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BACHELOR'S THESIS

Organic Compound Dependence on Magnetic Response of Nickel-Chlorine Based Hybrids

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Figure 1: $NiCl_3$ Propylammonium Hybrid

Abstract

In this thesis, nickel based hybrids which exhibit one dimensional magnetism are discussed. Magnetic and dielectric measurements are taken on different hybrids. The dielectric measurements did not provide consistent data and were therefore not fitted or analyzed. The magnetic data gave different responses per hybrid. Two models were proposed to describe this behaviour. The *chain-end* model describes that nickel chains end within the crystal and that the average length as well as the length distribution will give different responses. The *residual spin* model describes that only chain lengths of odd parity will contribute to the low temperature Curie behaviour. The average length and the length distribution can be tuned by using different organic compounds for the synthesis.

Contents

1	Introduction	7
1.1	ORGANIC, INORGANIC	7
1.2	HYBRIDS	7
1.2.1	MOTIVATION	8
1.2.2	STRUCTURE	8
2	THEORY	9
2.1	SYNTHESIS	9
2.2	MAGNETISM	9
2.2.1	INTRODUCTION	9
2.2.2	PARAMAGNETIC RESPONSE	11
2.2.3	THREE DIMENSIONAL ORDERING	11
2.2.4	LOW DIMENSIONAL ORDERING	11
2.3	DIELECTRICITY	13
2.3.1	GENERAL INTRODUCTION	13
2.4	CONJUGATED SYSTEM SYNTHESIS	14
2.4.1	MOTIVATION FOR SYNTHESIS	14
2.4.2	MECHANISM	14
3	EXPERIMENTAL	16
3.1	DIELECTRIC MEASUREMENTS	16
3.1.1	MEASUREMENT SETUP	16
3.1.2	RESULTS	16
3.2	MAGNETIC MEASUREMENTS	16
3.2.1	MEASUREMENT SETUP	16
3.2.2	SUPERCONDUCTING QUANTUM INTERFERENCE DEVICE	17
3.2.3	RESULTS	18
3.3	SYNTHESIS OF TEREPTHALIMINE	19
3.3.1	ANALYSIS	20
4	CONCLUSION	22
4.1	CHAIN ENDING MODEL	22
4.2	RESIDUAL SPIN MODEL	22
4.3	FURTHER RESEARCH	24
5	ACKNOWLEDGEMENTS	28
A	STUCTURES	29
B	MEASUREMENT SETUP	31

1 Introduction

This Bachelor's thesis will focus on the magnetic and dielectric response of nickel based hybrids, and the suggestion for a new conjugated hybrid. It will start with an introduction to hybrids, followed by an explanation of magnetism. Subsequently, paramagnetism and magnetic interactions in multiple dimensionalities will be explained. It will then provide an introduction to dielectric behaviour. A motivation for the synthesis will be given, including a reaction pathway. It will end up with the discussion of the result and preliminary conclusions.

1.1 ORGANIC, INORGANIC

Most chemical compounds can be put into two distinctive categories; The organic and the inorganic compounds. Organic chemistry is about the chemistry of carbon atoms. Living organisms largely consist of carbon based chemicals, hence the link with the word *organic*. Proteins for example are organic molecules. While inorganic compounds can also be found inside living beings, they are mostly associated with lifeless objects. Rocks and metals are examples of inorganic objects.

Both have different chemistry and therefore behave differently. Large differences are their magnetic and dielectric behaviour. While inorganic materials can have a strong magnetic response or a high conductivity, most organic molecules do not. Organic materials are often used as insulators and nonmagnetic materials. As Anne Arkenbout[3] put it nicely: 'Organic materials isolate the inorganic conductor that transports electricity to your coffee machine'. Recently, organic materials have been used as conductors [4, 15, 15], ferroelectrics[5, 13, 14] or semiconductors[6, 17]. The major advantage of organic materials is that their molecular structure can be altered easily and precisely.

Organic chemistry has been conducted for over two hundred years and has been mapped thoroughly. Therefore, changing one functional group to another is very easy and can have major results on the physical properties. Organic molecules have an even number of electrons, which are all paired. This will lead to almost no magnetic response, as well as insulator behaviour[8]. Although inorganic chemistry is also well known, inorganic constructs are harder to synthesize, if possible at all. Therefore, it is harder to customize inorganic products the way organic products can be customized. However, it is easier for inorganic compounds to have an odd number of spins. This can contribute to high conductivity or high magnetic response. A possibility that can combine the best of both worlds is hybrids.

1.2 HYBRIDS

A hybrid is a system that consists of multiple and different 'building bricks'. In this case, a hybrid is a material that consists of both an organic and an inorganic material. Hybrids can contain the best of both worlds. They can have a good magnetic response and the flexibility of organic materials, while still being a semiconductor or a conductor. This means that they can have a wide variety of applications, for instance in spintron-

ics. Hybrids can be created using different organic and inorganic materials, each with different properties and structures. For example, nickel based hybrids form a sandwich structure where the nickel chlorine complexes form chains, whereas manganese or iron based hybrids have inorganic sheets instead of chains. This thesis will focus on the nickel based hybrids.

1.2.1 MOTIVATION

Because of the properties described above, these hybrids can be used in certain fields such as spintronics[18], where a difference in spin direction of electrons can be made by applying magnetic fields. The motivation for this research lies in the research of *Anne Arkenbout*[3]. Arkenbout discovered pseudo one dimensional structures in nickel based hybrids. This thesis will focus on the influence of the organic part on the magnetic and dielectric response of pseudo one dimensional nickel based hybrids.

1.2.2 STRUCTURE

The hybrids in question are —as stated earlier— nickel based. The composition of these hybrids are $NiCl_3RNH_3$. This means that for the structure to be electrically neutral, the nickel is in the +2 oxidation state. As is discussed later, this will lead to its magnetic properties.

As stated earlier, the hybrids discussed form sandwich materials. Sheets of inorganic materials are separated by sheets of organic material. This means that the structure can be changed by changing the organic part, which controls layer-layer distance. In the nickel based hybrids, the inorganic part forms sheets of chains, which are in turn separated by organic material. The chains are not bonded to each other and thus are separated. The inorganic part is nickel chloride complexes, bonded to each other by face sharing octahedra. The inorganic part is bonded by ammonium groups from the organic part. The organic part can therefore be any compound which contains an ammonium group. Changing an organic part will in turn change the structure of the entire hybrid by altering the layer-layer and chain-chain separation.

Because the nickel atoms are contained within an octahedron, the d-orbital of nickel is split into two different energy levels. Two e_g levels and three t_{2g} levels[12]. This will provide a loss of degeneracy for the d-orbitals. This loss will result into a full occupation of the lower orbitals, having a total of zero spin and a partial occupation of the higher orbitals. This last term will result into an $S = 1$ system, hence the magnetism. The in-chain interaction (super exchange) occurs via three single chlorine atoms, thus an exchange path of length one. The inter-chain interaction occurs via two chlorines and a nitrogen atom. The interaction between chains in separate layers occurs via the entire organic molecule and intermediate chlorine atoms. The interaction between chains is weak due to the long interaction path, and therefore is negligible. Because this interaction is weak, the system will behave one dimensional, hence the one dimensional magnetism discussed later. The key to changing the magnetic or dielectric properties is to change the organic part because this will change the structure of the hybrid.

2 THEORY

2.1 SYNTHESIS

Synthesis of the hybrids stated in the previous section is relatively simple. The hybrids assemble themselves by crystallization from solution. The metal halide and ammonium halide are dissolved in a polar solvent such as ethanol in stoichiometric ratio. Heating to 50°C is usually necessary to dissolve all the product. The solution is subsequently put into a stove at 55°C . Over the course of several days, the solvent is slowly evaporated, allowing the hybrids to crystallize. The slower the evaporation of the solvent, the more time for crystallization and the bigger the crystals. So if the crystal yield is not good enough, evaporation could occur at a lower temperature setting or under a vacuum desiccator.

Care needs to be taken when storing the hybrids, because the crystals can react with water. Reaction with water results in a green crystalline compound, followed by solvation of the hybrid. This reactivity differs per used organic compound. The methylammonium hybrid reacts with water fairly quickly, whereas the phenylethylammonium hybrid is not as reactive and can be kept exposed to the atmosphere for several hours before decomposing, enabling the possibility for the creation of beautiful pictures. This can be prevented when the hybrid is kept in a stove at 65°C or in vacuum.

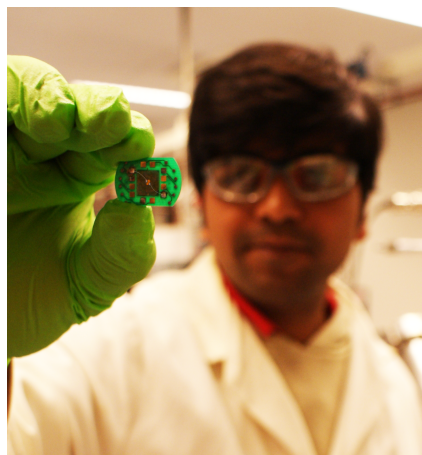


Figure 2: S. Giryapura holding a sample holder containing a hybrid. A closeup can be seen in section 3.

2.2 MAGNETISM

Magnetism is a property of materials to respond at the atomic or subatomic level to an applied magnetic field. Although magnets are commonly associated with ferromagnets, every material exhibits a magnetic response to an applied field. Ferromagnets are materials with can hold a magnetic field, even in the absence of an external magnetic field. Most materials respond only slightly to a magnetic field, hence the lack of association with magnetism.

2.2.1 INTRODUCTION

One of the common parameters which is associated with magnetism is the magnetic susceptibility χ . The magnetic susceptibility is a parameter which determines how a sample responds to an applied field. If the total field \vec{B} is given by the sum of the applied field \vec{H} and the induced field \vec{M} in the sample,

$$\vec{B} = \mu_0(\vec{H} + \vec{M}) \quad (1)$$

The magnetic susceptibility is defined as

$$\vec{B} = \chi \vec{H} \quad (2)$$

Or

$$\chi = \frac{\vec{B}}{\vec{H}} \quad (3)$$

So the magnetic susceptibility is an encapsulation of the magnetization of the material, assuming that the magnetization is a function of the applied field.

SOURCE OF MAGNETISM

But what is the cause of magnetism? As stated by Ampère's Law[19]:

$$\oint \vec{B} \cdot d\vec{r} = \mu_0 I_{encircled} \quad (4)$$

The magnetic field can be related to an electric current. This means that induced currents in a sample can result in a magnetic field. This is often not related to magnetism because the induced current will die out before the resulting field can be measured. Furthermore, during measurement the applied field is not changed, so there is no change in flux Φ_B . The lack of flux change will result in an absence of current in the sample.

However, by application of a magnetic field, the orbital motion of the electrons around the nucleus (as long as the orbital the considered electron currently occupies is associated with angular momentum) is disturbed. This means that due to equation 4, there is a resulting field which opposes the applied field. This is called a diamagnetic contribution. This contribution is independent of temperature and is usually very low [8, p. 301].

Most magnetism is caused by two different magnetic moments of electrons in the material. The nuclear magnetic moment is usually neglected because it is around 1000 times smaller than the electron contribution. The two different magnetic moments are the orbital magnetic moment and the spin magnetic moment. The orbital magnetic moment is caused by the electron revolving around the nucleus, as given by equation 4. Usually, the orbital angular momentum of an electron is zero. This is because the orbital momentum eigenstates are not eigenstates of the Hamiltonian. The eigenstates of the Hamiltonian of the electron are linear combinations of the orbital momentum eigenstates, usually leading to eigenstates with zero angular momentum.

The spin magnetic moment is caused by the spin of an electron. The classical picture is an electron spinning its own axis, which can also be described by a current flowing through a ring. In reality however, the electron is described as a point particle, which of course would not have a classical angular momentum and therefore would not have a magnetic moment. The inherent spin magnetic moment is therefore a purely quantum mechanical phenomenon.

2.2.2 PARAMAGNETIC RESPONSE

Paramagnetism is a very common phenomenon. When not considering interactions between spins in a lattice, the only response of those spins is by an external applied magnetic field. Thus the magnetization itself has no influence on the orientation of the spins. Application of an external field to a randomly organized spin system breaks up degeneracy because of:

$$U = -\vec{\nu} \cdot \vec{B} = m_j g \mu_B B \quad (5)$$

Where g is given by the Landé equation, m_j is the azimuthal quantum number and μ_B is the Bohr magneton. Considering only spin half systems with no angular momentum, there is a difference in energy between the up and down state. Their relative occupation depends on temperature. This approximation will lead to the *Curie Law* $M = \frac{CB}{T}$. where C is the Curie constant.

2.2.3 THREE DIMENSIONAL ORDERING

When considering local interactions, the situation changes. Because the neighbouring spins interact with each other, they can have a tendency to be parallel or antiparallel. According to the mean-field approximation, the field experienced by a magnetic atom is proportional to the magnetization. The total magnetization is then a function of the applied field and the interaction (which is usually called the exchange field). This will change the magnetic susceptibility to:

$$\chi = \frac{C}{T - T_c} \quad (6)$$

Which is called the *Curie Weiss Law*. The function diverges at $T = T_c$. Below this temperature, there is a spontaneous magnetization. The thermal fluctuations of the spins are of insufficient energy to disrupt the magnetic ordering. The constant T_c is called the *Curie Temperature* and describes the interaction between spins. If it is negative, the ordering will be antiferromagnetic and if it is positive, it will result in a ferromagnetic ordering.

2.2.4 LOW DIMENSIONAL ORDERING

At lower dimensionalities, the response is different. When only accounting for nearest neighbour interactions in two or one dimensions, long range order is suppressed. There are different ways to approximate this problem. These are the Heisenberg and Ising models. Both are described by the Hamiltonian:

$$\hat{H} = -2J \sum_{i>j} [aS_{z,i}S_{z,j} + b(S_{x,i}S_{x,j} + S_{y,i}S_{y,j})] \quad (7)$$

Where J is the interaction or exchange constant. For taking different values for a and b , different spin parameters can be taken into account. If $a = 1, b = 0$, the *Ising Model* is obtained, while $a = b = 1$ gives the *Heisenberg Model*. The *Heisenberg Model* model is a

semiclassical system, where spins can take any value in a three dimensional volume. The *Ising Model* constrains the spins to a single dimension, taking the form of a scalar. If $a = 0, b = 1$, the planar *Heisenberg Model* is obtained, which constrains the spins to lie on a plane. The J in the equation is the exchange constant. This constant can be positive or negative, resulting in ferromagnetic or antiferromagnetic order respectively[10].

The main difference thus is dimensionality. The characteristics of each model are different, and solving these models gives two different results. A real system can be designated as either a *Heisenberg Model* or an *Ising Model* by looking at the paramagnetic response. If the system is isotropic, then the magnetic susceptibility should be the same in each direction. This translates to a *Heisenberg Model*, whereas a non isotropic response translates to a planar or *Ising Model*.

Solving the *Ising Model* for several dimensionalities gives the results in the image below. Solving the *Heisenberg Model* gives other results as stated in the same image. Notice the difference in the two dimensional system, for the *Ising Model* predicts a singularity, whereas the *Heisenberg Model* does not. The one dimensional case of the *Heisenberg Model* cannot be solved exactly, but can be approximated numerically using a polynomial[9].

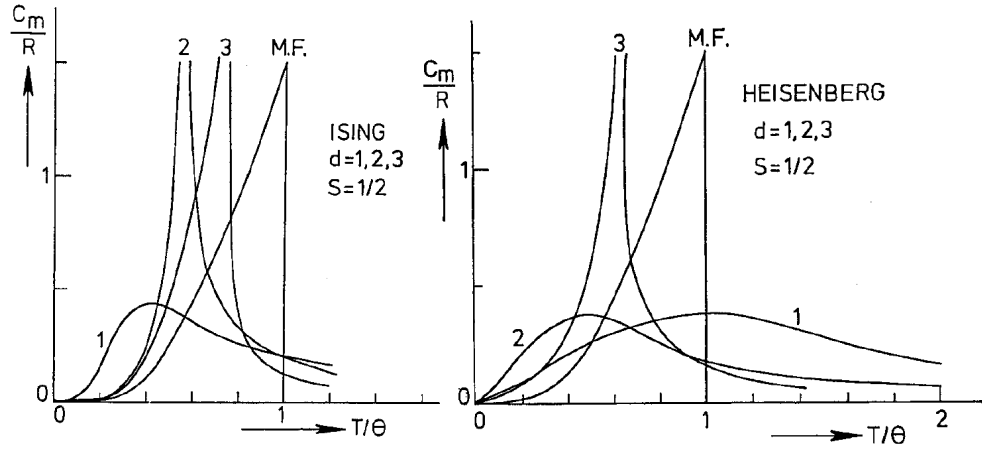


Figure 3: The *Ising* next to the *Heisenberg* model. Note that on the y-axis is not χ but molar heat capacity. The difference between the different models result in the absence of a singularity in the two dimensional model in the *Heisenberg model*.

Because the nickel based hybrids behave one dimensional, there is a possibility of a haldane gap. In both $S = \frac{1}{2}$ and $S = 1$ one dimensional systems, the ground state is nonmagnetic. This is due to pairing of the spins. This will form a singlet ground state, which has a total of zero spin. In $S = \frac{1}{2}$ systems, this is called a *Spin Peierls Transition*, whereas in $S = 1$ systems, this is called a *Haldane Gap*. In the nickel hybrid, there is a possibility of a *Haldane Gap*, but a deviation from ideal one dimensional behaviour was found at low temperatures[3, ch 4]. To find out what exactly happens at low temperature, a suggestion was made to synthesize a fully conjugated system, which

has the possibility for the onset of long range order.

2.3 DIELECTRICITY

Dielectricity describes how a material responds to an electric field, just like magnetization describes how materials respond to magnetic fields. A dielectric is a material that does not allow flowing current, but polarizes instead. This means that because of this polarization, the resulting field can be different than the applied field. A dielectric in an electric field behaves just like a diamagnet behaves in a magnetic field. The induced polarization is the opposite of the applied field, therefore reducing the resulting field. Thus:

$$\vec{P} = -\chi_E \vec{E} \quad (8)$$

Where \vec{P} is the induced polarization, χ_E is the dielectric susceptibility and \vec{E} is the applied electric field.

2.3.1 GENERAL INTRODUCTION

Usually, dielectricity is not described by the dielectric susceptibility but by the relative permittivity. When using a parallel plate capacitor, the capacitance is given by:

$$C = \epsilon \frac{A}{d} \quad (9)$$

Where ϵ is the permittivity of vacuum. When changing the vacuum between the capacitor plates to a dielectric, the relative permittivity is given by:

$$\epsilon_r = \frac{C_{dielectric}}{C_{vacuum}} \quad (10)$$

Where $C_{dielectric}$ is the capacitance of the capacitor with a dielectric between the plates and C_{vacuum} is the capacitance without the dielectric. The relative permittivity is a function of polarizability. The higher the polarizability, the lower the resulting field due to the higher polarization. This will result into more energy stored per applied voltage. The polarizability can depend on multiple factors. It differs per used material, but it also depends on temperature.

When increasing the temperature, the system expands, leaving more distance between capacitor plates. This will result into a lower measured capacitance. It has to be noted that this can be easily corrected by factoring in the expansion in the calculation. The other temperature dependent effect is that the thermal expansion causes an increase in polarizability because the distance between atoms increases. This allows for more movement of the electrons, resulting in an increased dielectric constant.

Magnetic ordering can also result in a dielectric response. If a material orders magnetically, this will lay constraints on the electrons in the material, changing the dielectric constant of the compound.

2.4 CONJUGATED SYSTEM SYNTHESIS

Because the layer-layer separation can be changed by using different organic ligands, the interactions between chains can be modified. This will alter the magnetic response because it affects the dimensionality. Another possibility is the addition of conjugated systems. Conjugated systems have the property of allowing super exchange, leading to a very high interaction constants.

Because amine groups can be changed to imine groups, it is possible to create a system of high conjugation in the form of terephthalimine. The amount of conjugation of this molecule can be altered without greatly distorting the original geometry. The three different possibilities are terephthalimine, terephthalamine and diaminocyclohexane. Hybrids created with these organic ligands will have their difference in magnetic response related solely to the amount of conjugation.

2.4.1 MOTIVATION FOR SYNTHESIS

The preferred compound could not be bought or obtained otherwise. Therefore another pathway to obtaining terephthalimine needed to be found. It is known that when adding ammonia to an aldehyde, an imine can be formed. Because it is possible to get pure terephthalaldehyde, this can be the starting material for the reaction. When adding ammonia to the compound, this could lead to the final product[1].

2.4.2 MECHANISM

First the aldehyde group absorbs a proton, forming an alcohol with a carbocation which is stabilized through resonance. This step can also take place without protonation, yielding a hemiaminal intermediate. Further clarification is needed however, because the reactions below need to happen twice, once to every side of the molecule. The R group depicts the rest of the conjugated system.

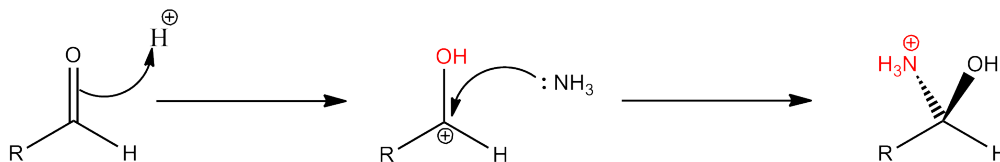


Figure 5: Protonation of the aldehyde followed by attack of the ammonia.

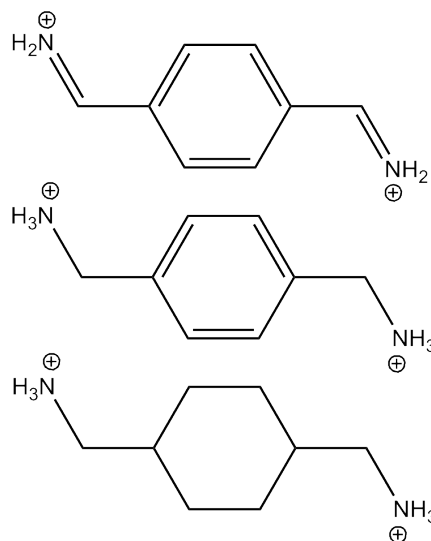


Figure 4: From top to bottom: Terephthalimine, Terephthalamine and paradiaminocyclohexane.

Amonia subsequently attacks the carbocation, forming an imminium group. The compound then deprotonates at the ammonium group and reprotonates the alcohol group. Dehydration follows, yielding an iminium ion, stabilized through resonance.

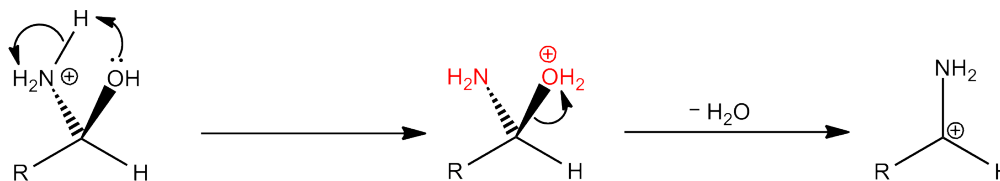


Figure 6: Deprotonation and reprotonation, dehydration leading to the formation of the iminium ion.

The lone pair on the nitrogen then attacks the carbocation forming a iminium ion. Deprotonation then ensues, forming the imine product.

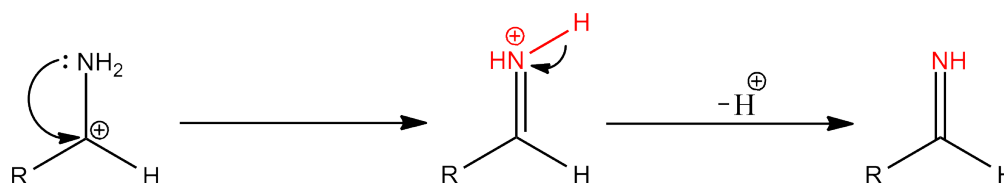


Figure 7: Attack of the lone pair, forming a double bond, followed by deprotonation.

Addition of concentrated hydrochloric acid could reprotonate the imine, yielding a diiminium ion. Single sided protonation is also possible but may be averted if sufficient acid is added. The protonated compound is stabilized very well through resonance.

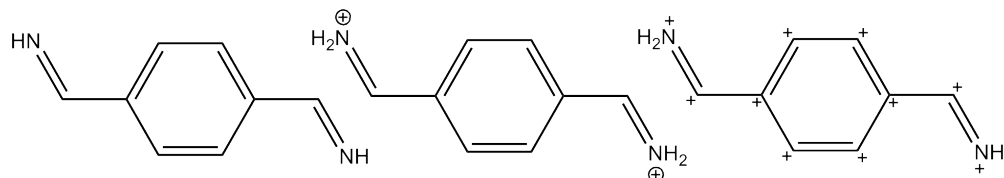


Figure 8: Distribution of positive charge through the compound. On the left the unprotonated compound, in the center the protonated compound. On the right is the charge distribution, note that the plus signs do not equal an entire electron charge but a partial one.

3 EXPERIMENTAL

Both dielectric and magnetic measurements were done after synthesis of the hybrid. Measurements were performed on nickel based hybrids containing different organic compounds. The next section will discuss the measurement setup of the dielectric and magnetic measurements including the results, as well as the synthesis of the conjugated system.

3.1 DIELECTRIC MEASUREMENTS

3.1.1 MEASUREMENT SETUP

Dielectric measurements were performed on an Advanced Research Systems CS204NE Cryostat using an Agilent E4980A Precision LCA Meter (picture found in appendix). First, a glass plate was stuck to the sample holder using varnish. The single crystal sample was subsequently put on the glass plate using varnish. Platinum wires ($0.01mm$) were soldered to the sample holder and then attached to two corners of the crystal using silver paint.

The sample was first put under vacuum $10^{-4}mbar$ and then cooled to $8K$ using a closed cycle helium refrigerator. The measurement was started and the cooling was shut down. Measurements were performed at $600KHz$ and $2V$ to minimize losses, and the capacitance versus temperature was measured over the course of 2 days.

3.1.2 RESULTS

The results obtained from the dielectric measurements were questionable to say the least. Measurements performed on the same crystal yielded different results each time. Measurements performed on different crystals also behaved the same way. Because the measurements did were not reproducible, it was not possible so draw conclusions from this behaviour. The compounds measured were nickel-phenylethylammonium and nickel-phenylmethyammonium.

3.2 MAGNETIC MEASUREMENTS

3.2.1 MEASUREMENT SETUP

Magnetic measurements were performed using a Quantum Design Superconducting Quantum Interference device (workings of the *SQUID* are discussed in the next subsection). To measure, a crystal was put into a gelatin capsule, using dried cotton to keep the

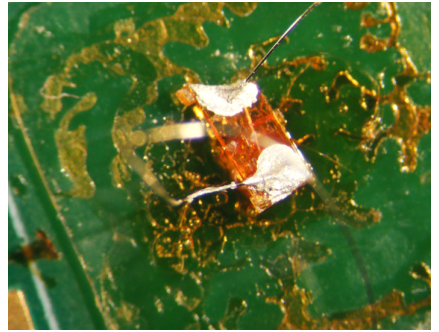


Figure 9: Nickel phenylethylammonium hybrid prepared sample under microscope. From contact to contact is approximately 1 mm. The platinum contacts are soldered to the corners of the sample holder (invisible on picture)

crystal aligned and in place. The cotton was first dried overnight in a stove at 120°C to prevent magnetic contribution of water. Holes were made in the capsule to allow the evacuation of air.



Figure 10: Sample contained within a cotton containing capsule inside a straw, next to a 20ct coin for size comparison. The sample is green because it has reacted with water.

The capsule was put into a plastic straw and fixed by making holes next to the capsule, preventing movement. Holes were made in the two ends of the plastic straw, allowing the evacuation of air. The bottom end of the straw was sealed using scotch tape to prevent the sample from falling out. The straw is homogeneous and therefore has no contribution to the change of magnetic flux.

The sample was fixed to a holder and inserted slowly into the squid. Measurements were performed under vacuum. The sample was centered with 0.5mm accuracy using a 200Oe field and subsequently cooled down to 2.5K . The measurement was started and the magnetic susceptibility versus temperature was measured over the course of eight hours.

3.2.2 SUPERCONDUCTING QUANTUM INTERFERENCE DEVICE

A superconducting quantum interference device (or *SQUID*) is a device used for measuring the magnetic moment of a sample at various temperatures and fields. Although the name of the measurement device implies that its workings are somewhat difficult, there is a very easy explanation for the workings of the device. This is only a simplified explanation however, and the true workings of the *Josephson Junction* are more difficult. For full understanding, *Introductory Solid State Physics* by Kittel[8, p. 289] provides a concise explanation.

At the heart of the *SQUID* is a superconducting loop containing a *Josephson Junction*[2]. The Josephson Junction functions as a current to voltage converter, converting induced current to a readout voltage. This superconducting loop is cooled using liquid helium to keep it superconducting. Inside the helium, there is another superconductor, a superconducting coil generating a magnetic field. This magnetic field can induce a magnetization in the inserted sample. Moving this sample through the superconducting loop will give a response, allowing the measurement of the magnetization.

The Electromotive Force given by Faraday's Law is stated as:

$$EMF = -\frac{d\Phi_B}{dt} \quad (11)$$

Because the flux inside a superconducting loop is constant, a current must flow to counteract the loop, stated by equation 4. The loops inside the *SQUID* are arranged in such a way that the total current change after moving the sample through the loops is zero.

This is achieved by first placing a clockwise loop, followed by a two counter clockwise loops, followed by another clockwise loop. The current is persistent, because the loop is a superconductor. Because the change of flux due to the applied field is zero, the sole contribution is the magnetization of the sample itself. It however is necessary to keep the applied field inside the coil as homogeneous as possible.

3.2.3 RESULTS

The general response obtained was similar in most cases. The high temperature region was fitted to a Curie-Weiss function, as for the low temperature region. The ratio of high temperature to low temperature Curie constant was 20 for the methylammonium hybrid and 5 for the ethylammonium hybrid. Other hybrids had values in between of the former mentioned. This can be explained in the following manner; the high temperature fit corresponds to all the nickel chain spins who at that temperature have enough energy to behave paramagnetically. At low temperatures, only the uncoupled spins can behave paramagnetically. This corresponds to the nickel chains in the hybrid being terminated inside the crystal. The in chain spins exhibit one dimensional magnetism, whereas the chain ends behave paramagnetically.

The average chain length can be deduced by comparing the Curie constant of high temperatures to the Curie constant at low temperatures. At low temperatures, only the paramagnetic spins have significant magnetization, which can be fitted by the Curie law. At high temperatures, the Curie constant is determined from the Curie-Weiss law. The chain length of the nickel chains is between 10 and 40, as illustrated in figure 11. The ratio of chain nickel spins to chain ending spins lies between 5 and 20 in that case. The one dimensional exchange constant differs per organic material used. The height of the one dimensional peak is regulated by the one dimensional exchange constant. In the propylammonium hybrid, there is a clear one dimensional peak, whereas in the ethylammonium hybrid, a peak is barely visible. However, the ethylammonium hybrid cannot be fitted using a Curie-Weiss function as well, suggesting that the hybrid exhibits weak one dimensional behaviour. Also, behaviour is not consistent in the propylammonium hybrid. Some crystals show strong one dimensional behaviour, while in others, one dimensional behaviour is barely visible. This means that hybrids have different behaviour from crystal to crystal. This can be explained by the proposed chain ending model (see conclusion). Since the magnetic response is dependent on the chain length[20], a different distribution will give a different response. Because the response for odd chain lengths is lower than the response for even chain lengths, more clarification is needed.

If the organic layer has the same unit length as the inorganic chain, there is no preference for chain termination. If this is not the case, there can be preferred sites for chain termination. In the ethyl based hybrid, a consistent low one dimensional response was measured. If the difference in unit length between the organic and inorganic layer is of a specific value, there can be a preference for odd numbered chains. This will give a lower response as compared to even numbered nickel chains.

The magnetic response is in this case dependent on the organic component of the hybrid. The difference in unit length between the organic and inorganic component is

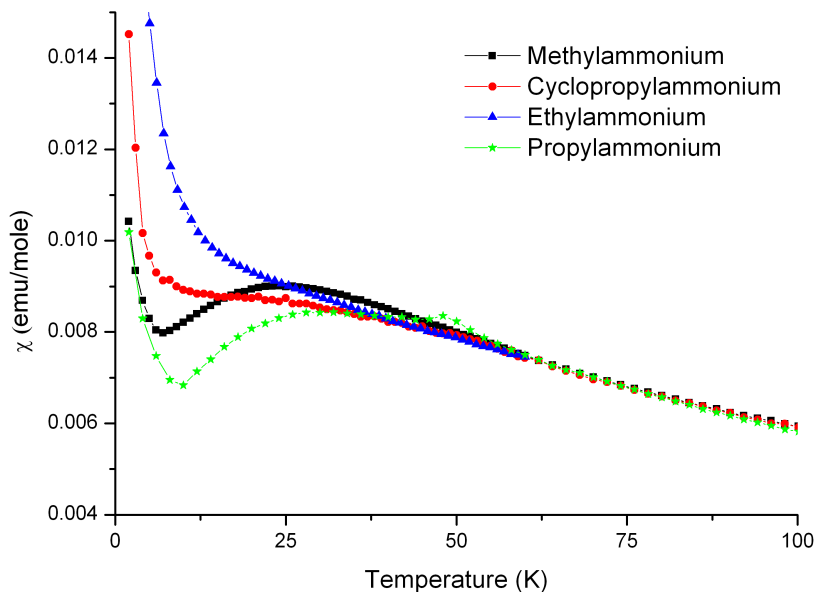


Figure 11: Dependence of magnetic response on the change of organic compound. The high to low temperature Curie constant ratio from top to bottom according to the legend is: 20, 15, 10, 5. The peak in the propylammonium hybrid is an artifact.

the key in changing the distribution of the chain lengths. However, the average chain length can possibly be changed by changing the synthesis conditions of the hybrids.

3.3 SYNTHESIS OF TEREPHTHALIMINE

To a three way flask equipped with a dropping funnel, cooler and gas inlet with capillary, 100mL of ethanol was added. The ethanol was enriched with 2% of diethyl ether, to convert any inserted water to ethanol. The gas inlet was connected to a mixture of argon and ammonia, of which the ratio could be controlled. Argon diluted ammonia was then bubbled through the ethanol for 20min to saturate the ethanol with ammonia [1].

During the saturation of ethanol, 1.86g, 14.1mmol of terephthalaldehyde was added to 90mL of enriched ethanol and added to the dropping funnel. A few drops of the solution was then added to the saturated ethanol, but no effect was visible. The mixture was then heated to the boiling point of ethanol. The addition of the solution was subsequently continued while the gas mixture flow was maintained. After addition of all the solution, the reaction mixture turned pale yellow. According to the literature [1], the final product would not dissolve in ethanol, so the reaction had not yet yielded any product.

The argon flow was then stopped and the ammonia flow was increased. The reaction mixture was left to reflux for another 80min after which the solution had become white due to a white precipitate in the mixture. The ammonia flow was stopped and the

ethanol was removed using decantation and drying in a stove at 60°C . The product was added to separate flasks, containing THF, chloroform, benzene, toluene, diethylether and benzylamine. The compound did not dissolve in any liquid. Solvation was needed to do NMR analysis.

3.3.1 ANALYSIS

Addition of hydrochloric acid to a mixture of methanol and the ending product did yield a solution, and dissolved the product. Deuterated hydrochloric acid was added to a solution of deuterated ethanol. The solvation of the product can be explained by the protonation of the compound. Prononation can occur either once or twice, on each imine group, to form a mono-imonium or di-imonium. The product was dissolved in the mixture and an NMR measurement was taken.

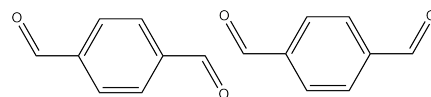


Figure 12: Cis and trans configurations of terephthalaldehyde.

The NMR spectrum was compared to a spectrum of the pure starting compound. This spectrum shows that the system adopted a cis or trans configuration, as seen in figure 3.3.1. It is also assumed that terephthalimine will also adopt two different configurations as well. The aldehyde peaks present in the spectrum of the starting compound had disappeared completely in the spectrum of the product. The rest of the peaks were hard to assign, since there were many more than can be accounted for. These peaks can be explained if the assumption of different configurations as well as different protonation amounts. If both protonation possibilities are considered (so doubly and singly protonated), as well as both cis and trans configurations, the total number of proton peaks is 26, not considering splitting. Because this vast amount of peaks are hard to assign, a different method was used to test the composition.

To purify the product further, approximately 200ml of ethanol was added to the product, and the mixture was stirred vigorously for 5hours. After stirring, the mixture was put into separate 50ml centrifuge flasks and centrifuged for 10min at 4500rpm. This caused the product to precipitate. The supernatant was decanted and the precipitate was put into a stove at 65°C to dry overnight. 40mg of product was sent for elemental analysis.

The result showed that oxygen was still present in the sample. The oxygen to nitrogen ratio was approximately one. Because no aldehyde peaks were present in the NMR spectrum, this means that a side reaction could have occurred. It is possible that the hemiaminal intermediate was still present in the sample. It is also possible that evacuation of water during the reaction was not successful, causing formation of a hemiacetal next to the formation of the desired product. This seems unlikely, because the terephthalhemiacetal is likely to dissolve in ethanol and would be removed by the purification procedure described in the preceding paragraph.

The result of the experiment still remains unknown. Suggestions for a better reaction would be the following: Because of the possible backwards reaction, care must be taken to keep any water out of the reaction, and to remove any water formed during the reaction,

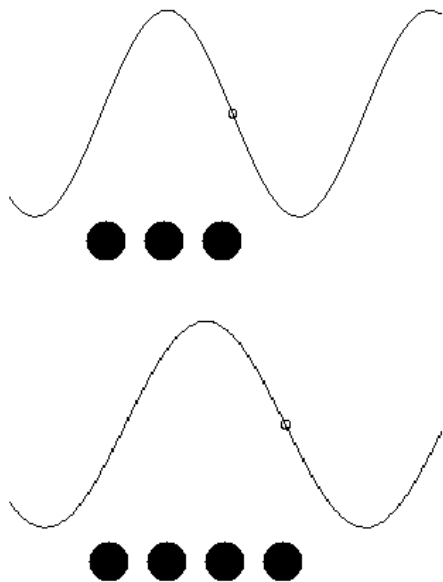
possibly by performing the reaction in diethylene glycol, at a higher temperature, above the boiling point of water. After the reaction, the product should be washed with dry ethanol to remove the ethylene glycol. Hydrochloric acid gas should then be added to protonate the compound. A hydrochloric acid solution is discouraged because this is a mixture which contains water.

4 CONCLUSION

4.1 CHAIN ENDING MODEL

In this thesis, the one dimensional behaviour of nickel based hybrids was measured. The magnetic response differs from hybrid to hybrid. The model that can explain this behaviour is the *Chain Ending Model*. The chain ending model states that nickel chains end within the crystal. The endings of the chains behave as paramagnetic impurities, whereas the nickel atoms inside the chain show one dimensional magnetism. Nickel chains of different length give a different response because of the ratio of end units to chain units. Different chain lengths were measured by comparing Curie constants at different temperatures.

The chain ends behave as though they were paramagnetic impurities and can be fitted with the Curie function. This is compared with the Curie constant at high temperatures, where all the nickel spins have enough energy to behave according to Curie-Weiss. These two constants were compared, yielding chain lengths. The ratio of Curie constants were fitted to be between 4 and 20. The proposed chain lengths are 10, 20, 30 and 40 for ethylamine, cyclopropylamine, propylamine and methylamine, respectively. Chains of different length will give a different response. Thus different distributions all summing to a total chain length of 20 will give a different one dimensional behaviour as can be seen in figure 13. The organic part of the hybrid is the key to changing the chain length distribution, which will affect the magnetic response of the hybrids. Different organic layers can have a preference to odd chain lengths or even chain lengths, creating a lower or higher response respectively. It is suggested that a periodic potential of different periodicity can be forced by organic ligands. Different organic compounds can give rise to different potential wells, each fitting different amounts of nickel complexes.



Changing synthesis conditions of the hybrids might have influence on the length distribution or on the chain length. Temperature dependence may be a large contribution. This because the thermal energy of the nickel complexes might overcome the periodic potential of the organic compound at higher temperatures. According to this theory, it is possible that when synthesized at a specific temperature—different for every hybrid—all the hybrids will converge to a single general response. At other temperatures, every hybrid will have its own distinctive response.

4.2 RESIDUAL SPIN MODEL

Another possible explanation of the measured magnetic behaviour is the *Residual Spin*

Figure 14: Different potentials can favour different chain lengths. The above potential prefers an odd number of nickel atoms per chain, whereas the lower potential will prefer an even number of nickel atoms per chain.

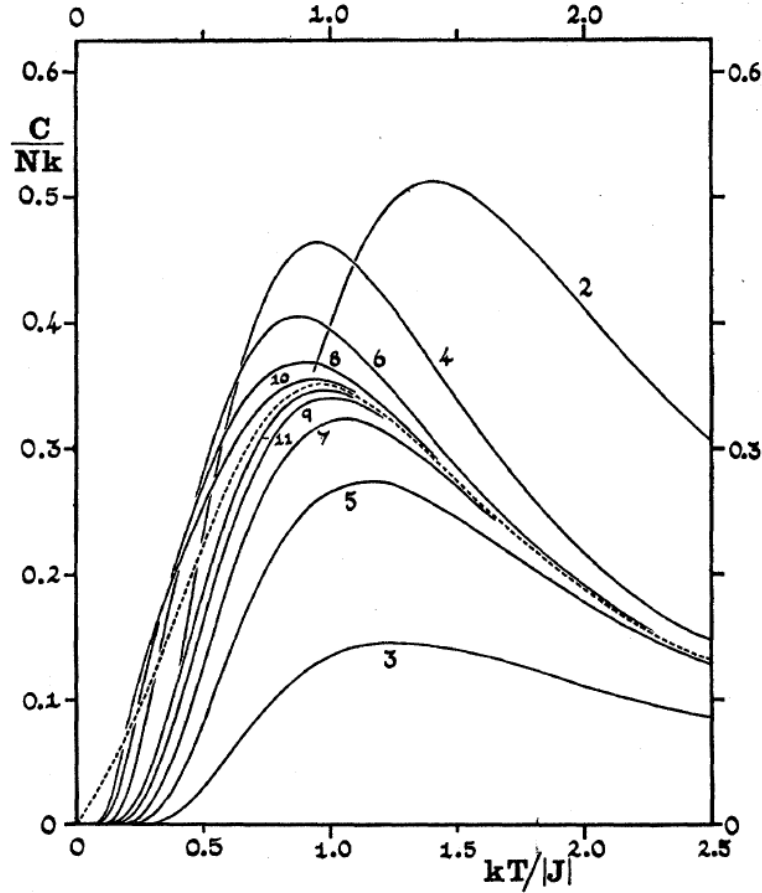


Figure 13: Variation of specific heat with temperature for antiferromagnetic Heisenberg chains. Graph by J. Bonner, M. Fisher[20].

Model. The residual spin model assumes that the susceptibility of linear open chains is the same as predicted for the circular linear systems[20]. This model states that the low temperature peak is not caused by chain endings which have unpaired spins, but by unpaired spin, inherently present in the chain. In a chain of even length, all the spins can pair, resulting in a total spin of zero, whereas a chain of odd length will have a single unpaired spin which will result into a residual spin. According to the literature, shorter odd chains will behave Curie-like, whereas even chains and very long chains exhibit one dimensional behaviour. At low temperatures, the odd chains will behave as a single system with residual spin, resulting into a Curie-like contribution to the magnetization.

Even chains will not give this Curie-like contribution because at low temperatures, all the spins are paired. Different organic ligands will favour different chain length or parity, because of the potential they cause.

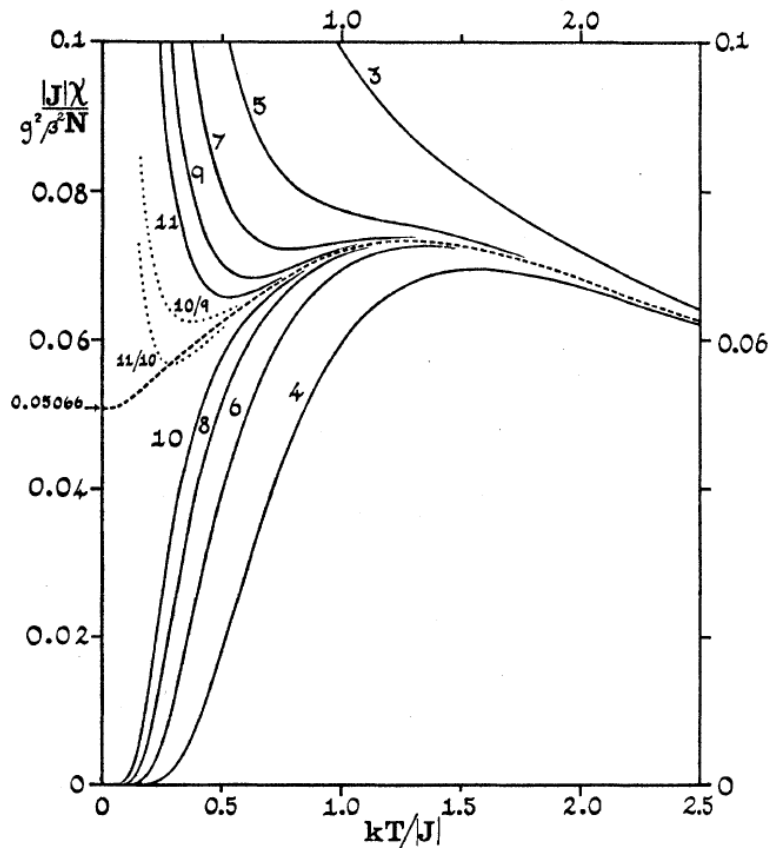


Figure 15: Susceptibility versus chain length in one dimensional ring systems. Odd rings will have a residual spin and will diverge at low temperatures.

4.3 FURTHER RESEARCH

To confirm this theory, it is necessary to synthesize hybrids at different conditions and measure the change in response. However, all the nickel based hybrids are synthesized in ethanol. Water is not usable for hybrid synthesis because this will oxidize nickel, prohibiting hybrid formation. This will not allow a very wide range of synthesis temperatures, since liquid ethanol is necessary. To synthesize hybrids at a wider temperature interval, it is necessary to use different solvents. However, this might bring along solvent effects, which will effect the synthesis of the hybrids, possibly changing the response. Another possibility of usable solvent is diethylene glycol. Diethylene glycol has a higher boiling point and thus allows for the synthesis of hybrids at a wider temperature range.

However, diethylene glycol has a high viscosity, which will also affect synthesis.

A way to test the models is by measuring the response in different directions. If the *Chain Ending Model* is correct, at low temperatures, the chain endings should behave paramagnetically. Because paramagnets are isotropic, the low temperature Curie constant should be the same in each direction.

This might also be applicable to the *Residual Spin Model*. If a chain of odd length is cooled, it might behave as a paramagnetic impurity. The behaviour of the chain might be fully paramagnetic. If this is the case, the behaviour should also be isotropic.

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A STRUCTURES

Structures were resolved using single crystal diffraction by T.W. Poortman [11].

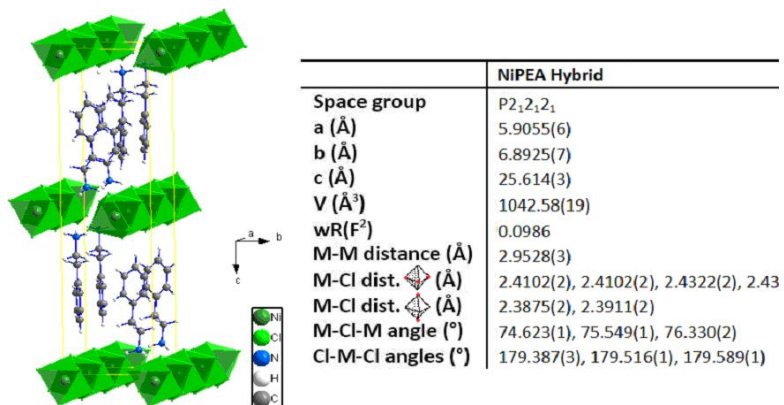


Figure 16: Nickel phenylethylammonium hybrid structure

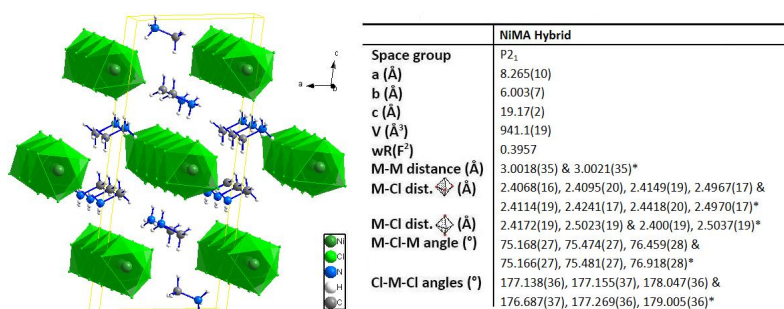


Figure 17: Nickel methylammonium hybrid structure

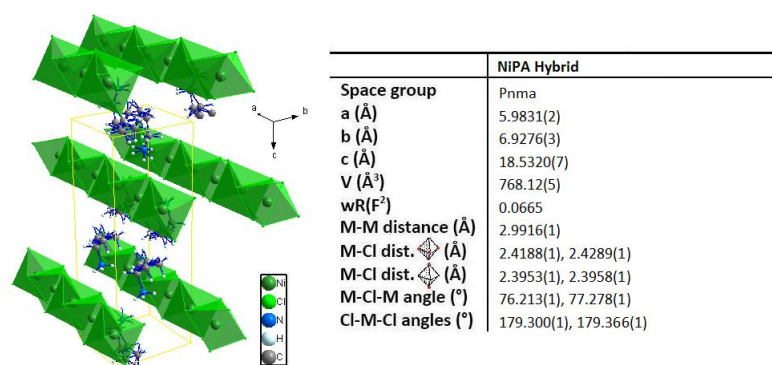


Figure 18: Nickel propylammonium hybrid structure

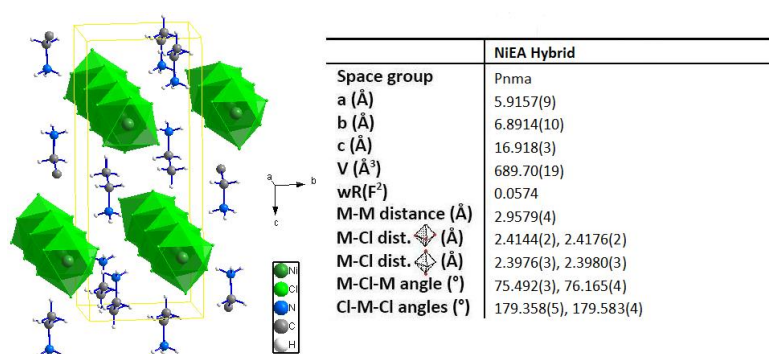


Figure 19: Nickel ethylammonium hybrid structure

B MEASUREMENT SETUP

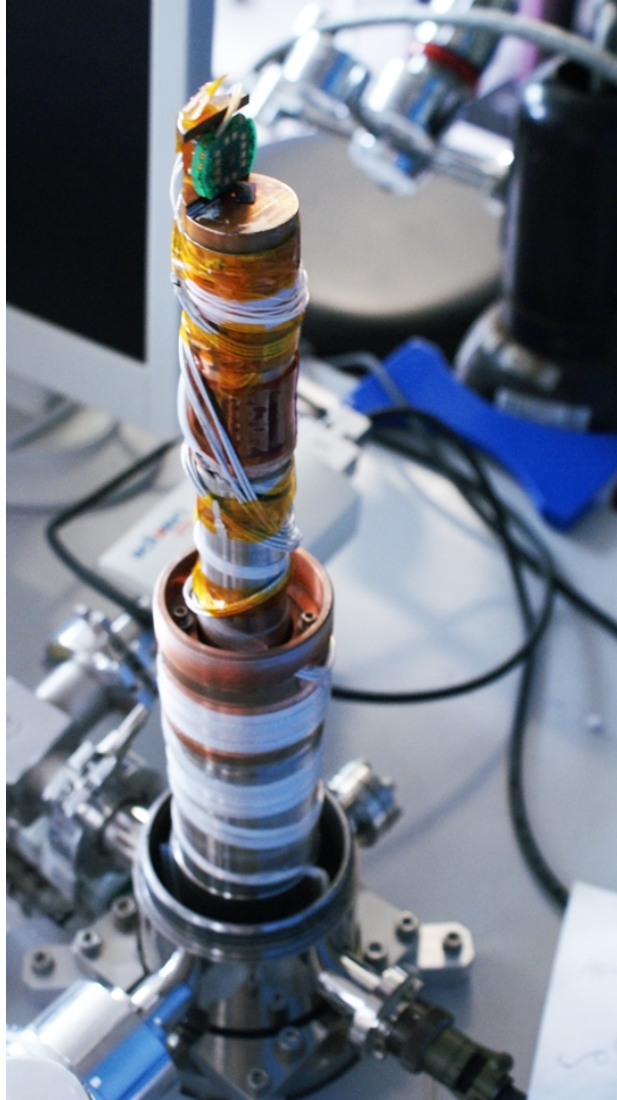


Figure 20: Advanced Research Systems CS204NE Cryostat or Coldfinger, used for measurement of capacitance. On top is the sample holder, allowing a connection between the measurement station outside of the probe station. Two temperature sensors are used to measure the temperature, one behind the sample holder and one further below. Neither is visible. The apparatus is closed using a cover that is screwed on, followed by a larger cover which is not screwed on.

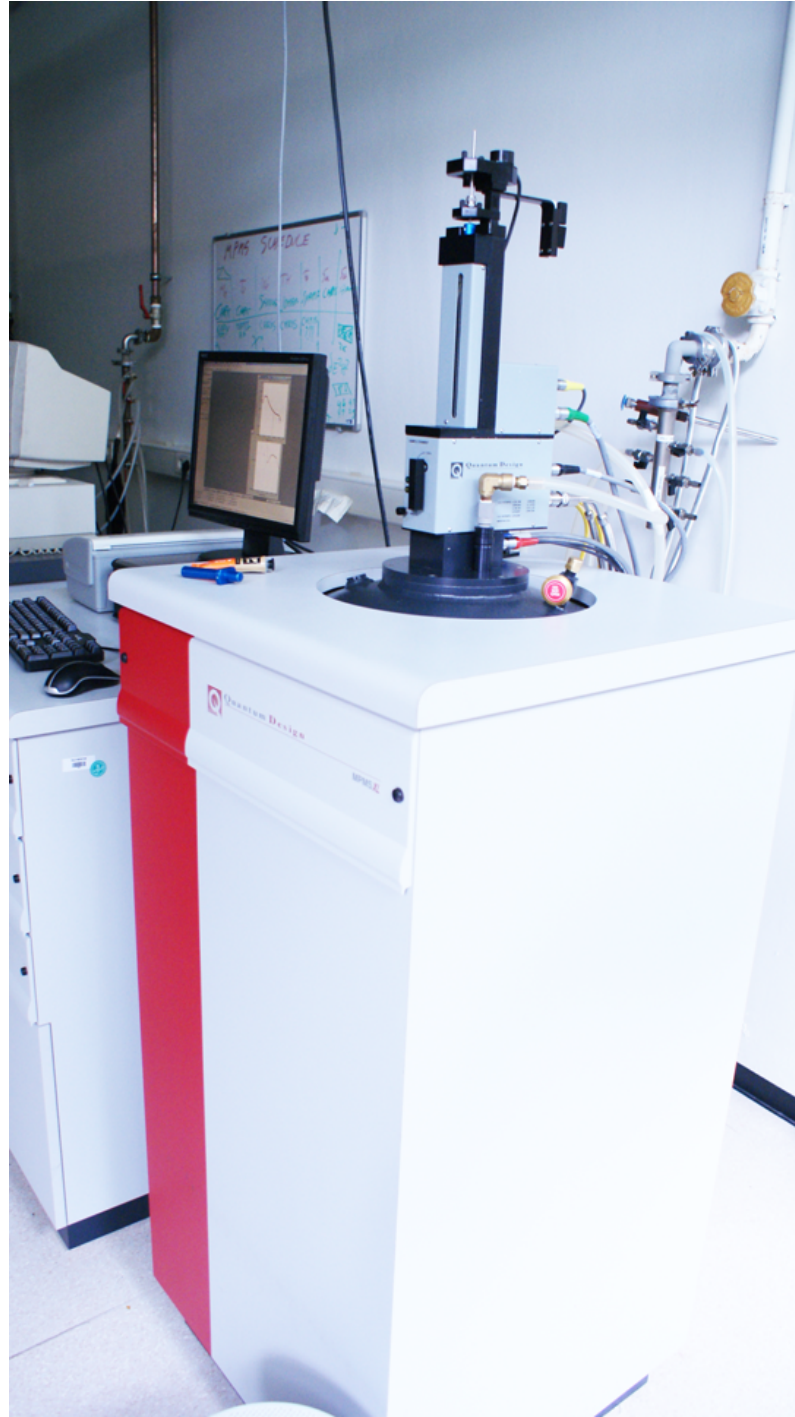


Figure 21: Quantum Design Magnetic Properties Measurement System or SQUID. The sample is introduced in the top part of the machine and lowered —through an airlock— further down into the apparatus. Measurement occurs in the heart of the device, which is isolated in the central housing.