle cryocooler. Its small mass makes it uniquely suited for many manipulator and goniometric applications. This cooler is ideal for small heat loads. It is used to compress the liquid helium that used in the cooling process in the cryostat.

c) **The vacuum pump:**
   The vacuum pump is used to suck the air from the cryostat, as we need to cool the sample in vacuum.

d) **The cryostat (closed cycle refrigerator):**
   The major components of the closed cycle cryostat are the expander, compressor, vacuum shroud, and radiation shield. The expander, commonly referred to as the cold head or cold finger, is where the Gifford-McMahon refrigeration cycle takes place. It is connected to a compressor by two gas lines and an electrical power cable. One of the gas lines supplies high pressure helium gas to the expander, the other gas line returns low pressure helium gas from the expander. The compressor provides the necessary helium gas flow rate at the high and low pressure for the expander to convert into the desired refrigeration capacity. The vacuum shroud surrounds the cold end of the expander in vacuum limiting the heat load on the expander caused by conduction and convection. The radiation shield is actively cooled by the first stage of the expander and insulates the second stage from the room temperature thermal radiation being emitted from the vacuum shroud.

A full schematic description of the connection of the cooling system is present in (fig 3.1).
Fig. 3.1 the cooling system parts and the connections
3.5.1 **How to run the Cryostat**

- **Mounting sample:**
  - Mount sample holder with the prepared sample.
  - Connect electrical leads coming from the sample to the connector at the cryostat.

- **Close cryostat:**
  - Impose the heat shield on the heat stage.
  - Connect the tube from the pump to the pumpout port on the expander skirt.
  - Switch on the pump
  - Open slowly the vacuum valve.

---

![Fig. 3.2 the sample holder](image1)

![Fig. 3.3 the vacuum valve](image2)

Fig. 3.4 the cold finger
Cooling:
- Turn on the water cooler.
- Turn on the compressor,
- Start measurement to collect data on the cooling run.
- There are two temperature sensors within the cryostat: sensor “A” reads the temperature at the sample and can be controlled by the temperature controller, sensor “B” reads the temperature close to the 1st heat stage.
- When the temperature has reached the base temperature, stop the cooling measurement

Heating:
- Start the heating measurement.
- Stop “store data” when the temperature has reached its final value
- Set setpoint to room temperature (300 K).

Open cryostat:
- Turn off compressor, turn off water cooler.
- Check both temperature sensors “A” and “B”
- Open the vacuum valve slowly and let air into the cryostat.
- Remove the vacuum shroud and the heat shield.

Evacuate Vacuum Shroud
- Attach a vacuum valve to the NW fitting on the refrigerator. Connect the valve to a vacuum pump capable of pumping to less than 0.05 torr ultimate pressure.
- At 0.05 torr, start the refrigerator.
- At 150 K on the refrigerator 2nd stage, cut off the refrigerator from the vacuum pump.

Changing Samples and Start up
- For a closed cycle system, turn off electrical power to the compressor(s). This turns off power to the refrigerator.
- Allow the refrigerator to warm to room temperature.
- Relieve the vacuum in the vacuum shroud. Allow the pressure to rise to atmospheric.
- Remove the vacuum shroud from the skirt of the refrigerator. The shroud is held only by the friction of the double O-ring seal.
- Unscrew the radiation shield from its adapter on the first stage heat station.
• Mount the sample. Unscrew the holder for sample mounting, it from the second stage heat station. See the section Sample Mounting.
• Wipe a light coat of vacuum grease on the male threads of the radiation shield adapter.
• Screw the radiation shield onto it adapter. Align the shield openings with the sample holder. The radiation shield threads do not need to bottom on the adapter.
• Press the vacuum shroud onto the skirt of the refrigerator. Align the shroud windows with the opening(s) in the radiation shield.
• If all other system components are ready for operation, begin to pump the insulating vacuum.
• When the vacuum reaches 0.05 torr, start the refrigeration system.
• For a closed cycle system, start the compressor(s). The valve motor in the refrigerator should also start.
• When the refrigerator temperature reaches 150K, close the isolating vacuum valve.

Fig. 3.5 the heat sensors

Fig. 3.6 the DAC connected to the cold finger
**Shutdown**

- For a closed cycle system, turn off electrical power to the compressor(s). This turns off power to the refrigerator.
- Allow the refrigerator to warm to room temperature.
- Relieve the vacuum in the vacuum shroud. Allow the pressure to rise to atmospheric.
3.6 The resistivity system:

In order to measure the resistance of the sample under high pressure we connect the 4 probes from the cell to the multimeter and nanovoltmeter in order to get the readings of the current and potential difference of the sample inside the cell. In the following is a brief description of these units:

a) Nanovoltmeter:
The two-channel (Keithley 2182A) Nano volt meter is optimized for making stable, low noise voltage measurements and for characterizing low resistance materials and devices reliably and repeatably. It provides higher measurement speed and significantly better noise performance than alternative low voltage measurement solutions. Here we use the (Keithley 2182A) to measure the voltage drop on the sample with a very high accuracy.

b) Multimeter:
The (Fluke 8846A) digital multi meter performs the functions you would expect to see in a multifunction DMM, including measuring volts, ohms, and amps. Basic V dc accuracy of up to 0.0024 %, 10 A current ranges, and a wide ohms range give an unbeatable combination of measurement capability (fig 3.9b). Here we use (Fluke 8846A) to measure the current passing through the sample with a very high accuracy.

c) Electronic switch:
This electronic switch is a fast switch in range of (millisecs) to change the polarity of the current during the data collection.

d) Current source:
Here we use a (knick) current source. In this source we control the current manually starting from 0.1 µA to 1 mA according to the sample type and the resistivity (fig 3.9c).

e) National instrument digital analog converter:
It is used to transfer the signal from the devices to the computer to deal with the lab view program which calculates the resistivity.

f) Temperature controller:
It is used to control the cooling and heating rate in the cryostate.

A full description of the connection of the resistivity system is presented in (fig 3.8).
Fig. 3.8 the resistivity system parts and the connections
Fig. 3.9 a) Nanovoltmeter, b) Multimeter, c) Current source, d) temperature controller
3.6.1 **How to use the program?**

In order to collect the data of the current intensity and the potential difference and to control the temperature (heating rate and cooling rate) we connect all this circuit to a computer and we use the LabVIEW program to do this job automatically and calculate the resistance. The program also draws a relation between the resistance and the temperature. Figure (3.10) shows the interface of the program.

![Fig. 3.10 The interface of the program.](image)

1- Start the program  
2- Turn (store data) on  
3- Fill in the sample information  
4- During the heating process click on the (Ramp) button and turn it on.  
5- Turn off the (permanently refresh) button [MAKE SURE IT BECOMES GREEN]

We use the cooling information to check that everything is fine (the plotting graph is smooth and as expected) and we collect the experimental data from the heating process that is why we turn the ramp off during cooling and we turn it on during heating.
3.6.2 **Precautions:**

1- Don’t leave anything red in the program before you leave
2- Make sure that the temperature controller part in the program is set to zone controlled

3.6.3 **How to compare between the different data points?**

In order to compare between the data we use a plotting program called (Gnuplot) this program draw graphs directly from the text file (the output file of the LabVIEW program).

The lab view program save the data in 5 columns (time, temperature, voltage, current, and resistance) respectively, so we mainly need to compare the (R vs T) data so we use the (Gnu plot) program.

We can play around with the scale of any of this axis (using log scale or reciprocal values) for more information read the help in the program.
3.7 **Pressure measuring system:**

To determine the pressure inside the DAC possesses we use the ruby fluorescence method. We incident a laser beam through the transparent diamonds to excites the ruby chips to emit fluorescence light. This light is then collected by a fiber optics wire and transferred to a spectrometer (HR4000 Spectrometer) to analyze the signal and send it to the computer. In principle, this fluorescence spectrum consists of two lines (R1 and R2) which have a wave length of 692.70 nm and 694.32 nm at ambient pressure, respectively. By increasing pressure, these lines shift to higher wavelengths. We take the R2-line as reference line to determine the pressure using the following equation:

\[
P(\text{GPa}) = 380.8 \left\{ \left( \frac{\Delta \lambda \text{ (nm)}}{694.32 \text{ (nm)}} + 1 \right)^{\frac{5}{2}} - 1 \right\} \text{ (GPa)}
\]

(3.1)

Whereas \( \Delta \lambda = \lambda - \lambda_0 \) with \( \lambda_0 = \lambda (p = 0 \text{ GPa}) = 694.32 \text{ nm} \). This conforms the drawn through line in Figure 3.11(a) which is the result of x-ray diffraction measurements on Ag, Cu, Mo and Pd [30]. For pressures below 30 GPa one can use the more simple equation, assuming the following linear approximation [21][19]:

\[
P (\text{GPa}) = 2.746 \times \Delta \lambda \text{ (nm)} \text{GPa}
\]

(3.2)

The big disadvantage of this method is that we cannot measure the pressure in-situ. We can only determine the pressure at room-temperature and outside the measuring apparatus. However, the pressure was determined before and after each measurement due to different thermal expansion coefficients of various parts of the cell, pressure can increase at low temperatures.

According to references [31] and [32], the effect of temperature on the pressure is less than 10% between 25 and 300 K so it will not affect our measurement that much.
Figure 3.11(b). Schematically illustrate the experimental equipment to determine the pressure. Where a powerful diode laser light goes through the optical path of a microscope and excites the ruby chips to emit fluorescence light. After that the light will be focused by several lenses on a fiber optics wire and transmitted to the monochromator, which reads out the interesting wavelengths. All the light is then absorbed by a photomultiplier behind the monochromator which amplifies the signal. The signal will be sent to an analog-digital converter which prepares the signal for the PC, where the spectrum will be presented and the pressure calculated.

3.7.1 **Using the system:**

1- Place the cell under the microscope with the lower side up
2- Turn on the laser
3- focus the laser beam on the ruby chips
4- start the computer program (ocean optics)
5- start the counting
### 3.7.2 Analyze the spectrum:

![Fig. 3.12 Laser fruresense pattern of Rubby at room temperature for selected pressures up to 12.7 GPa.](image)

1. move the cursor to the position of the center of the peak (corresponding to \( R_2 \))
2. get the wave length at this point
3. substitute in the pressure equation

### 3.7.3 Precautions:

1. check that the laser beam is in the center of the cross in the eye piece
2. take care of the wires as it may break while measuring the pressure
3. make sure the fiber optic tube is as much straight as you can (no right angles)
3.8 **Structure analysis system (X-Ray system)**

In order to measure the structure parameters for the sample and detect any deformation take place while we increase the pressure we use the very bright, highly coherent x-rays from a synchrotron source.

3.8.1 **Energy dispersive x-ray diffraction**

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy.

Here we use the x-ray diffraction as a tool to determine the adjustment of atoms in a crystal from which we can get information about the lattice parameters of the examining sample.

This method is based on Bragg’s law of reflection which state that

\[ n \lambda = 2d \sin \theta \]

where \( n \) is the order of diffraction, \( \lambda \) the wave length, \( d \) the distance between successive grating elements, called the grating spacing and \( \theta \) the half diffraction angle.

Consider two waves that are in phase, sharing the same frequency and with amplitudes \( A_1 \) and \( A_2 \). Their troughs and peaks line up and the resultant wave will have amplitude \( A = A_1 + A_2 \). This is known as constructive interference.

If the two waves are \( \pi \) radians, or 180°, out of phase, then one wave's crests will coincide with another wave's troughs and so will tend to cancel out. The resultant amplitude is \( A = |A_1 - A_2| \). If \( A_1 = A_2 \), the resultant amplitude will be zero. This is known as destructive interference.

In our case the Constructive interference occurs when the x-ray beam incident on the grating element with an angle that satisfy Bragg’s law.

There are many methods to perform x-ray diffraction measurements under high pressure. Commonly the Debye-Scherrer method will be used, as in this method we use the sample as a powder, other methods require single crystals.
which are not easy to produce and often will be destroyed by applying pressure.

So according to Bragg’s equation we can perform the x-ray diffraction method in two ways, first the angle dispersive x-ray diffraction in which we choose a monochromatic beam that hit the sample and change the angle until we get the constructive interference. For some parts of these crystallites, Bragg’s law is satisfied and constructive interference occurs. Hereby every grating plane produces, due to the statistic distribution of the crystallites, an own diffraction cone (Debye-Scherrer ring) with an aperture angle which is typical for each grating plane. Today such a Debye-Scherrer ring will be detected either with a rotating detector or an image plate.

Second the energy dispersive x-ray diffraction by fixing the angle and hit the sample by white x-ray beam. Here we use synchrotron radiation to examine the lattice parameters of the samples under pressure. An energy dispersive detector is mounted behind the sample in a fixed angle to collect all diffraction lines from many grating planes of the sample which strike the detector under the diffraction angle $\theta$. These different angles correspond to different energies and can be evaluated in the PC. The diffraction lines appear at specific energies, $E$, which are related to the corresponding interplanar spacing ($d$) by the Bragg’s equation

$$E \cdot d = \frac{h \cdot c}{2 \cdot \sin \theta} = \frac{6.1993 \text{ keV} \cdot A^0}{\sin \theta}$$

Here ($h$) is Planck’s constant, ($c$) is the speed of light.

This equation shows the relationship between the incident energy $E$ and the $d$ values.

Each of these 2 ways has its own advantages and disadvantages; for the angle dispersive x-ray diffraction way the resolution is quite better than the second way also, the angle dispersive diffraction shows no fluorescence lines and can reduce texture effects to a minimum, While for the energy dispersive x-ray diffraction method the resolution of this method is a bit lower. Frequently the texture leads to troubles in spectra since only a part of the whole Debye-Scherrer ring is measured. Additionally fluorescence peaks can appear which can overlap with some diffraction peaks. But for this method the advantage is that at the same time we can measure all diffraction patterns and visualized them immediately on the monitor. This makes changes in the spectra apparent quite fast. Moreover, the time to measure a spectrum is much less than for the angle dispersive x-ray diffraction.
3.8.2 **Equation of state**

In physics and thermodynamics, an equation of state is a relation between state variables [33]. More specifically, an equation of state is a thermodynamic equation describing the state of matter under a given set of physical conditions. It is a constitutive equation which provides a mathematical relationship between two or more state functions associated with the matter, such as its temperature, pressure, volume, or internal energy. Equations of state are useful in describing the properties of fluids, mixtures of fluids, solids, and even the interior of stars.

In order to determine the lattice parameters, the elastic bulk modulus $B$ as well as to study possible structural phase transitions under high pressures we perform the energy dispersive x-ray diffraction measurements. The bulk modulus in units of pressure is an important parameter relating the change of volume with pressure. $B$ is defined as

$$B = -V \frac{\partial P}{\partial V} |_T$$

Whereas $V$ stands for the volume of the unit cell and $P$ the applied pressure at constant temperature. Generally, $B$ increases when the crystal is compressed. The actual state for solids under strong compression can be described by several equations of state (EOS) [34]. For YbNiO$_3$ examined in this thesis, it is sufficient to assume a linear pressure dependence of $B$ due to a small change of the volume, according to the propse of Murnaghan [35][36]. Then $B$ reduces to:

$$B = B_0 + B'_0 \cdot P$$

So the equation of state can be obtained by integration as follow:

$$\int_{V_0}^{V} \frac{dV}{V} = \int_{0}^{P} \frac{dp}{B} = \int_{0}^{P} \frac{dp}{B_0 + B'_0 \cdot P}$$

$$\ln \frac{V_0}{V} = \frac{1}{B'_0} \ln \left( \frac{B_0 + B'_0 \cdot P}{B_0} \right) = \ln \left( \frac{B_0 + B'_0 \cdot P}{B_0} \right)^{\frac{1}{B'_0}}$$

$$\frac{V_0}{V} = \left( \frac{B_0 + B'_0 \cdot P}{B_0} \right)^{\frac{1}{B'_0}}$$

$$V_0 = V \left( \frac{B_0 + B'_0 \cdot P}{B_0} \right)^{\frac{1}{B'_0}}$$
Whereas $V_0$ is the value of the unit cell at $p = 0$ GPa. The Murnaghan EOS is valid for changes in the volume up to $V/V_0 \leq 0.85$. For larger volume changes one has to introduce additional parameters as shown in [37], which lead e.g. to the Birch-Murnaghan equation of state [38].

3.8.3 **Beam line F3 at Hasylab**

As mentioned before we need a high energy x-ray beam to determine the lattice parameters under high pressure at room temperature of the sample using the energy dispersive x-ray diffraction method, for this reason we use synchrotron radiation (SR) at beamline F3 of Hasylab in Hamburg (Figure 3.13).

![Figure 3.13: Schematic sketch of the different accelerators at DESY (Deutsches ElektronenSynchrotron) in Hamburg. The linear accelerator (LINAC) and the synchrotron (DESY) accelerate electrons and positrons, respectively before they are pipelined into the storage ring (DORIS). The abbreviations EMBL and Hasylab are different experimental halls. Here the bending magnet of the storage ring DORIS emits white SR beam which is received by the beamline F3, then the beam is optimized for energy-dispersive powder diffraction. It is especially geared for work with high pressure diamond anvil cells.](image)

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As we deal with a small sample, we adjust the beam to be well-defined beam sizes down to $20 \times 20 \, \mu\text{m}$. Also we optimize the equipment for background suppression.

In this beamline the detector is made up from Ge with a resolution about 1\% and the scattered radiation in the horizontal plane at angle up to $(2\theta = 30)$. Also to reduce the Compton scattering from the diamonds and improves the resolution we use an adjustable double-slit system. This system rotates with the detector and allows rapid changes in the diffraction angle. A Huber diffractometer serves for sample translation, rotation and tilting, and for detector alignment (angle changes) in the energy-dispersive mode. The precision of the translations is below $1\mu\text{m}$, which of the rotations and tilts 0.5 mill degrees.

For the data collection we use a PC coupled to the multi-channel analyzer, which is also to store the data in the energy-dispersive experiments [39][40][41].

Further instrumentation specifications:

- Source: 4.5 GeV by bending magnet, $E_c = 16$ keV
- Beam characteristics: white beam
- Beam size: $< 200 \, \mu\text{m}$ adjustable; vertical electron beam divergence 0.11 mrad FWHM
- Detector: Ge semiconductor (solid state)
- Angular range: $0 < 2\theta < 30^\circ$ (horizontal only)
- Energy resolution: $\Delta d/d = 10$ milli above 26 keV
Chapter 4

High Pressure Studies on YbNiO$_3$

The transition metal oxide YbNiO$_3$, the subject of the present high pressure study is known as a Mott-insulator. The physical properties of such class of materials are determined by strong electronic correlation due to the Coulomb repulsion between the d electrons of the transition metal. We, thus, think that before presenting the basic properties of RNiO$_3$ compounds, it is useful to briefly mention the important aspects of Mott-insulators.

4.1 Mott insulators transition in metal oxides

Although the nearly free electron approximation is able to describe many properties of electron band structures, one consequence of this theory is that it predicts the same number of electrons in each unit cell. If the number of electrons is odd, we would then expect that there is an unpaired electron in each unit cell, and thus that the valence band is not fully occupied, making the material a conductor.

In 1937 Jan Hendrik de Boer and Evert Johannes Willem Verwey pointed out that a variety of transition metal oxides that are predicted to be conductors by band theory (because they have an odd number of electrons per unit cell) are in fact insulators [42]. Nevill Mott and R. Peierls (1937) [43] predicted that this anomaly can be explained by including interactions between electrons.
Materials such as CoO that have an odd number of electrons per unit cell are insulators, in direct conflict with this result. This kind of material is known as a Mott insulator.

Mott insulators are a class of materials that are expected to conduct electricity under conventional band theories, but which in fact turn out to be insulators when measured (particularly at low temperatures). This effect is due to electron-electron interactions which are not considered in the formulation of conventional band theory.

In 1949, in particular, Mott proposed a model for NiO as an insulator, in which conduction can be understood based on the formula [43]

\[(\text{Ni}^{2+}\text{O}^{2-})_2 \rightarrow \text{Ni}^{3+}\text{O}^{2-} + \text{Ni}^{1+}\text{O}^{2-}\.\]

In this situation, the formation of an energy gap preventing conduction can be understood as the competition between the Coulomb potential $U$ between 3d electrons and the transfer integral $t$ “hopping integral” which describes the hopping of 3d electrons between neighboring atoms of 3d electrons between neighboring atoms. The total energy gap is then

$$E_g = U - 2zt_{dd},$$

where $z$ is the number of nearest-neighbor atoms.

Now it is possible to distinguish two cases of insulators (Mott-Hubbard insulator and the charge-transfer insulator), depending on the charge-transfer excitation energy $\Delta$ and the Coulomb repulsion $U$. This situation is schematically shown in Figure 4.1.

So if the oxygen 2p-orbitals are low in energy (Figure 4.1 (a)), $\Delta$ will be much larger than $U$, then the lowest charged excited states are those which correspond to the transfer of a d-electron from one TM site to another: $(d_n + d_n \rightarrow d_{n-1} + d_{n+1})$. This process costs the energy $U$. As we have seen, we obtain an insulating ground state for $U >> W$ (W denotes the bandwidth), which is known as a Mott-Hubbard insulator. Certainly, this hopping does not happen directly from one TM ion to the next, but via the oxygen p-states. With some support of perturbation calculations it is possible to introduce an effective d–d hopping matrix element

$$t_{dd} = \frac{t_{pd}^2}{\Delta},$$

In general, Mott insulators occur when the repulsive Coulomb potential $U$ is large enough to create an energy gap. One of the simplest theories of Mott insulators is the 1963 Hubbard model.
In charge transfer insulators the 2p-orbitals are close to the 3d-levels (Figure 4.1(b)), $\Delta$ becomes much smaller than $U$ and the lowest charged excited states are those where an electron of a 2p-level will be transferred into a 3d-level of an adjacent TM ion. Therefore results in a hole at the oxygen site for one electron per TM ion and ($\Delta/t >> 1$), we obtain again an insulating ground state, which is defined as charge transfer insulator.

From magnetic properties point of view, there is no significant difference between charge-transfer insulators and Mott-Hubbard insulators. However, differences appear in their excitation spectra as well as in their transport properties.

We can easily summarize the difference in these two types of insulators as follows:

For ( $U/W > \Delta/W$) the band gap is of $p-d$ type and the anion or ligand $p$-band is located between the lower and upper Hubbard bands. This gap is a charge-transfer gap and the corresponding compounds are charge-transfer insulators. In this case, the band gap is proportional to $\Delta$.

If ( $U/W < \Delta/W$), the band gap is of $d-d$ type and thus a Mott-Hubbard insulator.

According to this two limiting cases, Zaanen, Sawatzky and Allen [45] suggested the following phase diagram:
They have a band gap of the magnitude U. The straight line $U\Delta$ separates the Mott-Hubbard and the charge-transfer regimes. The diagram also contains a metallic region near the $\Delta/W$-axis (d-metals) or near the $U/W$-axis (p-metal). This classification scheme is very useful for oxide materials science.

4.2 Basic Properties of RNiO$_3$ (YbNiO$_3$) at ambient pressure

4.2.1 Structural aspects

From the chemical crystallography [46] it is found that the series of rare-earth nickelates (RNiO$_3$) crystallize with the oxygen in the face centers the Ni cation in 6-fold coordination, surrounded by an octahedron of anions, and the R cation in 12-fold cub octahedral coordination, this structure is called perovskite type structure. The general chemical formula for perovskite compounds is ABX$_3$, where 'A' and 'B' are two cations of very different sizes, and X is an anion that bonds to both. The 'A' atoms are larger than the 'B' atoms. Here A stands for the rare earth cation, B stands for the Ni, and X stands for the Oxygen anion (the legend). The relative ion size requirements for stability of the cubic structure are quite stringent, so slight buckling and distortion can produce several lower-symmetry distorted versions, in which the coordination numbers of A cations, B cations or both are reduced. ABX$_3$ compounds consists of corner-shared BX$_6$ octahedra (B = cation), located at the edges of a simple cubic lattice and with a larger A cation in the body centre of the unit cell. If the ratio between the bond length
between (A and X) and (B and X) is \( \sqrt{2} \) so this structure will be an ideal perovskite structure.

![Diagram of ABX₃ perovskite structure]

Fig. 4.3 Two different views of the ideal cubic ABX₃ perovskite structure. The red spheres are X atoms (usually oxygen), the blue spheres are B-atoms (a smaller metal cation) and the orange spheres are the A-atoms (a larger metal cation).

Here in the RNiO₃ it is found that the A atom is very small and the NiO₆ octahedral was found to be ideal along the series are tilted to fill extra interstitial space. So the unit cell will be distorted from the cubic structure and smaller in size the relation of distortion between the relative distances \( d_{B-X} = d_{\text{Ni-O}} \) and \( d_{A-X} = d_{\text{R-O}} \) can be calculated from geometry and is defined as the tolerance factor \( t \) [47] which is defined as

\[
t = \frac{d_{A-X}}{\sqrt{2} \cdot d_{B-X}}
\]
It can be calculated from the equilibrium (A-X) and (B-X) bond lengths for ambient conditions from the sums of the ionic radii which are listed in tables [48] from x-ray data at room-temperature and ambient pressure. Experimentally, it is observed that when $t$ is slightly less than 1 unity, the NiO$_6$ octahedra are rotated around the (1 1 1) cubic axis (see Figure 4.4) [49]. Is $t$ even smaller, than a tilt of the octahedra around the (1 1 0) and (0 0 1) cubic axes is observed which results in the orthorhombic GdFeO$_3$-structure [50] and for much smaller $t < 0.7$, nonperovskite structures are preferred [51].

The variation of the lattice parameters as a function of the tolerance factor is shown in Figure 4.5. From this picture we can see that the orthorhombic distortion, which becomes even more important with decreasing R$^{3+}$ radius, is stable from $t \approx 0.932$ (Lu) to $t \approx 0.975$ (Pr). For LaNiO$_3$ the high value of $t = 0.986$ allows stabilizing the less distorted rhombohedral structure. The boundary between these two phases has been localized at $t = 0.980$ [1].
4.2.2 Electronic states of 3d metal ion:

The degeneracy of d levels of a single transition metal (TM) ion ($l = 2$) is fivefold ($2l + 1$). Due to Coulomb repulsion these states are oriented in the space to minimize the energy between them, they take the directions ($d_{x^2-y^2}$, $d_{z^2}$, $d_{xy}$, $d_{xz}$, $d_{yz}$). In a crystal, the spherical symmetry of the ion will be reduced due to the strong anisotropic crystal field (CF) and the fivefold orbital degeneracy is lifted. This leads to a splitting of the energy levels and is called the crystal field splitting ($\Delta_{CF}$). Now when the transition metal ion attracts oxygen ions (which are called ligands) forming a transition metal oxide the crystal field is determined by the coulomb repulsion with oxygen octahedra.
From Figure 4.6 we can see that the oxygen atoms are located in the axes (x, y, z) which mean that electrons that lies in the TM ion orbitals which adjusted directly towards the oxygen ions will experience a higher energy due to coulomb repulsion with the oxygen ion than the electrons in the orbitals which lies aligned between the oxygen orbitals.

So the electrons in \( (d_{x^2-y^2}, d_{z^2}) \) orbitals which form the \( e_g \) levels and point directly to the oxygen are higher in energy than the electrons in the \( (d_{xy}, d_{xz}, d_{yz}) \) which forms the \( t_{2g} \) levels and with loops between the oxygen position; these \( t_{2g} \) orbitals have a small probability density in the p-orbitals as they are lower in energy. We need to mention that both the \( e_g \) and \( t_{2g} \) orbitals are degenerate in an octahedral symmetry (see Figure 4.6(c)). This crystal field splitting between the \( t_{2g} \) and the \( e_g \) levels is often defined as \( 10D_q \). Typical values for the magnitude of the crystal field splitting are \( \Delta_{CF} \approx 1 - 2 \text{ eV} \).
4.2.3 Jahn-Teller effect

The Jahn–Teller effect describes the geometrical distortion of non-linear molecules under certain situations. This electronic effect is named after Hermann Arthur Jahn and Edward Teller, who proved, using group theory, that non-linear degenerate molecule cannot be stable [53]. The Jahn-Teller theorem [53] states that a system of interacting electrons and nuclei in a degenerated electronic state is unstable, because the system can always reduce its energy by distorting in such a way as to remove the degeneracy [54]. The linear reduction in energy due to the removal of degeneracy will ultimately be balanced by the initial quadratic increase in elastic energy [55] and a new position of equilibrium will be reached with a permanent distortion of the system. This means that e.g. regular octahedra may be deformed into a tetragonal distortion to lift the cubic symmetry, see Figure 4.7(a). This means that any non-linear molecule with a degenerate electronic ground state will undergo a geometrical distortion that removes that degeneracy, because the distortion lowers the overall energy of the complex.

We can describe the energy gain as a function of distortion \( \alpha \) by perturbation theory as

\[
E(\alpha) = -A \alpha + (B \alpha^2 / 2)
\]

Here \((-A\alpha)\) represents the splitting of the degenerate levels due to the perturbation, while \((B\alpha^2/2)\) represents elastic deformation energy. Here \((A)\) is considered as electron phonon coupling, and \((B)\) describes the bulk modulus. This means that at some finite \( \alpha \) we can get minimum energy. See (Figure 4.7(b)).

For the cubic Ni\(^{+3}\)-ion in YbNiO\(_3\) for example, a possible distortion consists of an elongation of the oxygen octahedron by the value of \((2\alpha)\) in \(z\)-direction and a common compression of \((\alpha)\) in \(x\)- and \(y\)-direction. The splitting of the energy levels caused by the Jahn-Teller effect (see Figure 2.7(c)) can be described in a similar way like the crystal field. Elongation in \(z\)-direction reduces the Coulomb repulsion between the ligands and the electrons in the \(d_{z}^2\)-orbital. This leads to an energy reduction of the \(d_{z}^2\)-orbital. While, a compression in \(xy\)-plane of the octahedron causes a stronger Coulomb repulsion for an electron in the \(d_{x^2-y^2}\)-orbital, this leads to an increase of energy. This means, that the \(d_{x^2-y^2}\)-orbital will be energetically lower than the \(d_{x^2-y^2}\).
As the neighbors of TM ions in perovskites have common oxygen ligands so they experience the deformation forces and interact with a corresponding deformation, which leads to a reduction of the crystal symmetry, i.e. a structural phase transition. This effect is called the cooperative Jahn-Teller effect or orbital ordering. Orbital ordering means a fixed pattern of orbital occupations at every atomic site in the crystal.

**Fig. 4.7** Tetragonal deformation of $O_6$-octahedra stabilizing one particular orbital: (a) Elongation: stabilizing $d_{z^2}$-orbital (and vice versa a compression: stabilizing $d_{x^2-y^2}$ orbital). (b) A perturbation $\alpha$ reducing the symmetry: a linear term which represents the splitting of the degenerated levels (energy gain) and a quadratic term representing the energy loss. (c) Splitting of the energy levels of the $d$-orbitals of a Mn$^{3+}$-ion due to the crystal field and the Jahn-Teller effect. Taken from [56].
4.2.4 **Phase diagram of RNiO$_3$**

We can describe the structural, electronic and the magnetic properties phase transition using the RNiO$_3$ phase diagram (Figure 4.8). The phase diagram shows the change of the transition temperatures ($T_{MI}$) and ($T_N$) with the size of the R$^{3+}$ ion. For the largest rare earth ion (R= La), the system is metallic paramagnetic and crystallizes in a rhombohedral type structure. The orthorhombic ($P_{bmm}$) members of the RNiO$_3$ series exhibit a metal insulator transition at $T_{MI}$ which increases with decreasing the ionic radius of the R$^{3+}$ ion (R= Pr,……, Lu). The temperature-induced MI transition in RNiO$_3$ series has been ascribed to the opening of a small charge transfer gap at $T<T_{MI}$ which is intimately connected an orthorhombic ($P_{bmm}$) to monoclinic ($P_{21/n}$) structural transition [3]. The transition to a monoclinic symmetry on crossing $T_{MI}$ to the insulating state implies two independent Ni-sites and the presence of a charge ordering ($2\text{Ni}^{3+} \rightarrow \text{Ni}^{3+\alpha} + \text{Ni}^{3-\alpha}$) [4,5].

As shown in the phase diagram, the insulating phase exhibits antiferromagnetic order below $T_N$.

![Fig. 4.8 Modified phase diagram of the RNiO$_3$ series from [57]. The relation shows the change of the transition temperatures ($T_{MI}$) and ($T_N$) as a function of the size of R$^{3+}$ ions.](image-url)
<table>
<thead>
<tr>
<th>Element</th>
<th>La</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Y</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>0.9856</td>
<td>0.9751</td>
<td>0.9711</td>
<td>0.9642</td>
<td>0.962</td>
<td>0.9452</td>
<td>0.9354</td>
<td>0.9318</td>
</tr>
<tr>
<td>$T_N$ (K)</td>
<td>0</td>
<td>130</td>
<td>200</td>
<td>225</td>
<td>205</td>
<td>145</td>
<td>138</td>
<td>130</td>
</tr>
<tr>
<td>$T_M$ (K)</td>
<td>0</td>
<td>130</td>
<td>200</td>
<td>400</td>
<td>463</td>
<td>582</td>
<td>595</td>
<td>599</td>
</tr>
<tr>
<td>Radius $R^{+3}$ (pm)</td>
<td>117.2</td>
<td>113</td>
<td>112.3</td>
<td>109.8</td>
<td>108.7</td>
<td>104</td>
<td>100.8</td>
<td>100.1</td>
</tr>
</tbody>
</table>

Tab. 4.1 represents the data of the ionic radius, tolerance factor, and the transition temperatures in RNiO$_3$ compounds.

4.3 Motivation for high pressure studies on YbNiO$_3$

As mentioned before, the temperature-induced MI transition in RNiO$_3$ series is connected with structural changes and simultaneous charge ordering. However, a common physical picture for the driving mechanism of the thermally-induced MI transition is still far from being fully understood.

Previous high pressure studies showed that, the transition temperature $T_M$ of the MI transition can be suppressed with external pressure stabilizing the metallic state to lowest temperatures. This observation has been found not only in NdNiO$_3$ and PrNiO$_3$ [58], but also in RNiO$_3$ with small $R^{3+}$ radius (EuNiO$_3$, [7] and LuNiO$_3$, [8]). Thus, a promising approach for a better understanding of the driving mechanism of the MI transition is to investigate the effect of pressure on the transport, magnetic and structural properties of RNiO$_3$ with small $R$, e.g. YbNiO$_3$. Up to now nothing is known about the pressure response of the transport, magnetic, and structural properties of YbNiO$_3$. Thus, such a study should help to develop a common physical picture of the mechanism of the pressure-induced IM transition in these compounds. In particular, to provide better understanding of the following interesting aspects:

(i) The pressure-induced insulator metal (IM) transition and its possible connection with the structural phase transition and charge ordering; both are observed at the temperature-induced MI transition.

(ii) Whether the expected metallic state at high pressure is magnetic or nonmagnetic.
4.4 *High pressure resistivity measurements on YbNiO$_3$*

In this section, we are going to present and discuss the results of the electrical resistance measurements on YbNiO$_3$ under high pressure as well as the effect of pressure on $T_N$ in the sample as obtained from electrical resistivity measurements. In the next section, we present the structural stability of YbNiO$_3$ under high pressure and discuss possible mechanisms for the pressure-induced insulator to metal (IM) transition in the YbNiO$_3$.

YbNiO$_3$ samples used in this thesis were prepared by Dr. J. A. Alonso et al. (Instituto de Ciencia de Materiales de Madrid, CSIC, Canto Blanco, Madrid, Spain) by solid state reactions as polycrystalline powders. Their preparation is described elsewhere [3,5]

As it is shown in the phase diagram (Fig. 4.7) YbNiO$_3$ is at room temperature a paramagnetic insulator with an antiferromagnetic ordering temperature of $T_N = 138$ K and MI transition temperature of $T_{MI} = 595$ K at ambient pressure. It exhibits at $T_{MI}$ a structural distortion from of the orthorhombic phase to a monoclinic with the appearance of charge ordering of the Ni$^{3+}$ ions.

### 4.4.1 Pressure-induced insulator metal transition

Figure 4.9 shows the pressure dependence of the electrical resistance of YbNiO$_3$ between 8.0 and 300 K at different pressures up to 12.4 GPa. YbNiO$_3$ reveals a semiconducting like behavior ($dR/dT < 0$) at the ambient pressure because the value of its $T_{MI}$ at ambient pressure is much higher than room temperature. By increasing the pressure above 1.2 GPa to 6.6 GPa, $R (T)$ strongly decreases with increasing pressure and the magnitude of the slope of the curve ($dR/dT$) gradually decreases. At the same time, the absolute value of the resistance decreases dramatically by more than 6 orders of magnitude at low temperatures, indicating a gradual change towards a metallic like state.

For $p \geq 8.2$ GPa one observes a metallic like behavior ($dR/dT > 0$) or a phase transition from the insulating to a metallic state. From the geometry of the contacted sample inside the sample chamber of the DAC, we roughly estimate the specific resistance ($\rho$) of YbNiO$_3$ of the order of 0.49 m$\Omega$cm for $p = 8.2$ GPa at 4.2 K and $\approx 0.16$ m$\Omega$cm for $p = 12.4$ GPa at 4.2 K. These values are higher than those typical for metallic systems, but comparable with those reported for other members of the RNiO$_3$ series. For example, the value of $\rho$ in the metallic state of PrNiO$_3$ and NdNiO$_3$ amounts to $\rho \approx 0.4$ m$\Omega$cm and $1.3 \times 10^{-3}$ m$\Omega$cm at 300 K, respectively [46,59]. This is a common feature for all investigated RNiO$_3$ samples in the metallic state.
4.4.2 **Reversibility of the pressure-induced insulator metal transition in YbNiO₃**

We report in the following on a second high pressure experiment on YbNiO₃ to account for the reversibility of the pressure-induced IM transition. This physical aspect becomes important after the very recent high pressure report on the pressure dependence of the transition temperature of the IM transition in YNiO₃ and LuNiO₃ [60]. In this work, the authors performed high pressure resistivity measurements on second-sintered RNiO₃ (R=Eu, Y, and Lu) samples, where the samples are sintered 2 times at high temperatures, in a multianvil module in the temperature range between 700 K and 300 K. They found that the pressure dependence of $T_{\text{IM}}$ is smaller than previously reported in Ref. [8]. The authors discuss their results of LuNiO₃ and YNiO₃ in an analogy to the orbital ordering insulator LaMnO₃ instead of charge ordering model introduced by [8]. They further suggest that their observation is not related to the nature of the second-sintered samples but due to the different pressure conditions in mutianvil and diamond anvil cells. They argue that the high pressure measurements on LuNiO₃ were performed on powdered sample using DAC under nearly nonhydrostatic pressure which may result in reduction of the sample, i.e. an intrinsic change of the chemical...
composition and thereby leads to the observed pressure-induced MI transition in LuNiO$_3$ at low pressure of about 6 GPa.

![Graph showing the pressure dependence of the electrical resistance of YbNiO$_3$ between 300 and 4.2 K up to 17.0 GPa.](image)

Fig. 4.10 Pressure dependence of the electrical resistance of YbNiO$_3$ between 300 and 4.2 K up to 17.0 GPa.

To provide a clear answer to such an assumption, we have performed a second high pressure resistivity experiment on our powdered sample (YbNiO$_3$) in a DAC across the pressure-induced IM transition to about 17 GPa and released the pressure to ambient pressure again. If the sample would have been reduced under nearly nonhydrostatic pressure, as suggested by [60], the pressure-induced IM transition should be irreversible. This means that the high-pressure metallic state should remain after releasing pressure. This second high-pressure resistivity measurements on the same powdered YbNiO$_3$ sample in the same DAC up to about 17 GPa are shown in Fig. 4.10. These measurements have been performed in collaboration with the University of Cologne in Germany where measurements are extended to 4.2 K. The results are similar to those of the first measurements (s. Fig. 4.9) and confirm that the pressure-induced IM transition occurs above 8 GPa.
In Fig. 4.11, we now show the pressure and temperature dependence of the resistivity as the pressure is gradually released to ambient pressure. This Figure clearly demonstrates that the pressure-induced IM in YbNiO$_3$ is indeed reversible. As it is evident from Fig. 4.11, upon releasing pressure in the metallic state at $p = 12$ GPa to ambient pressure, the sample returned back to its initial insulating state. This finding clearly shows that the intrinsic nature of the sample is not affected at all by the pressure conditions in the DAC as suggested by [60]. We thus feel that the contradiction between the two reports may be due to the different sintering process of the samples. It could be also related to a different behavior of the sample under high pressure at high temperatures up to about 800 K, which might affect thermodynamic balance of the sample during the measurements.
4.4.3 Pressure dependence of $T_N$ in YbNiO$_3$

As we have recently shown in LuNiO$_3$ [8] and related RNiO$_3$ compounds [61], the resistivity exhibits a local maximum at a temperature $T_{\text{max}}$ which is related to $T_N$. Following our data analysis, we were able to observe such a maximum above 5 GPa at about 180 K (see Fig. 4.12). No maximum could be observed below that pressure due to a dominating semi conducting like behavior of the sample. The maximum has been determined at different pressure values by fitting locally a polynomial function (9th grade) at the R(T) curve close to the maximum (i.e. in a temperature interval of roughly 40 K with the maximum in the middle of this interval). The maximum temperature is found where the first derivative of this polynomial fit equals zero.

![Graph showing pressure dependence of YbNiO$_3$ resistivity](image)

Fig. 4.12 Pressure dependence of the electrical resistance of YbNiO$_3$ between 300 and 4.2 K at 4.2 GPa and 5.0 GPa. While at 4.2 GPa there is no maximum visible, a clear maximum around 180 K can be observed at 5.0 GPa.

The values of $T_{\text{max}}$ as deduced from the R(p,T) measurements up to 12.4 GPa are plotted in Fig. 4.13. The value of $T_N$ (138 K) at ambient pressure is also included. As is evident from the figure, $T_{\text{max}}$ strongly increases with increasing pressure, reflecting a corresponding increase of $T_N$. This is
what one would expect for local moment behavior. However, the analysis of the initial change of $T_N$ with pressure indicates that the pressure-induced increase of $T_{\text{max}}$ ($T_N$) is larger in the insulating state ($p \leq 8.2$ GPa) than that in the metallic state ($8.2 < p < 12.4$ GPa). Such a large positive coefficient ($dT_N/dp > 0$) has been also found in LuNiO$_3$ and SmNiO$_3$ confirms the localized character of the 3d-states of RNiO$_3$ (R = Sm,..,Lu) in the insulating state.

The different pressure dependence of $T_{\text{max}}$ observed in the insulating and metallic states is due to the fact that the nature of the magnetic ground state in these two phases is essentially different: while magnetism in the insulating state is determined by superexchange interactions between localized 3d electrons, it is governed in the metallic state by itinerant 3d electrons, e.g. by a spin density wave-like state. Accordingly, the large increase of $T_{\text{max}}$ with pressure in the insulating state can be explained by the increase of the effective hopping which results in an increase of the effective exchange interaction and a large increase of $T_N$. On the other hand, it is difficult to predict the strength of the pressure dependence of $T_N$.

![Fig. 4.13 Pressure dependence of the values of $T_{\text{max}}$, where the resistance of YbNiO$_3$ goes through a maximum, and which is related to the onset of magnetic order. Antiferromagnetic ordering at ambient pressure sets in at $T_N = 138$ K in YbNiO$_3$. Dashed lines are linear fits to the data in the insulating state ($p \leq 8.2$ GPa) where $T_{\text{max}}$ increases with 8.6 K/GPa (red) and in the metallic state ($p > 8.2$ GPa) where $T_{\text{max}}$ increases with 4.3 K/GPa.](image-url)
in the pressure-induced metallic state. In the metallic state the dependence of $T_N$ on pressure is more complex, as pressure can affect the coupling constant, bandwidth and the shape of the Fermi surface. Such complicity may lead to a weaker pressure dependence of $T_N$ as observed in YbNiO$_3$. Finally, our results indicate that the high pressure metallic state in YbNiO$_3$ is magnetically ordered which is consistent with recent high pressure reports on EuNiO$_3$ [7] and LuNiO$_3$ [8].

4.5 High pressure x-ray diffraction measurements on YbNiO$_3$

In this section we are going to investigate the effect of the pressure on the lattice parameters (a, b and c) and the volume of the monoclinic unit cell in YbNiO$_3$ as obtained from our energy dispersive x-ray (EDX) diffraction measurements at 300 K at beamline F3 at Hasylab (Hamburg). This investigation should give an answer to the question whether the observed pressure-induced IM transition in YbNiO$_3$ is connected with a structural phase transition.

![Fig. 4.14 X-ray diffraction patterns of YbNiO$_3$ at room temperature for selected pressures up to 23.7 GPa. Data were taken in a diamond anvil cell setup at beamline F3, HASYLAB, Hamburg, Germany with $E_d$ = 103.257 KeVÅ. Asterisks mark undetermined reflections from an impurity phase of the sample.](image-url)
Figure 4.14 shows the x-ray diffraction patterns obtained from our EDX diffraction measurements at 300 K and up to 23.7 GPa. Due to the limited resolution of the EDX data, and very small monoclinic distortion in YbNiO$_3$ we were not able to observe the diffraction peaks corresponding to the monoclinic phase. However, to qualitatively investigate a possible change of the lattice structure with pressure, we have performed crude analysis assuming an undistorted orthorhombic structure and follow its stability with increasing pressure. On the basis of our analytical approach, the diffraction patterns are indexed according to the orthorhombic structure up to the highest pressure (see Fig. 4.14). The pressure is determined using Au marker in which the lattice parameter changes with the pressure (see Fig. 4.15).

![Graph showing the pressure dependence of the lattice parameter of Au marker](image)

_Fig. 4.15 the pressure dependence of the lattice parameter of Au marker_

The pressure-volume relationship of YbNiO$_3$ up to about 25 GPa at 300 K is displayed in Fig. 4.16. The data reveals within the experimental accuracy a smooth variation of the volume with pressure which can be described by Murnaghan equation with bulk modulus $B_0 = 197\pm8$ GPa and its derivative $B_0' = 5\pm1$. These values are similar to those obtained for RNiO$_3$ compounds with small R$^{3+}$ radius; e.g. YNiO$_3$ and LuNiO$_3$ [62].
To obtain more information on the structural stability of YbNiO₃, we show in Fig. 4.17, Fig. 4.18, and Fig. 4.19 the change of the lattice parameters a, c, and b, respectively. Here, we find within the accuracy of our measurements up to pressure of about 16 GPa a smooth variation of a, b, and c and the volume. In other words, there is no discontinuity in the pressure dependence of all lattice parameters in this pressure range that indicates a structural anomaly or phase transition around the critical pressure (about 8 GPa) at which we observe a pressure-induced IM transition in YbNiO₃.
Fig. 4.17 Pressure dependence of the lattice parameter $a$ of the approximated unit cell of YbNiO$_3$ (see text) for pressures up to 25 GPa taken in a diamond anvil cell setup.

Fig. 4.18 Pressure dependence of the lattice parameter $c$ of the approximated unit cell of YbNiO$_3$ (see text) for pressures up to 25 GPa taken in a diamond anvil cell setup.
From these results we can conclude that the observed pressure-induced IM transition in YbNiO$_3$ is not connected with any structural change. This finding is consistent with that reported from previous high pressure studies on EuNiO$_3$ [7] and LuNiO$_3$ [8]. Moreover, the results imply that the stability of the monoclinic phase up to 16 GPa and thereby the existence of charge ordering in the metallic magnetic state as recently suggested for LuNiO$_3$ [8].

Finally, we would like to mention that we find an anomalous change of the lattice parameter $b$ (s. Fig. 4.19) above 16 GPa which can be taken as an evidence for a structural phase transition in YbNiO$_3$. This would mean that above 16 GPa we have achieved the expected structural phase transition from monoclinic to the “real” orthorhombic structure. This suggestion is supported by the fact that such a structural phase transitions have been observed in RNiO$_3$ compounds with small $R^{3+}$ radius at the same or close to 16 GPa (e.g. 16 GPa for LuNiO$_3$, [62] and 14 GPa for YNiO$_3$ [63]. For an experimental verification of the suggested structural phase transition in YbNiO$_3$ angle resolved x-ray diffraction experiments are highly desired. Such experiments are underway.

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**Fig. 4.19** Pressure dependence of the lattice parameter $b$ of the approximated unit cell of YbNiO$_3$ (see text) for pressures up to 25 GPa taken in a diamond anvil cell setup. The red arrow marks a change in the pressure dependence of the $b$-axis, red lines correspond to linear fits of the data for $0 < p < 17$ GPa and $17 < p < 25$ GPa.
Chapter 5

Summary and Outlook

The thesis deals with the investigation of the effect of pressure on the electronic, magnetic and structural properties of the magnetically ordered Mott-insulator YbNiO$_3$. This compound belongs to the interesting family of transition metal oxides RNiO$_3$ (R= rare earth) with perovskites structure, in which the metal insulator (MI) transition can be induced at ambient pressure as a function of temperature and the transition temperature ($T_{MI}$) increases with decreasing the size of the R$^{3+}$ ion. This temperature-induced MI transition in RNiO$_3$ series is connected with structural changes and a simultaneous charge ordering of the Ni$^{3+}$ ions. Furthermore, the RNiO$_3$ series display antiferromagnetic (AF) order at low temperatures, where the transition to a magnetically ordered state at $T_N$ is also related to the size of the R$^{3+}$ ion. For large R$^{3+}$ ions (R = Pr, Nd) the MI transition is accompanied by AF ordering of the (Ni) sub lattice (i.e. $T_N \approx T_{MI}$), whereas for smaller R$^{3+}$ (R = Sm $\rightarrow$ Lu) $T_N$ is much smaller than $T_{MI}$ (e.g. for YbNiO$_3$, $T_N = 140$ K and $T_{MI} = 599$ K). According to the magnetic phase diagram RNiO$_3$ exhibit a crossover from antiferromagnetic insulator (R $\neq$ La) to nonmagnetic metal (LaNiO$_3$). However, a common physical picture for the driving mechanism of the thermally induced MI transition is still far from being fully understood.
External pressure has been shown to induce an insulator to metal transition in RNiO$_3$ compounds with small R$^{3+}$ as recently observed in EuNiO$_3$ and LuNiO$_3$ and thereby provides valuable information for a better understanding of the driving mechanism of the MI transition. It was, thus, the aim of this work to investigate the effect of pressure on the transport, magnetic and structural properties of RNiO$_3$ with small R$^{3+}$, e.g. YbNiO$_3$. Such a study should help to develop a common physical picture of the pressure-induced IM transition in this class of materials.

The investigation of the pressure-induced IM transition in YbNiO$_3$ ($T_N = 140$ K and $T_{MI} = 599$ K and its possible relationship to structural phase transition has been carried out using high pressure electrical resistivity and x-ray diffraction measurements. The electrical resistivity has been measured up to about 20 GPa and at different temperatures between 300 and 8 K in a closed cycle cryostat. This experimental set up for high-pressure resistivity at variable temperatures and the associated optical system for the pressure determination have been successfully installed for the first time at the Physics Department. To achieve very high pressure a diamond anvil cell (DAC) has been used which allows one to obtain controlled and well-defined pressure data. A slightly modified, same type of DAC, has been used for the structural investigation under high pressure, which has been carried out by energy dispersive x-ray (EDX) diffraction measurements at 300 K up to about 23 GPa at beamline F3 at Hasylab in Hamburg, Germany.

The analysis of the temperature dependence of the electrical resistivity as a function of increasing pressure in YbNiO$_3$ shows a gradual transition from the insulating to a metallic behavior around 8 GPa, i.e. a pressure-induced IM transition. To account for the reversibility of the observed pressure-induced IM transition, we have performed a second high pressure resistivity experiment on YbNiO$_3$ in DAC across the pressure-induced IM transition up to about 17 GPa and released the pressure to ambient pressure again. We find a reversible behavior, i.e. the sample returned back to its initial insulating state after releasing pressure. If the sample would exhibit intrinsic changes under nearly non-hydrostatic pressure, as recently suggested by Ref. 60, the pressure-induced IM transition should be irreversible. This is indeed not the case in YbNiO$_3$.

We further were able to determine the pressure dependence of the magnetic ordering temperature of YbNiO$_3$ ($T_N$) from the corresponding change of the local maximum of the resistivity ($T_{max}$) since $T_{max}$ is related to $T_N$. We find that $T_{max}$ strongly increases with increasing pressure, reflecting a corresponding increase of $T_N$. This is what one would expect for a local moment behavior. $T_N$ increases from 138 K at ambient pressure to about 230 K at about 13 GPa and thus clearly indicates that the pressure-induced metallic state in YbNiO$_3$ is magnetically ordered. However, the analysis of the initial change of $T_{max}$ with pressure indicates that the pressure-induced increase of $T_{max}$ ($T_N$) is larger in the insulating state ($p \leq 8.2$ GPa) than that in the metallic state ($8.2 < p < 12.4$ GPa). Such a large positive coefficient ($dT_N/dp > 0$) has been also found in LuNiO$_3$ and SmNiO$_3$ and confirms the localized character of the 3d-states of RNiO$_3$ (R = Sm,..,Lu) in the insulating state. It would be very interesting to directly determine the pressure dependence of $T_N$ and the Ni magnetic moment of YbNiO$_3$ across the IM transition, e.g. by high
pressure neutron scattering measurements. Such experiments would shed a deeper insight on the nature of the high pressure metallic magnetic phase.

Finally, we have investigated the effect of pressure on the lattice parameters (a, b and c) and the volume of YbNiO₃ up to about 25 GPa as obtained from our EDX diffraction measurements. This investigation should give an answer to the question whether the observed pressure-induced IM transition at about 8 GPa in YbNiO₃ is connected with a structural phase transition or not. A crude analysis of pressure-volume relationship of YbNiO₃ up to about 25 GPa at 300 K reveals within the experimental accuracy a smooth variation of the volume with pressure and thereby excludes that the observed pressure-induced IM transition in YbNiO₃ is connected with a structural phase transition. This finding is consistent with that reported from previous high pressure studies on EuNiO₃ and LuNiO₃. However, high resolution angle resolved x-ray diffraction measurements would be necessary to proof our conclusion. Such experiments on YbNiO₃ are underway.
References

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