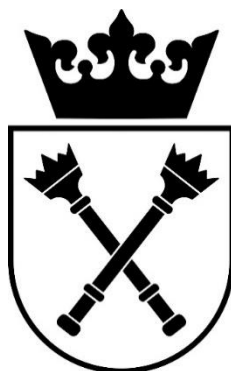


Magnetic properties of one-dimensional coordination polymers based on transition metal thiocyanates

Doctoral thesis
by

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Abstract

The magnetic properties of $M^{II}(\text{NCS})_2(\text{ligand})_2$ compounds show features characteristic for single spin chain models. The magnetic ions are connected into structural chains by NCS bridges. Apart from that, to every magnetic ion two other ligands are connected. The coordination of the bridges and ligands determines the geometry of the chain. The chains can be linear or corrugated. Between the neighboring chains, hydrogen bonds can be present.

In the framework of this thesis, there were investigated the magnetic properties of the compounds: $\text{Mn}^{II}(\text{NCS})_2(3\text{-bromopyridine})_2$, $\text{Ni}^{II}(\text{NCS})_2(3\text{-ethylpyridine})_2$, $\text{Co}^{II}(\text{NCS})_2(4\text{-(3-phenylpropyl)pyridine})_2$, $\text{Co}^{II}(\text{NCS})_2(4\text{-methoxypyridine})_2$, $\text{Co}^{II}(\text{NCS})_2(\text{aniline})_2$. These magnetic measurements are supported by thorough chemical characterization, calorimetric measurements, advanced theoretical analyses, and Monte Carlo simulations.

The Ni-based and Mn-based chains were investigated in a powder form, whereas the Co-based chains were investigated in a single crystal form. The single-ion properties are different for different magnetic ions, and they decide about the Heisenberg or Ising interaction in low temperatures. In all compounds, the intrachain exchange interaction is mediated through the NCS bridges. For Ni-based and Co-based chains, the intrachain interaction is ferromagnetic, for Mn-based chain it is antiferromagnetic. For the linear chains, the intrachain interaction is stronger than for the corrugated chains, which was assessed on the basis of the investigations of two isomers of $\text{Ni}^{II}(\text{NCS})_2(3\text{-ethylpyridine})_2$. The magnetic ordering in these systems is caused by the coexistence of magnetic interactions in the chains and between them. For the investigated systems, the ordering is observed for Ni-based and Co-based compounds, in the range from 1.3 to 6.5 K. Despite the magnetic ordering, the chain properties are observed for these systems, as the interchain interaction is significantly weaker than the intrachain interaction. The determined for Co-based compounds inter to intrachain interaction constant ratios are: 0.0032, 0.011 and 0.14 for $\text{Co}^{II}(\text{NCS})_2(4\text{-(3-phenylpropyl)pyridine})_2$, $\text{Co}^{II}(\text{NCS})_2(4\text{-methoxypyridine})_2$ and $\text{Co}^{II}(\text{NCS})_2(\text{aniline})_2$, respectively. For $\text{Co}^{II}(\text{NCS})_2(\text{aniline})_2$, the ratio is the largest and the interchain interaction are mediated within the crystallographic planes. For those reasons, the system is analyzed also within the 2D Ising model in this thesis.

The investigation of magnetic relaxations is the main purpose of this thesis. They are observed for the $\text{Co}(\text{NCS})_2(\text{ligand})_2$ chains. For the single crystals of these compounds, two relaxation processes were observed, one of which was assigned to the relaxation of single chains. The second relaxation process can be the relaxation of short fragments of chains like single molecules, a coherent rotation of 1D domains in a ferromagnetic chain or the spin waves excitations.

The single chain relaxation for all the Co-based compounds was analyzed. For $\text{Co}^{II}(\text{NCS})_2(4\text{-(3-phenylpropyl)pyridine})_2$, it was proven that the single spin relaxation, comprising on the relaxation of single chain, does not proceed according to the Orbach process. On that basis, the conventional approach to the analysis of the single chain

relaxation times was modified, and the Orbach process contribution was replaced with Raman, direct and quantum tunneling of magnetization processes. The single chain relaxation in $\text{Co}^{\text{II}}(\text{NCS})_2(4\text{-methoxypyridine})_2$ and $\text{Co}^{\text{II}}(\text{NCS})_2(\text{aniline})_2$ proceeds in the finite chains regime, as a consequence of the very long correlation length in the ordered systems.

The mechanisms of the single chain relaxation were possible to investigate thoroughly due to the access to the single crystal samples of Co-based compounds. The relaxations observed for single crystals were compared with the relaxations observed for the previously investigated powder samples. It turned out, that the relaxation processes in such quasi-one-dimensional systems are dependent on the form of the sample, it is, the length of the chains in the samples. Apart from that, for the monocrystalline samples the magnetic properties were measured along the specific directions, which enabled the experimental confirmation of the easy axis directions. The directions were known previously only from *ab initio* calculations.

Abstrakt

Własności magnetyczne związków $M^{II}(\text{NCS})_2(\text{ligand})_2$ wykazują cechy charakterystyczne dla modeli pojedynczego łańcucha spinowego. Jony magnetyczne są połączone w łańcuchy strukturalne poprzez mostki NCS. Oprócz tego, do każdego jonu magnetycznego przyłączone są dwa inne ligandy. Koordynacja mostków i ligandów determinuje geometrię łańcucha. Łańcuchy mogą być liniowe lub pofalowane. Pomiedzy sąsiednimi łańcuchami mogą być obecne wiązania wodorowe.

W ramach tej pracy, badane były własności magnetyczne związków: $\text{Mn}^{II}(\text{NCS})_2(3\text{-bromopyridine})_2$, $\text{Ni}^{II}(\text{NCS})_2(3\text{-ethylpyridine})_2$, $\text{Co}^{II}(\text{NCS})_2(4\text{-(3-phenylpropyl)pyridine})_2$, $\text{Co}^{II}(\text{NCS})_2(4\text{-methoxypyridine})_2$, $\text{Co}^{II}(\text{NCS})_2(\text{aniline})_2$. Pomiar magnetyczny są poparte dokładną charakterystyką chemiczną, pomiarami kalorymetrycznymi, zaawansowanymi analizami teoretycznymi oraz symulacjami Monte Carlo.

Łańcuchy oparte na jonach Ni i jonach Mn były badane w formie proszkowej, z kolei łańcuchy oparte na jonach Co były badane w formie pojedynczych kryształów. Własności pojedynczego jonu są różne dla różnych jonów magnetycznych i to one decydują o oddziaływaniach Heisenberga lub Isinga w niskiej temperaturze. We wszystkich związkach, wymienne oddziaływania wewnątrz-łańcuchowe są mediowane poprzez mostki NCS. Dla związków opartych na jonach Ni oraz jonach Co, oddziaływanie wewnątrz-łańcuchowe jest ferromagnetyczne, dla łańcucha opartego na jonach Mn oddziaływanie jest antyferromagnetyczne. Dla łańcuchów liniowych oddziaływanie wewnątrz-łańcuchowe jest silniejsze niż dla łańcuchów pofalowanych, co zostało ocenione na podstawie badań dla dwóch izomerów $\text{Ni}^{II}(\text{NCS})_2(3\text{-ethylpyridine})_2$. Porządkowanie magnetyczne w tych układach jest spowodowane współistnieniem oddziaływań magnetycznych w łańcuchach i pomiędzy nimi. Dla badanych układów, porządkowanie jest obserwowane dla związków opartych na jonach Ni oraz jonach Co, w zakresie od 1.3 do 6.5 K. Pomimo porządkowania magnetycznego, własności łańcuchowe są obserwowane dla tych układów, ponieważ oddziaływania między-łańcuchowe są znacząco słabsze niż oddziaływania wewnątrz-łańcuchowe. Dla łańcuchów opartych na jonie Co, stosunki stałych oddziaływań między do wewnątrz-łańcuchowych są odpowiednio: 0.0032, 0.011 i 0.14 dla $\text{Co}^{II}(\text{NCS})_2(4\text{-(3-phenylpropyl)pyridine})_2$, $\text{Co}^{II}(\text{NCS})_2(4\text{-methoxypyridine})_2$ i $\text{Co}^{II}(\text{NCS})_2(\text{aniline})_2$. Dla $\text{Co}^{II}(\text{NCS})_2(\text{aniline})_2$, ten stosunek jest najwyższy, a oddziaływania między-łańcuchowe są mediowane wewnątrz płaszczyzn krystalograficznych. Z tych powodów, w prezentowanej pracy ten układ jest analizowany również dwuwymiarowym modelem Isinga.

Badania relaksacji magnetycznych są głównym celem tej pracy. Są one obserwowane dla łańcuchów $\text{Co}(\text{NCS})_2(\text{ligand})_2$. Dla monokryształów tych związków, dwa procesy relaksacyjne zostały zaobserwowane, jeden z nich został przypisany do relaksacji pojedynczych łańcuchów. Drugim procesem relaksacji może być relaksacja krótkich

fragmentów łańcuchów jak pojedynczych molekuł, koherentna rotacja domen 1D w ferromagnetycznym łańcuchu lub wzbudzenia fal spinowych.

Relaksacje pojedynczych łańcuchów dla związków opartych na jonie Co zostały zanalizowane. Dla $\text{Co}^{\text{II}}(\text{NCS})_2(4-(3\text{-phenylpropyl})\text{pyridine})_2$, zostało udowodnione, że relaksacja pojedynczych spinów, składająca się na relaksację pojedynczego łańcucha, nie zachodzi według procesu Orbacha. Na tej podstawie, metoda konwencjonalna analizy czasów relaksacji pojedynczego łańcucha została zmodyfikowana i wkład procesu Orbacha został zastąpiony procesami Ramana, bezpośrednim oraz kwantowym tunelowaniem magnetyzacji. Relaksacja pojedynczego łańcucha w $\text{Co}^{\text{II}}(\text{NCS})_2(4\text{-methoxypyridine})_2$ i $\text{Co}^{\text{II}}(\text{NCS})_2(\text{aniline})_2$, zachodzi w reżimie skończonych łańcuchów, co jest konsekwencją bardzo długiej długości korelacji w układach uporządkowanych.

Mechanizmy relaksacji pojedynczych łańcuchów były możliwe do zbadania dokładnie, dzięki dostępowi do próbek monokrystalicznych związków opartych na jonie Co. Relaksacje obserwowane dla monokryształów zostały porównane z relaksacjami obserwowanymi dla uprzednio badanych próbek proszkowych. Okazało się, że procesy relaksacyjne w takich kwazi-jednowymiarowych układach są zależne od formy próbki, to jest, od długości łańcuchów w próbkach. Oprócz tego, dla próbek monokrystalicznych właściwości magnetyczne zostały zmierzone dla konkretnych kierunków, co umożliwiło eksperymentalne potwierdzenie kierunków osi łatwej. Wcześniej, te kierunki były znane tylko z obliczeń *ab initio*.

Table of contents

The purposes of the thesis	13
1. Introduction.....	14
1.1. Basics of magnetism	14
1.2. Molecular magnets	19
1.3. Magnetic relaxation in molecular systems	22
1.4. $M^{II}(NCS)_2(Ligand)_2$ family of compounds	26
1.5. Chain models.....	29
1.5.1. $Mn^{II}(NCS)_2(ligand)_2$ chains	29
1.5.2. $Ni^{II}(NCS)_2(ligand)_2$ chains	29
1.5.3. $Co^{II}(NCS)_2(ligand)_2$ chains	30
2. Research methods.....	32
2.1. Syntheses	32
2.2. Chemical characterization methods	32
2.3. SQUID Magnetometry.....	34
2.3.1. MPMS QD 5XL magnetometer	34
2.3.2. Samples preparation for measurements.....	38
2.3.3. Recalculation of the measured values and units	39
2.3.4. Diamagnetic corrections.....	39
2.3.5. Demagnetization	40
2.3.6. Relaxation time determination	41
2.4. Calorimetry	41
2.4.1. Physical Properties Measurement System	41
2.4.2. Samples preparation for measurements.....	46
2.4.3. Recalculation of the measured values and units	46
2.5. Algorithms and Libraries for Physical Simulations (ALPS)	46
3. Magnetic properties of $Mn^{II}(NCS)_2(3\text{-bromopyridine})_2$	48
3.1. Synthesis	48
3.2. Crystal structure.....	48
3.3. Magnetic properties	49
3.4. Summary	52

4.	Magnetic properties of $\text{Ni}^{\text{II}}(\text{NCS})_2(3\text{-ethylpyridine})_2$	53
4.1.	Syntheses	53
4.2.	Crystal structure	54
4.3.	Magnetic properties	57
4.4.	Summary	61
5.	Magnetic properties of $\text{Co}^{\text{II}}(\text{NCS})_2(\text{ligand})_2$ compounds	62
5.1.	Magnetic properties of $\text{Co}^{\text{II}}(\text{NCS})_2(4\text{-}(3\text{-phenylpropyl})\text{pyridine})_2$	62
5.1.1.	Synthesis	62
5.1.2.	Crystal structure	63
5.1.3.	Specific heat	65
5.1.4.	Magnetization curves	66
5.1.5.	Easy axis determination	67
5.1.6.	Magnetic susceptibility	68
5.1.7.	Magnetic relaxation	70
5.1.8.	Summary	81
5.2.	Magnetic properties of $\text{Co}^{\text{II}}(\text{NCS})_2(4\text{-methoxypyridine})_2$	82
5.2.1.	Synthesis	82
5.2.2.	Crystal structure	83
5.2.3.	Magnetization curves	86
5.2.4.	Specific heat	87
5.2.5.	Easy axis determination	89
5.2.6.	Magnetic susceptibility	90
5.2.7.	Magnetic relaxation	93
5.2.8.	Summary	106
5.3.	Magnetic properties of $\text{Co}^{\text{II}}(\text{NCS})_2(\text{aniline})_2$	107
5.3.1.	Synthesis	108
5.3.2.	Crystal structure	108
5.3.3.	Magnetization curves	111
5.3.4.	Specific heat	116
5.3.5.	Phase diagram	122
5.3.6.	Easy axis determination	123

5.3.7. Magnetic susceptibility.....	124
5.3.8. Magnetic relaxation.....	127
5.3.9. Summary.....	139
6. Realization of the thesis purposes	140
References	145

The purposes of the thesis

Molecular magnets are organic-inorganic hybrid systems, that can become in the future an alternative for the conventional magnetic materials in many applications, e.g. magnetic memory and high-density data storage.[1, 2] They are also considered potential materials for drug delivery systems [3] or qubits based on the single spin [4]. So far, the materials with the best performance for magnetic memory are materials displaying slow magnetic relaxation, e.g. Single Molecule Magnets based on lanthanides.[5-7] The magnetic behavior of Single Molecule Magnets is relatively easy to describe, apart from that, the lanthanides can display a high magnetic anisotropy.[8] As other candidates, there are considered structurally more complicated systems, such as chain molecular magnets. The slowing down of the dynamics of the spin chains was predicted in 1963 by Glauber.[9] The first experimental evidence of such a compound was delivered in 2002.[10] In the next years, many others were discovered.[11] Also, the magnetic chain behavior was observed for the ordered systems.[12] Currently, a lot of attention is given to the strategies of synthesis of such compounds and the impact of the crystal structure on their magnetic properties.[13] The magnetic behavior of spin chain compounds is complex and they can display some unique properties, not observed for Single Molecule Magnets. Nevertheless, the chain magnets display the most desirable effects in very low temperatures, usually below 10 K.[14] Therefore, their application in the industry is for now impossible. However, thorough investigations of such compounds can prove to be very useful – they can provide a lot of information, on how to design other compounds with the expected features or without the disturbing effects.

The subject of this thesis are the magnetic properties of molecular chain compounds with the general formula $M^{II}(NCS)_2(\text{ligand})_2$ ($M^{II} = Co^{II}, Ni^{II}, Mn^{II}$). Most of the compounds from this family are quasi-one-dimensional systems. They order magnetically which suggests that apart from the intrachain interaction, the weak interchain interaction is present. The main purposes of the thesis are:

- ❖ Development of the synthesis' method of large single crystals of $Co^{II}(NCS)_2(\text{ligand})_2$ for magnetic measurements.
- ❖ Determination of the influence of the crystal structure of the compounds and the electronic structure of the transition metal ions on the magnetic behavior of $M^{II}(NCS)_2(\text{ligand})_2$ spin chains.
- ❖ Investigations of the relaxation mechanisms in $Co^{II}(NCS)_2(\text{ligand})_2$ chains.

These purposes have been achieved by performing extensive magnetic investigations of the $M^{II}(NCS)_2(\text{ligand})_2$ compounds. These investigations are supported by thorough chemical characterization, calorimetric measurements, advanced theoretical analyses, and Monte Carlo simulations.

1. Introduction

In this chapter, there will be presented the most important aspects of molecular magnetism, necessary to understand the issues of this thesis, it is: the basics of magnetism, a description of molecular magnets, the theory of relaxation in low-dimensional molecular magnets, an overview of the $M^{II}(NCS)_2(\text{ligand})_2$ family of compounds and the models which are used in this thesis to describe the magnetic behavior of the studied systems.

1.1. Basics of magnetism

The magnetic response of an atom originates from two sources: spin of the electron, s , (the intrinsic angular momentum of the electron, the spinning of the electron around its own axis) and orbital angular momentum, l , (the movement of the electron around the nuclei). The magnetic moment of the electron is:

$$\mu_e = -\mu_B(l + gs), \quad (1.1.1)$$

where μ_B is Bohr magneton, the magnetic moment of an electron on the orbit, g is the factor, equal to 2.0023 for a free electron. The magnetic moment of the nuclei is not considered in this thesis. For a free ion, the total angular momentum is $J = L + S$ and the magnetic moment can be expressed (spin-orbit coupling not included) [15]:

$$\mu = \mu_B \sqrt{L(L+1) + 4S(S+1)}, \quad (1.1.2)$$

where L is the total orbital angular momentum of the ion, S is the total spin of the free ion. The magnetic moment can take other values, for example, the orbital angular momentum can be quenched, and spin-only magnetism will be observed. However, not necessarily the observed magnetic moment will correspond to the S value resulting from the ion electron configuration. It is because the energy levels among the subshell can split (e.g., for subshell d , it can split to t_{2g} and e_g), the unpaired electrons can pair and therefore the *effective spin* can be lower.

The total magnetic moment of the specific amount of material is called **magnetization**, M . [16] The basic unit is emu (electromagnetic unit, 1 emu = 1 erg/Gauss), per mole or mass unit. If M is proportional to the applied magnetic field, it makes sense to use **magnetic susceptibility**, χ , [15] which is the magnetization over the magnetic field strength, H :

$$\chi = \frac{M}{H}. \quad (1.1.3)$$

It can also be expressed per mole, volume, or mass unit. The magnetic field strength is related to the **magnetic induction**, B , [16] by the following equation:

$$B = H + 4\pi M = (1 + 4\pi\chi)H. \quad (1.1.4)$$

The temperature dependence of magnetic susceptibility is different for different types of magnetic materials.

Diamagnetism [15] is a result of the interaction of the paired electrons with the external magnetic field and has contribution to the magnetic susceptibility of every material in which the paired electrons are present. A purely diamagnetic material is composed of atoms or ions with only paired electrons. Diamagnetic material put in the magnetic field repels the magnetic field, it is, the density of the magnetic field strength lines is lower inside the material than outside the material. It is the same as the creation of the magnetic field opposite to the external magnetic field, therefore, the diamagnetic susceptibility is negative. It is also temperature independent and relatively small in comparison with the paramagnetic susceptibility, however, to obtain an accurate value of the paramagnetic susceptibility of the material, the diamagnetic contribution has to be estimated and subtracted from the measured susceptibility of the material. The estimation is easy to perform, as the diamagnetic susceptibilities of individual atoms, ions, bonds, etc., can be added to obtain the diamagnetic susceptibility of the whole compound. To do that, the so-called Pascal constants are used.[17] Only for superconductors the diamagnetic signal is large, but such behavior is usually absent in molecular magnets.

Paramagnetism [15] comes from the interaction of the unpaired electrons in atoms or ions with the external magnetic field. The lines of the magnetic field are denser inside paramagnetic material than outside of it. Contrary to the diamagnetic susceptibility, the paramagnetic susceptibility is positive and depends on the temperature, which describes the **Curie Law** [15]:

$$\chi = \frac{C}{T} = \frac{N_A g^2 \mu_B^2 S(S+1)}{3k_B T} = \frac{N_A \mu_{eff}^2}{3k_B T}, \quad (1.1.5)$$

where C is the Curie constant, N_A is the Avogadro number, k_B is the Boltzmann constant. The Curie constant can be expressed by the effective moment, μ_{eff} . This law is satisfied only for compounds, in which the magnetic centers do not interact with each other, and the magnetism originates only from spin, it is, the orbital magnetic moment is quenched or $L = 0$. If there is a magnetic interaction between the paramagnetic ions, the high-temperature magnetic susceptibility can be approximated by the **Curie-Weiss law** [15]:

$$\chi = \frac{C}{T - \theta}, \quad (1.1.6)$$

where θ is the Curie-Weiss temperature, which value indicates the type of interaction: for *negative* value, the interaction is antiferromagnetic, for *positive*, ferromagnetic.

In some cases, the material with all electrons paired can display some weak paramagnetic properties. This is caused by the mixing of the wave functions of the ground and not thermally populated excited states and is called temperature-independent paramagnetism (TIP).[15] The values of TIP susceptibility are positive and larger than the absolute value of diamagnetic susceptibility, however, similarly to diamagnetic susceptibility, it is not important at low temperature.

The total spin of an atom/ion is $S = n/2$, where n is the number of unpaired electrons. In the simplest scenario, the energy levels are $(2S+1)$ times **degenerated**, it is, there are $(2S+1)$ states with the same energy. This can be also orbitally degenerated. The degeneracy

may be removed by several factors, even in absence of magnetic field. One of them is the ligand field, and the effect is called Zero Field Splitting (ZFS).

Zero Field Splitting is an effect which partially creates the magnetic anisotropy of single ion.[2, 15] It is the result of the electrostatic field of the ligands surrounding the magnetic ion. The magnetic ion is positively charged, and it is attracted to the negatively charged ligands. However, the unpaired electrons of magnetic center also repel the electrons of ligands that do not participate in the creation of bonds. As the shapes of the orbitals are different depending on the subshell, the repulsion energy will be different, therefore, the degeneracy can be removed. It is fully removed for ions with even number of electrons on the unfilled shell (non-Kramers ions). It is partially removed for Kramers ions, which are the ions with odd number of electrons on the unfilled shell. For such ions, the energy levels are split into doublets. It means that there is still degeneracy for $+|m_s|$ and $-|m_s|$ states. To describe the anisotropy in the axial crystal field, there is used the second-order axial anisotropy parameter, D . If $D > 0$, the $|m_s|$ states with lowest values have the lowest energy, if $D < 0$, on the contrary. When the crystal field is not purely axial, i.e., there is rhombic contribution, the second-order rhombic anisotropy parameter, E , is also used. When both D and E are zero, the crystal field has cubic symmetry, and the energy levels are all degenerated. The crystal field Hamiltonian is:

$$\mathcal{H}_{CF} = D \left[S_z^2 - \frac{1}{3}S(S+1) \right] + E(S_x^2 - S_y^2). \quad (1.1.7)$$

Any remaining degeneracy can be further removed by applying the external magnetic field and this is called the **Zeeman effect**. [15] The Hamiltonian is:

$$\mathcal{H}_Z = \mu_B \mathbf{H} \hat{\mathbf{S}}. \quad (1.1.8)$$

However, the splitting of the energy level can be significantly different for different direction of this applied field, which is the manifestation of the magnetic anisotropy of the g -tensor. For relatively not complicated cases of single ions, the susceptibility can be approximated with solution of the Van Vleck's equation, where there are distinguished the parallel (for easy axis) and perpendicular (for hard axes) susceptibilities.

Spin-Orbit Coupling (SOC) is an interaction between the spin and orbital momenta.[2] The energy of SOC interaction is defined by the Hamiltonian:

$$\mathcal{H} = \lambda \mathbf{L} \cdot \mathbf{S}, \quad (1.1.9)$$

where λ is a constant, which takes the negative value if the shell of the ion with the unpaired energies is more than half full, and positive otherwise. SOC is only of little importance for ions with half-filled shells and light elements. This effect is especially important for example for lanthanides. SOC acts as a factor assisting the crystal field to split the energy level in zero magnetic field. The SOC effect is of low importance for Mn^{II} , medium importance for Co^{II} and great importance for Ni^{II} . [15]

Magnetic interactions can occur between the paramagnetic ions under different conditions. Magnetic centers are magnetic dipoles and they can interact directly through **magnetic dipole-dipole interaction**. [15] This interaction strongly depends on the distance between the magnetic centers and orientation of them to each other. It is important only

at the low temperature and is not enough to cause the spontaneous ordering at the high temperature.

The other type of interaction is the **exchange**.^[18] It occurs, when the magnetic centers are so close to each other that their orbitals overlap, it is, the wave functions of the electrons overlap. Considering two electrons, the linear combination of their wave functions is symmetric ($S = 1$, triplet state) or antisymmetric ($S = 0$, singlet state). The difference of the energies of these states defines the exchange constant, J :

$$J = \frac{E_S - E_T}{2}, \quad (1.1.10)$$

where E means energy, index S stands for singlet and index T stands for triplet. The effective Hamiltonian for the two electrons is therefore:

$$\mathcal{H}_{2e} = -2J\mathbf{s}_1 \cdot \mathbf{s}_2. \quad (1.1.11)$$

For many electrons, it converts into:

$$\mathcal{H} = -\sum_{ij} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j, \quad (1.1.12)$$

which is a Heisenberg Hamiltonian taking into consideration the exchange between every pair of spins in the system, where J_{ij} is the exchange constant between the i -th and j -th spins. Factor 2 disappears, to avoid doubling the same interaction (it is counted from the point of view of every electron). Therefore, if the energy of the singlet state is lower than the energy of the triplet state, the spins tend to align antiparallely, J is negative, and the interaction is called **antiferromagnetic**. In case when the triplet state has lower energy, spins align parallelly, J is positive, and the interaction is called **ferromagnetic**. The exchange interaction can be direct or indirect.^[18] **Direct exchange** is when the orbitals of the neighboring magnetic ions or atoms directly overlap. The **indirect exchange** is when the magnetic centers in a conducting material are not close enough to each other for the orbitals to overlap and the conducting electrons are an interaction medium. A conduction electron can be spin-polarized by the neighboring magnetic moment. Then, this electron can couple to the other magnetic moment. This interaction is called **RKKY interaction**, from the last names of their discoverers: Ruderman, Kittel, Kasuya, and Yosida.^[19-21] The J constant is proportional as:

$$J_{RKKY} \propto \frac{\cos(2k_F r)}{r^3}, \quad (1.1.13)$$

where r is the distance between the electron and the magnetic ion, k_F is the radius of the Fermi surface. The oscillatory character of the J constant decides the type of interaction. The sign convention is the same as above.

However, there are many magnetic materials, which are comprised not only of the magnetic centers. In this case, the exchange is also not direct. It is mediated by the non-magnetic ions, and the interaction is called **superexchange**.^[18] It originates from the mixing of the excited states. There are defined rules which allow determining the type of the superexchange interaction which are called the Goodenough–Kanamori–Anderson rules.^[22] In literature (and also in this thesis), superexchange is called simply **exchange**.

In a ferromagnet, spins are ordered parallelly. A system is in the ferromagnetic state only below the critical temperature, T_C . For ferromagnets, magnetic hysteresis is observed.

Antiferromagnet is comprised of spins ordered antiparallely, and for that reason, the magnetic moment cancels. The antiferromagnetic state is below the Nèel temperature, T_N , and below the critical field, H_c . The single molecule/ion magnets and the model spin chains do not order.

In the systems ordered ferromagnetically due to the exchange and dipole-dipole interactions, the **magnetic domains** are present.[15] The magnetic domains occurs to lower the total energy of the system. The borders of the domains are called the **domain walls**. In the one-dimensional systems, the domain walls are also present but not in three dimensions but in one. Such domain wall can be sharp (comprised of 2 spins only), and broad (comprised of more than 2 spins).[23]

Specific heat (C) is a very important physical quantity related to magnetic properties.[24] The general definition states that the specific heat is the amount of energy that is needed to make the temperature of the compound larger by one Kelvin. Anomalies in specific heat measurements can show if the compound orders magnetically. The basic contribution to the specific heat of the sample is the specific heat of the lattice, which originates from the vibrations of the crystal lattice.[15] The vibrations of the lattice are called phonons and can be treated both as a (quasi)particle and a wave.[25] From the experimental investigations, it is known that at high temperature, the specific heat of the inorganic solid materials is close to $3Nk_B$. In turn, in the low temperature, the specific heat decreases significantly with decreasing temperature, for insulators $C \propto 1/T^3$. To calculate the specific heat, it is assumed that the phonons are independent, and their energy depends on the frequency of the vibrations and the number of phonons. There are two main models which can be used to describe the lattice contribution: Einstein model and Debye model. The number of phonons ($\langle n \rangle$) in the thermal equilibrium is expressed with the Bose-Einstein distribution. The averaged energy for N oscillators with the same resonance frequency is:

$$E = 3N \langle n \rangle \hbar\omega. \quad (1.1.14)$$

where 3 comes from the 3 degrees of freedom for every atom. The specific heat in constant volume according to the **Einstein model** is then [24]:

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3Nk_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{\left(\frac{\hbar\omega}{k_B T} \right)}}{\left(e^{\left(\frac{\hbar\omega}{k_B T} \right)} - 1 \right)^2}, \quad (1.1.15)$$

In this approximation, it is assumed that all the phonons have the same frequency. In the **Debye model**, the oscillators with different frequencies are taken into consideration.[24] The energy is defined:

$$E = \int \mathcal{D}(\omega) \langle n(\omega, T) \rangle \hbar\omega d\omega, \quad (1.1.16)$$

where $\mathcal{D}(\omega)$ is the density of states. In the three-dimensional model it is equal to:

$$\mathcal{D}(\omega) = \frac{\omega^3 L^3}{2\pi^2 v^3}, \quad (1.1.17)$$

where $\left(\frac{L}{2\pi} \right)^3$ is the volume of the considered space and v is the group velocity of the phonons, which is assumed constant in the Debye approximation. Putting the density of

states and the average number of phonons into the energy equation and then differentiating the energy over temperature, the specific heat in the Debye model is:

$$C_V = 9Nk_B \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (1.1.18)$$

where θ_D is the Debye temperature characteristic for the substance.

The total specific heat of the magnetic material, apart from the lattice contribution, has also a magnetic contribution. To obtain it, from the total specific heat the lattice contribution has to be subtracted. For estimation of the lattice contribution at low temperatures, the individual Debye or Einstein models or the linear combination of the Debye and Einstein model can be used:

$$C_{lattice} = a_E C_{Einstein} + a_D C_{Debye}, \quad (1.1.19)$$

where a_E and a_D are the dimensionless amplitudes of the contributing specific heats. Such an approach includes the acoustic and the lowest branch of optical phonons.

Having the temperature dependence of the magnetic contribution to the specific heat, there are exposed all the anomalies providing much useful information. The most important is the information about the magnetic ordering manifested as a narrow maximum. Another effect possible to observe is the Schottky anomaly, which is the manifestation of the ZFS effect as a broad maximum. Finally, the exchange interaction, even in the absence of magnetic ordering, also leads to a broad maximum. The last case can be most clearly observed for isolated magnetic molecules and one-dimensional systems.

1.2. Molecular magnets

Molecular magnets are a class of magnetic compounds which are comprised of organic or organic and inorganic components.[2] In purely organic materials, the unpaired electrons come from the radicals, in the inorganic-organic systems – from the magnetic ions. They can be divided into two groups: molecular magnets which display magnetic relaxation and molecular magnets which do not display magnetic relaxation. Both groups can be also divided considering their dimensionality. In this thesis, there are concerned only the magnets with magnetic ions, therefore, the following discussion is conducted only for such molecular systems.

Molecular magnets are a relatively young topic of materials research, in comparison with conventional magnets. For example, magnetite was discovered in ancient times, whereas the first reports regarding molecular magnets comes from the beginning of the 20th century.[26, 27] The variety of molecular magnets is incredible. This is mostly due to the strong development of synthesis methods in recent years. The multifunctionality of molecular magnets is a feature that makes them materials with many possible applications, both as a replacement for conventional magnets and in new inventions. The multifunctionality, e.g. memory effect and optical transparency in one compound, can be achieved by the rational design of these systems using the so-called **building block**

approach.[28] In this approach, at the beginning the properties of the designed system are determined, then, the proper components to build it have to be chosen: the magnetic centers and their surroundings. After that, the compound has to be synthesized and at the end, the magnetic properties of the compounds should be measured, to find out if the expected properties were obtained. The building blocks have to be selected very carefully from the chemical point of view because not all of the blocks tend to join to the selected magnetic center. Usually, the connection is made by the directional bonds, like coordination bonds, or weaker, supramolecular interactions. The directionality of the bond is very important when in a compound the magnetic interactions between magnetic centers are expected. Therefore, all the above comes down to finding a proper way to synthesize the designed compound. Below, there are presented examples of molecular magnets based on transition

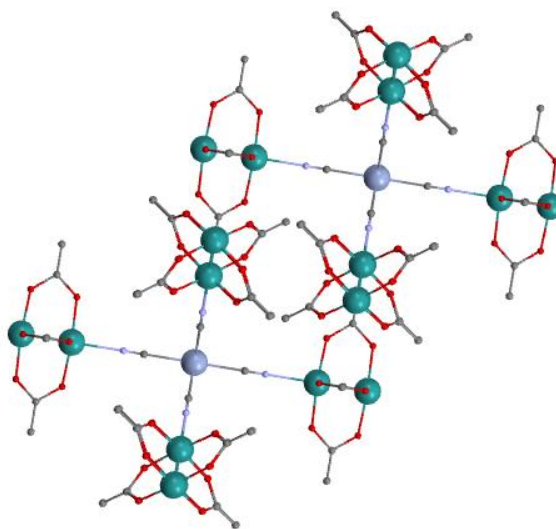


Figure 1.2.1 A fragment of the crystal structure of $[\text{Ru}^{\text{II/III}}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}^{\text{III}}(\text{CN})_6]$. View along crystallographic axis a . CCDC: 234876. (Ru – green, Cr – grey-blue, O – red, C – grey, N – light blue, H – omitted)

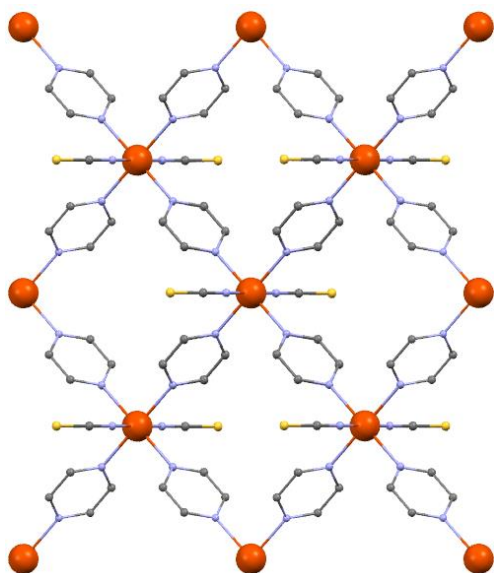


Figure 1.2.2 A fragment of a crystal structure of $\text{Fe}(\text{NCS})_2(\text{pyrazine})_2$. View along c axis, on the planes. CCDC: 1261052. (Fe – orange, C – grey, S – yellow, N – light blue, H – omitted)

metals, regarding their dimensionality. There are shortly discussed the aspects of their structures which have an impact on the magnetic properties.

3D molecular magnets are the compounds in which the magnetic centers are linked through non-magnetic organic/inorganic bridges into 3D networks. The compounds order magnetically. The example of such magnets are compounds with the general formula $[\text{Ru}^{\text{II/III}}_2(\text{O}_2\text{CMe})_4]_3[\text{Cr}^{\text{III}}(\text{CN})_6]$. [29] The compound crystallizes in $Im\bar{3}m$ space group. The magnetic exchange interactions are mediated along a , b and c crystallographic directions between Me^{III} and $\text{Ru}^{\text{II/III}}$ through the CN bridges (Figure 1.2.1). In a , b and c directions the interactions are the same due to the fact that this is a cubic crystal structure. The critical temperature is 33 K. Other example are the family of Prussian-blue analogues, some of them having critical temperatures close to 300 K. [30]

2D molecular magnets are the compounds in which the exchange magnetic interactions are present only in two dimensions, creating magnetic planes. An example of such plane is $\text{Fe}(\text{NCS})_2(\text{pyrazine})_2$. [31] The exchange interaction is mediated through the pyrazine ligands (Figure 1.2.2). The ordering is observed at 6.6 K.

1D molecular magnets are compounds in which the magnetic interactions are present only in one dimension. If such chain compound displays the slow magnetic relaxation, it is called **Single Chain Magnet (SCM)**. An example is $[\text{Co}(\text{hfac})_2\text{NaphNN}]_n$. [32] It is a very unique compound, as the blocking temperature (temperature below which the magnetic relaxation is observed) is very high as for a Co-based chain system: 13.2 K. The magnetic interaction is mediated through N-O-O-N bridges (Figure 1.2.3), there is no interaction between the chains and therefore no magnetic ordering is observed.

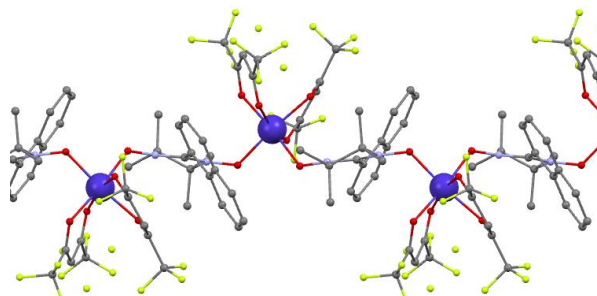


Figure 1.2.3 A fragment of a crystal structure of $[\text{Co}(\text{hfac})_2\text{NaphNN}]_n$. View along a axis, on the chain. CCDC: 1406569. (Co – blue, C – grey, N – light blue, O – red, F – light yellow, H – omitted)

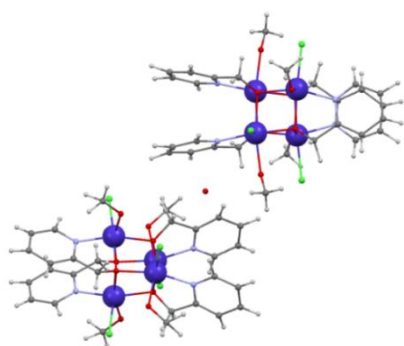


Figure 1.2.4 A crystal structure of $[\text{Co}_4(\text{hmp})_4(\text{MeOH})_4\text{Cl}_4]$. View along b axis. CCDC: 703422. (Co – blue, C – grey, N – light blue, O – red, Cl – green, H – omitted)

0D molecular magnets can be divided into two groups of compounds based on single molecules: with many magnetic ions and with one magnetic ion. If these compounds display magnetic relaxation, they are called **Single Molecule Magnets (SMM)** and **Single Ion Magnets (SIM)**, respectively. These compounds are of special interest, as they are the smallest molecular systems and for that reason are expected to be applied in the future in high-density data storage. [33-35] An example of SMM is $[\text{Co}_4(\text{hmp})_4(\text{MeOH})_4\text{Cl}_4]$ system. [36] The total spin of the molecule is 6, there is no interaction between the molecules and inside the molecules between Co ions (Figure 1.2.4). An example of SIM is $[\text{Mn}(\text{3-OEt-salme})_2]\text{BPh}_4$. [37] The single molecules do not interact with each other due to well-extended organic ligands (Figure 1.2.5).

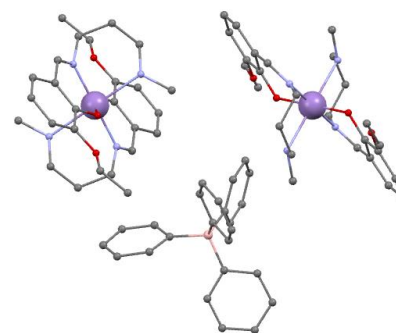


Figure 1.2.5 A crystal structure of $[\text{Mn}(\text{3-OEt-salme})_2]\text{BPh}_4$. View along a axis. CCDC: 1451873. (Mn – purple, C – grey, N – light blue, O – red, B – beige, H – omitted)

1.3. Magnetic relaxation in molecular systems

The slow magnetic relaxation is an effect observed for some of the molecular magnets with the magnetic centers characterized by the large magnetic anisotropy. **Slow magnetic relaxation in the discrete molecular compounds** is a very thoroughly investigated issue.[38-41] Below, there is presented in detail the process of the relaxation on the example of Co^{II} ion with $S = \frac{1}{2}$ effective spin.

In octahedral surrounding, the ground state for Co^{II} is ${}^4T_{1g}$. [27] The degeneracy is 12: $2S+1 = 4$ for $S = 3/2$, orbitally triply degenerated. Due to the distortion of the octahedron (e.g., tetragonal), the degeneracy is removed by ZFS and SOC which results in two quartets well separated by Δ from the lowest lying two Kramers doublets. [2] These doublets are also well separated from each other with δ , and for that reason, in approximation, this can be treated as ZFS involving the quartet state. [27] For Co^{II}-based compounds investigated in the framework of this thesis, Δ and δ are both large and D is positive. It means, that the lowest lying Kramers doublet is for $M_S = \pm 1/2$, i.e., the effective spin of the ion is $1/2$, not $3/2$. The formula for the energy gap, δ , incorporates the parameters from ZFS Hamiltonian and is [42]:

$$\delta = 2\sqrt{D^2 + 3E^2}. \quad (1.3.1)$$

The system displaying the slow magnetic relaxation possesses the strong **magnetic anisotropy**. The uniaxial anisotropy is preferred, however, for easy plane anisotropy it is also possible to observe relaxation. [39] The uniaxial anisotropy means, that there exist one distinguished direction along which, the magnetic moment tend to align, it is called easy axis. The magnetic moments align along this easy axis in two orientations: *up* or *down*. In the system of noninteracting paramagnetic ions with high anisotropy being in the equilibrium, there is an equal number of magnetic moments oriented *up* and *down*. When the magnetic field is applied in the *up* direction of an easy axis, the magnetic moments align with the field and only state *up* is populated. After the field is turned off, the spins come back to the equilibrium, however, it occurs with delay. The obstacle causing the delay is the **energy barrier** (Figure 1.3.1) resulting from the fact that between *up* and *down* states, there are excited states which are not preferred energetically (they have larger energy than the ground state). The energetically worst directions are called **hard axes**.

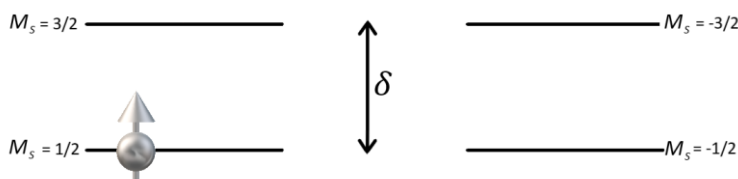


Figure 1.3.1 A scheme of the lowest energy levels for Co^{II} ion, after the turning off the magnetic field. Only the $M_S = \frac{1}{2}$ state is populated.

Crossing the energy barrier, it is, the relaxation of magnetic moment, can occur through the interaction of the spins with phonons. The relaxation is called then **spin-lattice relaxation**. [26] The interaction of the spin with the crystal lattice is one of the two most probable ways of relaxation in the solid state materials. The other is quantum tunneling. [2] There are also known spin-spin relaxation, however, such processes are very fast. [43] Their observation is almost impossible using the commonly used SQUID magnetometry. In this thesis, the author focuses exclusively on the spin-lattice and quantum tunneling relaxation.

There can be distinguished three pathways of spin-lattice relaxation. [15, 26] The first pathway is crossing the barrier just by acquiring the needed amount of energy from phonons. It is called **Orbach process** and its relaxation time, τ , is described by the Arrhenius law:

$$\tau_{Orbach}^{-1} = \tau_0^{-1} \exp\left(-\frac{\delta}{k_B T}\right), \quad (1.3.2)$$

where δ is the energy barrier. A scheme of this process is presented in Figure 1.3.2. The energy acquired by the spin needs to be the same as the energy barrier. It means, that only the phonons of the specific energy will interact with the spins.

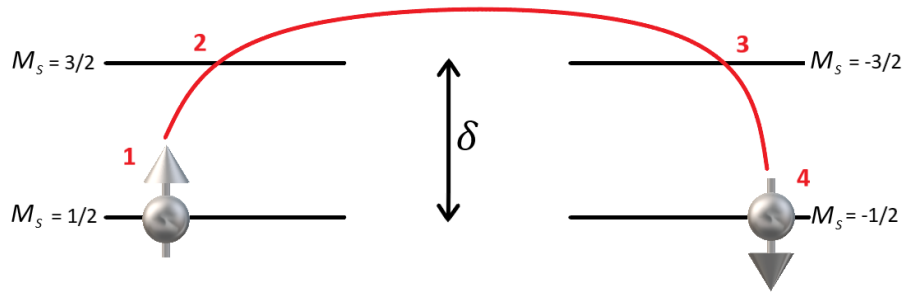


Figure 1.3.2 The scheme of the Orbach process. 1 → 2 – phonon absorption. 3 → 4 – phonon emission.

The process which does not require the specific energy to be acquired is the **Raman process**. [26] The mechanism is similar, but there are the virtual energy levels used (Figure 1.3.3). The relaxation time is:

$$\tau_{Raman}^{-1} = CT^n, \quad (1.3.3)$$

where C and n are constants. For Kramers ions, n should be 9. [26]

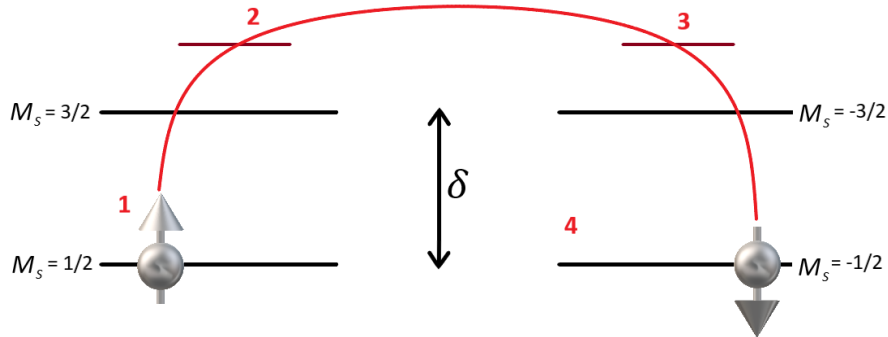


Figure 1.3.3 The scheme of the Raman process. The dark red lines - virtual energy levels. 1 → 2 – phonon absorption. 3 → 4 – phonon emission.

Raman and Orbach processes do not need the external field to occur and are two phonon processes, contrary to the **direct process**. [26] In this process, the field is needed to split the energy levels (remove the degeneracy) lying on the opposite sides of the energy barrier (Figure 1.3.4). The relaxation occurs directly between the initial and final states, no intermediate levels are used. Only one phonon is needed – it is absorbed or emitted, depending on the splitting. The relaxation time is:

$$\tau_{direct}^{-1} = AH^4T, \quad (1.3.4)$$

where A is a constant, and power 4 is characteristic for Co^{II} ions. [42]

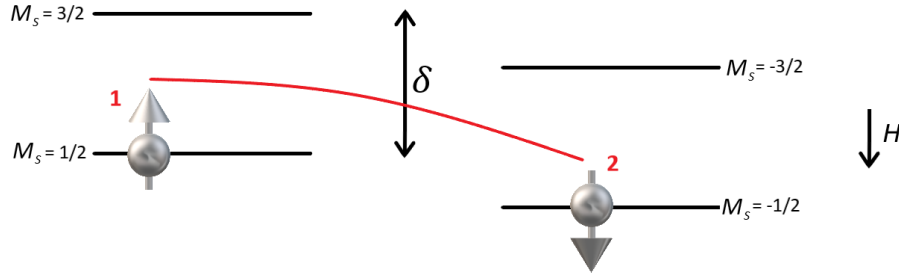


Figure 1.3.4 The scheme of the direct process. 1 → 2 – phonon emission.

There is also another possible pathway of relaxation that does not require a phonon (Figure 1.3.5). It is called **quantum tunneling of magnetization** and it can occur without the external magnetic field, or at the external field, which is needed to equate the levels lying on the opposite sides of the barrier. [2] The relaxation time is:

$$\tau_{qtm}^{-1} = \frac{B_1}{1+B_2H^2}, \quad (1.3.5)$$

where B_1 and B_2 are constants.

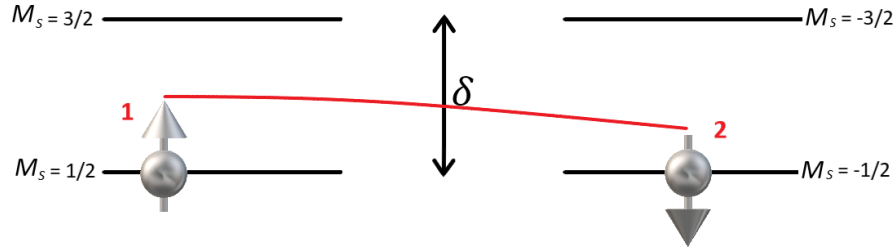


Figure 1.3.5 The scheme of the quantum tunneling of the magnetization at $H = 0$. 1 → 2 - no phonon emission or absorption.

The **total relaxation time** can be therefore described with one equation built from the above four formulas:

$$\tau^{-1} = \tau_{Orbach}^{-1} + \tau_{Raman}^{-1} + \tau_{direct}^{-1} + \tau_{qtm}^{-1} = \tau_0^{-1} \exp\left(-\frac{U}{k_B T}\right) + CT^n + AH^4T + \frac{B_1}{1+B_2H^2}, \quad (1.3.6)$$

where U is the effective energy barrier. There are summed inverse relaxation times, as they are proportional to the probability. It means that the longer the time, the lower probability of this process and the lower its contribution to the total relaxation time. The relaxation pathways of the discrete compound can be determined experimentally by measuring the

relaxation times and then fitting equation 1.3.6 to the field and temperature dependence. They can be also predicted partially if the energy level scheme is known.

The relaxation in non-discrete systems is more complicated, as long-range magnetic interaction plays a very important role. In 1D systems, the relaxation time is comprised of two components: the first one is connected with the single spin relaxation, the second one with the interactions creating the chain. Below, there is presented a theory of **single chain relaxation**, called in this thesis a *conventional approach*. It works for chains based on e.g. Mn(III) ions [10], [44], and some based on Co^{II} ions [45].

The chains in the system are described with two physical quantities.[46] The first one is L , the **length of the chain**. It is the physical length of the chain, literally, the distance between the two neighboring structural defects. The second quantity is the **correlation length**, ξ . It is half of the distance between the two domain walls in the chain. The compared quantities are L and 2ξ . When $L < 2\xi$, the chains are called **finite**. When $L > 2\xi$, the chains are called **infinite** (Figure 1.3.6). This nomenclature is based on the presence of defects. For the infinite size regime, the defects' presence can be neglected.

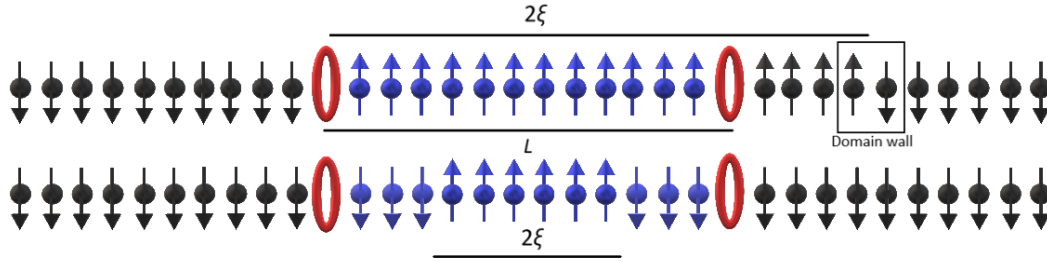


Figure 1.3.6 The spin chains. Top: **finite** chain. Bottom: **infinite**.

The correlation length increases with decreasing temperature. Therefore, in lower temperatures, the chains in one system are finite, and at the higher, infinite. The change between these two regimes of chains is called **crossover**. It manifests in the change of the dominant relaxation processes because finite and infinite chains relax with different energy barriers. For a finite chain, the relaxation time in the *conventional approach* is:

$$\tau_{finite} = \tau_0 \exp\left(\frac{\Delta_\xi + \Delta_A}{k_B T}\right), \quad (1.3.7)$$

and for the infinite is:

$$\tau_{infinite} = \tau_0 \exp\left(\frac{2\Delta_\xi + \Delta_A}{k_B T}\right), \quad (1.3.8)$$

where Δ_ξ is the energy needed to create a domain wall, and Δ_A is the energy originating from the magnetic anisotropy of the single magnetic ion. Δ_A is in the *conventional approach* identified with the energy barrier in the Orbach process of the single spin relaxation. This energy is needed for a domain wall to propagate along a chain. The difference of factor 2 by the Δ_ξ for these regimes originates from the starting point of the relaxation. A finite chain relaxation starts at the defect. An infinite chain relaxation starts with a single spin flip in a chain, which means that the two domain walls are created and for that reason, a factor 2 appears. At the crossover temperature, $2\xi \approx L$ and there is a change of the regime. For a

perfect chain behaving according to this model, the crossover is possible to detect in the Arrhenius plot of the relaxation times (Figure 1.3.7).

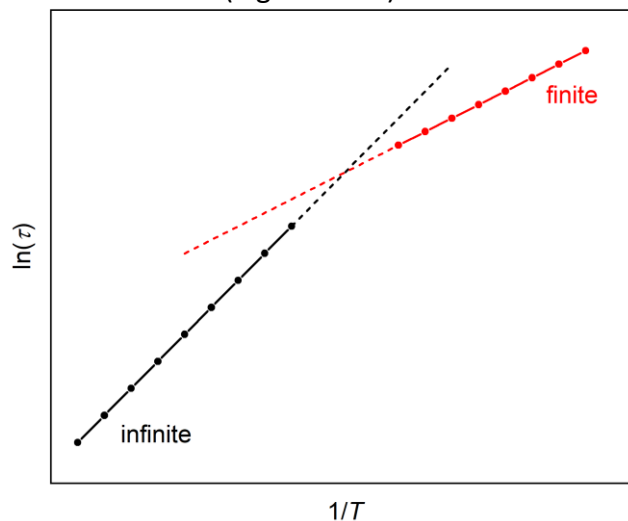


Figure 1.3.7 A schematic Arrhenius dependence of the relaxation times for a model Single Chain Magnet.

The *conventional approach* works only for chains, in which single spins relax according to the Orbach process. For other chains, the crossover may fall outside of the available temperature or relaxation time range, or the observed dependences deviate from linear.

The relaxation time of the chain depends on the external magnetic field. For a system in which there is no magnetic interaction between the chains, the maximal time is at the zero field. In the case of the chains in a system that orders ferromagnetically, the maximal time is also at zero field. For chains ordered antiferromagnetically, the maximum appears at the critical field of the metamagnetic transition.[47]

1.4. $M^{II}(NCS)_2(Ligand)_2$ family of compounds

To obtain a chain molecular magnet there are specific requirements to be met. The most important requirement is that the magnetic exchange must be present only in one dimension, along the chains. Therefore, it is necessary to obtain a proper, linear crystal structure, which is not an easy task, as sometimes to do that, some special techniques of synthesis are needed. For the $M^{II}(NCS)_2(Ligand)_2$ family, which is the subject of this thesis, it is also the case. To find a recipe for the synthesis it is necessary to find a proper molar ratio of $M(NCS)_2$ salt and the ligand and the proper solvent or the mixture of solvents.[48] During these trials, there are many other compounds with diverse compositions obtained. Most of the side compounds are discrete,[49] however, there were encountered some 2-dimensional compounds (both structurally and magnetically), for example $Fe(NCS)_2(4\text{-acetylpyridine})_2$ and $Ni(NCS)_2(4\text{-acetylpyridine})_2$ [50], $Co(NCS)_2(4\text{-$

bromopyridine)₂ [51], Co(NCS)₂(4-*tert*-butylpyridine)₂ and Ni(NCS)₂(4-*tert*-butylpyridine)₂ [52], Co(NCS)₂(ethylisonicotinate)₂ and Co(NCS)₂(ethylisonicotinate)₂ [53]. The structure and exchange interactions are therefore not easy to control and in many cases the method of synthesis used for one compound does not work for another one. The method of synthesis must be matched individually. The goal is to obtain the magnetic ions connected with each other into chains by the NCS bridges, and with two ligands connected to every magnetic ion. An example of the chain is presented in Figure 1.4.1.

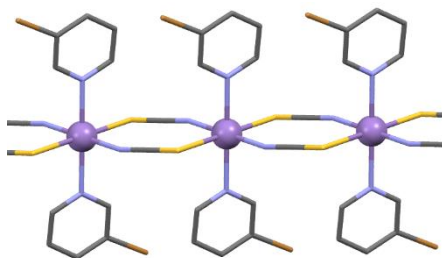


Figure 1.4.1 Mn(NCS)₂(3-bromopyridine)₂ spin chain.[54] Purple: Mn^{II} ions; yellow – S, blue – N, grey – C, orange – Br, H – omitted.

For this family, the interaction is supposed to be mediated through the NCS bridges only, along the structural chain. However, in most of the cases, there are created new interaction pathways, for example through the hydrogen bonds between the ligands of the neighboring chains. These interactions are significantly weaker than the intrachain interaction, but the presence of intra and interchain interactions result in the magnetic ordering of the compounds, so in the general view, the 1-dimensional character is lost. But not in all cases. Sometimes, the interchain interactions are weak enough to be neglected, despite the ordering, and the chain properties are preserved. Such compounds are called quasi 1D systems.

The magnetic exchange along the chains in the described compounds can be ferro-(Ni^{II}(NCS)₂(ligand)₂ or Co^{II}(NCS)₂(ligand)₂) or antiferromagnetic (Mn^{II}(NCS)₂(ligand)₂). There are few factors deciding the type and strength of interactions. Depending on the magnetic ion, its effective spin and the ligands, the crystal field is different and can cause significantly different magnetic anisotropy, as easy-axis or easy-plane. If the coordination of the M^{II} ion is *trans-trans-trans*, the chain is linear and the relatively strong intrachain interaction is mediated, when it is *cis-cis-trans*, the chain is corrugated, and the strength of interaction is significantly weaker. The type and strength of magnetic interactions, along with the type of the magnetic ion, are also deciding when it comes to the slow magnetic relaxation phenomenon. From the already performed investigations, it seems like for [M^{II}(NCS)₂(ligand)₂]_n family, the single chain relaxation is observed only for compounds based on Co^{II}, due to the strong anisotropy of the single Co^{II} ions. For Ni(NCS)₂(ligand)₂ and Mn(NCS)₂(ligand)₂ chains, the relaxation is not observed, as the single ions do not have a proper anisotropy.[15, 53, 55]

The compounds for which the magnetic investigations are included in this thesis are presented in Table 1.4.1. The symbols will be used in the following chapters. All the investigations presented in this thesis have been published or will be published soon.

Table 1.4.1 The list of the compounds investigated in the framework of this thesis. CN - the group of prof. Christian Näther from Christian Albrechts Universität zu Kiel, MF – author of the thesis.

Compound, symbol	Sample form, provider, symbol	Ordering	Single chain relaxation	Reference
$[\text{Mn}(\text{NCS})_2(3\text{-bromopyridine})_2]_n$ Mn-1	powder, CN, Mn-1-p	Not observed down to 1.8 K.	Not observed.	[54]
$[\text{Ni}(\text{NCS})_2(3\text{-ethylpyridine})_2]_n$ (linear chains) Ni-1	powder, CN, Ni-1-p	Yes	Not observed.	[56]
$[\text{Ni}(\text{NCS})_2(3\text{-ethylpyridine})_2]_n$ (linear and corrugated chains) Ni-2	powder, CN, Ni-2-p	Yes	Not observed.	[56]
$[\text{Co}(\text{NCS})_2(4\text{-(3-phenylpropyl)pyridine})_2]_n$ Co-1	single crystal, CN, Co-1-c	Yes	Yes	[57]
$[\text{Co}_x\text{Cd}_{1-x}(\text{NCS})_2(4\text{-(3-phenylpropyl)pyridine})_2]_n$, $x = 0.013$ CoCd-1	powder, CN, CoCd-1-p	No	No, but single spin relaxation is observed.	[57]
$[\text{Co}(\text{NCS})_2(4\text{-methoxypyridine})_2]_n$ Co-2	single crystal, MF, Co-2-c	Yes	Yes	[58]
$[\text{Co}(\text{NCS})_2(\text{aniline})_2]_n$ Co-3	single crystal, MF, Co-3-c	Yes	Yes	In preparation.

In the framework of this thesis, the Ni^{II} and Mn^{II} compounds are investigated only in the powder (polycrystalline) form, the Co^{II} compounds are investigated in the single crystal form. The single crystal research started with an accidental synthesis of **Co-1-c**. The other single crystals of Co compounds were synthesized in the hope to obtain more information about the magnetic relaxation in these compounds. For Ni^{II} -based and Mn^{II} -based compounds, the relaxation is not observed, and for that reason, the synthesis of single crystals for magnetic measurements has not been a priority. The investigations of the powder samples of the Co^{II} based compound were conducted and were already published [59-61]. Here, the conclusions and some of the results from these publications are used for comparison. The **Co-1-c** investigations are supported by the investigations of the powder sample of magnetically diluted compound, **CoCd-1-p**. The **Co-2-c** and **Co-3-c** investigations are supported by the investigations of the powder samples obtained by crushing the crystals.

1.5. Chain models

In this subsection, there are presented models which are used in this thesis for a description of the chain behavior, depending on the magnetic ion.

1.5.1. $\text{Mn}^{\text{II}}(\text{NCS})_2(\text{ligand})_2$ chains

The ground state of single Mn^{II} ion in octahedral coordination, ${}^6\text{A}_{1g}$, is non-degenerated orbitally. The magnetism originates from spin only, as $L = 0$. The spin is $S = 5/2$. It is a Kramers ion. The ZFS is usually very small.[15]

In the case of $\text{Mn}^{\text{II}}(\text{NCS})_2(\text{ligand})_2$ compounds, the analysis is based on the chains composed of classical isotropic spins, between which, there is Heisenberg antiferromagnetic interaction.[62] For Mn^{II} ions, the analytical expression for such a chain is scaled to $S = 5/2$. The Hamiltonian is:

$$\mathcal{H}_{\text{Mn}} = -J \sum_i \mathbf{s}_i \mathbf{s}_{i+1} + g\mu_B \mathbf{H} \sum_i \mathbf{s}_i, \quad (1.5.1)$$

where J is the magnetic exchange constant, $\mathbf{s}_i$ is the i -th spin, and g is the g -factor. The magnetic susceptibility is:

$$\chi = \frac{N_A \mu_B^2 g^2 S(S+1)}{3k_B T} \left(\frac{1+P}{1-P} \right), \quad (1.5.2)$$

where P is:

$$P = \coth \left(\frac{JS(S+1)}{k_B T} \right) - \frac{k_B T}{JS(S+1)}. \quad (1.5.3)$$

1.5.2. $\text{Ni}^{\text{II}}(\text{NCS})_2(\text{ligand})_2$ chains

The ground state of Ni^{II} ion in octahedral coordination is ${}^3\text{A}_{2g}$, $S = 1$. In this case, the zero field splitting effect can be very large and for the compounds considered in this thesis, such effects are manifested in the very low temperature, below 20 K.[27] Ni^{II} is a non-Kramers ion. The exemplary *ab initio* calculations for $\text{Ni}(\text{NCS})_2(\text{ligand})_2$ compound, show the easy-plane anisotropy.[53]

There is no simple way to model the magnetic behavior of such a compound at low temperature, as there is no analytical solution of e.g., magnetic susceptibility for a chain of $S = 1$ spins. Therefore, the $\text{Ni}(\text{NCS})_2(\text{ligand})_2$ behavior is modeled with the formula derived from the simulation. The starting point is that at the high temperature, the ZFS is neglected, and all the spins are treated as isotropic. The used Hamiltonian is the sum of the Heisenberg chain Hamiltonian with isotropic spins with Zeeman term:

$$\mathcal{H}_{\text{Ni}} = -J \sum_i \mathbf{s}_i \mathbf{s}_{i+1} + g\mu_B \mathbf{H} \sum_i \mathbf{s}_i, \quad (1.5.4)$$

where J is the magnetic exchange constant along the chain, $\mathbf{s}_i$ is the i -th spin, and g is the g -factor. The magnetic susceptibility was calculated on that basis by using DMRG and quantum Monte Carlo methods. The result of the simulation was described by the author of the thesis, using the Padé approximation with an additional exponent governing the $T = 0$ limit [63]:

$$\chi = \frac{N_A \mu_B^2 g^2}{k_B T} \left(\frac{a_0 + a_1 x + a_2 x^2}{1 + b_1 x + b_2 x^2 + b_3 x^3} \right)^c, \quad (1.5.5)$$

where $x = J/T$, c is the exponent and is equal to -0.81086, $a_0 = 1.65273$, $a_1 = 2.05175$, $a_2 = 2.84018$, $b_1 = 2.88478$, $b_2 = 4.65762$, $b_3 = 4.30349$. The equation can be used only when the exchange along the chain is ferromagnetic, the susceptibility is measured at small field and the fit is performed in the (relatively) high-temperature regime.

1.5.3. $\text{Co}^{II}(\text{NCS})_2(\text{ligand})_2$ chains

The *ab initio* calculations of the single ion properties for Co^{II} ions in some of the $\text{Co}(\text{NCS})_2(\text{ligand})_2$ compounds, predict the strongly anisotropic ground state doublet, resulting from the crystal field of N_4S_2 coordination.[64] At the low temperature, the effective spin is 1/2, not 3/2 as it would result from the electron configuration of Co^{II} ion. The chain properties of the $\text{Co}(\text{NCS})_2(\text{ligand})_2$ compounds manifest themselves in most cases at temperatures below 10 K, so in such low temperature, only the ground states of Co^{II} ions are populated, and therefore, the exchange interaction can be anisotropic. If the exchange constant in one direction is significantly larger than in the remaining two, the exchange can be treated like the Ising type. The ZFS effect is not as significant as for the Ni^{II} , therefore, for the description of the magnetic susceptibility, ZFS can be neglected in the total Hamiltonian. Therefore, there is used the Hamiltonian for Ising chain with $S = 1/2$ and the Zeeman term:

$$\mathcal{H}_{Co} = -J \sum_i s_i^z s_{i+1}^z + \mu_B \sum_i \mathbf{H} \hat{g} s_i, \quad (1.5.6)$$

where tensor $\hat{g}$ represents the g factors for the directions perpendicular to the easy axis (g_x, g_y , in general $g_\perp$) and parallel to the easy axis (g_z). The analytical susceptibility equations for isolated chains were obtained by M. Fisher.[65] For directions perpendicular to the easy axis – perpendicular susceptibility:

$$\chi_\perp^{chain} = \frac{N_A \mu_B^2 g_\perp^2}{2J} \left[\tanh\left(\frac{J}{4k_B T}\right) + \left(\frac{J}{4k_B T}\right) \text{sech}^2\left(\frac{J}{4k_B T}\right) \right], \quad (1.5.7)$$

and for direction parallel to the easy axis – parallel susceptibility:

$$\chi_\parallel^{chain} = \frac{N_A \mu_B^2 g_\parallel^2}{4k_B T} \exp\left(\frac{J}{2k_B T}\right). \quad (1.5.8)$$

The weak interchain interaction, zJ' , is included for both susceptibilities in the following way:

$$\chi_j = \frac{\chi_j^{chain}}{\left(1 - \frac{zJ'}{N_A g_j^2 \mu_B^2} \chi_j^{chain}\right)} + \chi_0, \quad (1.5.9)$$

where χ_0 is the temperature-independent paramagnetic susceptibility. Therefore, the equation for the total susceptibility of a powder sample is:

$$\chi = \frac{\chi_\parallel + 2\chi_\perp}{3}. \quad (1.5.10)$$

For a single crystal, the susceptibility can be analyzed similarly as for the powder sample, it is, performing measurement for 3 perpendicular directions and average arithmetically the susceptibility. However, it is possible to fit simultaneously the susceptibility for these 3 directions, but only for systems in which there is one type of chains. In such approach, there are two coordinate systems, between which the correlation needs

to be determined. The coordinate system of the main axes of susceptibility is denoted with x , y and z , where z is the direction of an easy axis. The coordinate system connected with the susceptibilities for the directions of measurements ($\mathbf{X}$, $\mathbf{Y}$, $\mathbf{Z}$) can be associated with the (x, y, z) system by the following rotation matrix parametrized with the proper Euler angles [66]:

$$\mathbf{R} = \begin{pmatrix} \cos \alpha_1 \cos \alpha_3 - \sin \alpha_1 \cos \alpha_2 \sin \alpha_3 & -\cos \alpha_1 \sin \alpha_3 - \sin \alpha_1 \cos \alpha_2 \cos \alpha_3 & \sin \alpha_1 \sin \alpha_2 \\ \sin \alpha_1 \cos \alpha_3 + \cos \alpha_1 \cos \alpha_2 \sin \alpha_3 & \cos \alpha_1 \cos \alpha_2 \cos \alpha_3 - \sin \alpha_1 \sin \alpha_3 & -\cos \alpha_1 \sin \alpha_2 \\ \sin \alpha_2 \sin \alpha_3 & \sin \alpha_2 \cos \alpha_3 & \cos \alpha_2 \end{pmatrix}. \quad (1.5.11)$$

The magnetization along the direction of measurements can be therefore expressed:

$$\begin{pmatrix} M_1 \\ M_2 \\ M_3 \end{pmatrix} = \mathbf{R} \begin{pmatrix} 0 \\ 0 \\ M_{ea} \end{pmatrix}, \quad (1.5.12)$$

where M_{ea} is the magnetization of an easy axis:

$$M_{ea} = \sqrt{M_1^2 + M_2^2 + M_3^2}, \quad (1.5.13)$$

The Euler angles can be calculated from:

$$\tan \alpha_1 = -\frac{M_1}{M_2}, \quad (1.5.14)$$

$$\tan \alpha_2 = \frac{\sqrt{M_{ea}^2 - M_3^2}}{M_3}. \quad (1.5.15)$$

The third angle, α_3 , is fitted as it describes the rotation of x and y axes around z axis. The susceptibility tensor in (x, y, z) system is:

$$\chi_{xyz} = \begin{pmatrix} \chi_x & 0 & 0 \\ 0 & \chi_y & 0 \\ 0 & 0 & \chi_z \end{pmatrix}, \quad (1.5.16)$$

and the recalculation to the susceptibility in ($\mathbf{X}$, $\mathbf{Y}$, $\mathbf{Z}$) is:

$$\chi_{XYZ} = \mathbf{R} \cdot \chi_{xyz} \cdot \mathbf{R}^T. \quad (1.5.17)$$

For the Co^{II} -based chain compounds investigated in the framework of this thesis, the intrachain interaction is ferromagnetic, it is, J is larger than 0. For such chains, the parallel susceptibility is dominant over perpendicular susceptibility.

The specific heat in the Ising model is [15]:

$$C = R \left(\frac{J}{k_B T} \right)^2 \text{sech}^2 \left(\frac{J}{2k_B T} \right). \quad (1.5.18)$$

2. Research methods

In this chapter, there are gathered methods used in the investigations performed by the author for this thesis. The main methods are magnetometry and calorimetry, therefore, they are widely described. However, the author also synthesized some of the samples and performed for them the chemical characterization. This chemical characterization consisted of confirmation of the single crystal structure and verification of the purity of the samples. For that reason, these methods are treated in this thesis as support to the main research and are concisely described. Another supporting method are calculations of magnetic properties using the ALPS package.

2.1. Syntheses

All the samples were obtained from solution. In this way it is possible to obtain polycrystalline (powder) samples and small single crystals for Single Crystal X-Ray Diffraction. In case of large single crystals for magnetic measurements, the samples were also obtained from the solution, but the slow evaporation method was used. The individual recipes for the samples are given in the proper compound sections. Samples **Co-2-c** and **Co-3-c** were synthesized by the author of the thesis, the rest by the group of prof. Christian Näther.

2.2. Chemical characterization methods

For all the compounds, the crystal structures were determined by the group of prof. Christian Näther, on the small crystals, unsuitable for magnetic measurements. For **Co-2-c** and **Co-3-c**, which were used for magnetic investigations, the crystal structure was confirmed by the author of the thesis, with support of dr hab. Dawid Pinkowicz, prof. UJ, from Faculty of Chemistry, Jagiellonian University.

The crystal structures of compounds investigated in the framework of this thesis were determined by using the **X-Ray Diffraction** (XRD) method. The XRD method is based on the diffraction of the waves phenomena.[24] To explore the crystal structures, the diffracted waves have to have lengths comparable with the distances between the atoms. This effect enables to determine the position of the nuclei, electron density and from that, the parameters of the unit cell and symmetry of the structure. As the x-ray radiation source, usually the copper or molybdenum anticathode are used, which have strong $K\alpha_1$ lines with wavelengths 1.541 Å and 0.709 Å, respectively. According to a simplified model, the initial beams are reflected by the parallel atomic layers, but only in a small part. The diffracted beams interfere constructively only when the initial radiation fall under the specified angles, which are associated with the interlayer distance, d , by the **Bragg law**:

$$2d\sin(\theta) = n\lambda, \quad (2.2.1)$$

where θ is the angle between the initial beam and the atomic layer, λ is the wavelength and n is the row of the reflection. This equation expresses the differences of the optical path lengths between the waves. To obtain an interference pattern from which the crystal structure can be determined, it is necessary to perform an experiment for many angles or many wavelengths. Technically, it is easier to perform this experiment at the constant wavelength for different angles, as then, only one source of radiation (e.g. Cu or Mo anticathode) is necessary. The continuous source of X-ray radiation can be a synchrotron, however, due to the low accessibility of such equipment, the vast majority of X-ray diffraction is performed at one wavelength for different angles.

For **Single Crystal X-Ray Diffraction** (SCXRD),[24] the single crystal is mounted on the special holder which is then attached to the goniometer. The crystal has to be centered before the measurement. The diffraction pattern is 'an image of the crystal structure' in the reciprocal space. To obtain the crystal structure from the diffraction pattern, it is necessary to transform it to the real space. The procedure starts with the determination of the reflection intensities from the pattern.[67] The intensity is equal to the square of the structure factor, which is in turn associated by the Fourier transform with the **electron density** in the real space. The structure factor is defined with the complex number, so knowing the intensities from the experiment gives only the absolute value of this factor, the information about the phase is lost. This is called a **phase problem**. [67] There exists many methods of solving this problem, as theoretical (direct method, Patterson function) and based on experiment (e.g. heavy metal replacement). On the basis of electron density, the model of the structure is built and then it is refined.

The SCXRD measurements performed by the author in the framework of this thesis, concern only two samples: **Co-2-c** and **Co-3-c**. The measurements were performed to confirm if the crystal structure corresponds to the expected one, previously determined by the group of prof. Christian Näther, and to confirm the monocrystalline character of the sample. The measurements were performed using a Bruker D8 QUEST ECO diffractometer. The source of radiation was molybdenum anticathode (MoK α radiation, $\lambda = 0.709 \text{ \AA}$). The diffractometer is equipped with Triumpmh monochromator and a PHOTON III CPAD detector. The source and the detector move synchronically to collect the constructively interfered beams. The diameter of the initial beam is 700 μm , which enables measuring large single crystals. The crystal structure was determined and refined using the automated structure determination option. The crystal faces were determined with the Apex3 software.

For a **Powder X-Ray Diffraction** (PXRD),[24] the powder sample is e.g. in the capillary. There are collected the reflexes at the 2θ angles. The structure determination from a powder pattern is far more difficult than for a single crystal, due the random orientation of the crystals. Therefore, it is usually used as a method of confirmation of the purity of the sample. The PXRD pattern is simulated from the crystal structure and compared to the experimental pattern (positions and height of the peaks). If there are some

additional peaks or some of the present peaks are higher, it means that there is some contamination in the sample.

Powder X-Ray Diffraction measurements were performed using a powder diffractometer Bruker D8 Advance ECO. The source of radiation was copper anticathode (CuK α radiation, $\lambda = 1.541 \text{ \AA}$). The measurements were performed in the transmission geometry. The diffractometer is equipped with a SSD 160 detector. The measurements were performed to check the purity of the powder samples obtained from single crystals of **Co-2** and **Co-3**.

The purity of the samples was also checked by **Elemental Analysis** (EA). In EA, the sample is burned, and using gas chromatography, the amount of the created oxides is measured. Using this method, only the elements creating gas oxides can be detected. The measurements were performed to check the purity of the powder samples obtained from single crystals of **Co-2** and **Co-3**. The measurements were performed using the Elementar Vario Micro Cube CHNS analyzer, by a technical worker in the Faculty of Chemistry, Jagiellonian University.

2.3. SQUID Magnetometry

2.3.1. MPMS QD 5XL magnetometer

The magnetometer used for measurements is **Quantum Design Magnetic Properties Measurement System 5XL** (QD MPMS 5XL, Figure 2.3.1).[16] With this equipment, it is possible to perform measurements in a very wide range of temperatures, from 1.8 to 400 K. Such low temperatures are obtained due to a liquid helium cooling system. The field range is from 0 to $\pm 5 \text{ T}$. The measurement procedure can be easily programmed in the software MultiVu due to the control systems over the magnetic field and temperature setting. The Superconducting Quantum Interference Device (SQUID) enables measuring the magnetic moment with high sensitivity. It is incorporated into the equipment in a way enabling operation at the high fields, and simultaneously senses the change of the field of approximately 10^{-15} T . The SQUID uses the so-called Josephson junctions, which working principle is based on the Josephson laws. The behavior of the Josephson junction was predicted in 1962 by B.D. Josephson, and two years later it was experimentally proven by Anderson and Rowell.[16]



Figure 2.3.1 The Magnetic Properties Measurement System, Quantum Design, Institute of Physics, Jagiellonian University.

The **Josephson junction** is built from superconducting and non-superconducting (most often an insulator) material. They are combined into a device according to the order: superconductor – insulator – superconductor. The insulator is a very thin barrier between the superconducting blocks, thin enough to enable the tunneling of Cooper pairs through it.[68] Cooper pairs are pairs of electrons created in the superconducting state, they are described by the Bardeen–Cooper–Schrieffer theory.[69] Their current through the barrier can be described by the **I Josephson law**:

$$I(t) = I_c \sin \varphi(t). \quad (2.3.1.)$$

I_c is the critical current, it is, the maximal current that can flow through the junction without losing the superconducting state in the material. $\varphi(t)$ is the difference in phase between the wave functions of the Cooper pairs before and after tunneling through the junction.

The **II Josephson law**, [70] describes the phase behavior when the potential across the junction ($V(t)$) appears:

$$\frac{\partial \phi}{\partial t} = \frac{2eV(t)}{\hbar} = \frac{2\pi V(t)}{\phi_0}, \quad (2.3.2)$$

where ϕ_0 is the magnetic flux quantum. The voltage across the junction appears when the magnetic field is applied. Therefore, two Josephson effects can be distinguished: dc and ac. Dc effect is when the tunneling of Copper pairs occurs without the voltage across the junction, and ac, when the dc voltage across the junction is present. In the latter case, the alternating current with frequency V_{dc}/ϕ_0 flows through the junction.

SQUID is a device comprised of two Josephson junctions incorporated into a loop (Figure 2.3.2). When the current enters the loop and the magnetic field is not applied, it divides equally between the two branches. Applying the magnetic field results in the appearance of the screening current, I_s , circulating in the loop. This current generates the magnetic field in an opposite direction. Therefore, due to the screening current, the magnetic flux across the loop cancels to achieve the integer value. While the magnetic flux

crossing the junction is an integer of ϕ_0 , the screening current is 0 and there is no phase shift between the wave functions of the Cooper pairs in the two branches. Then, the interference of these functions is constructive and the total current at the way out of the loop is then maximal. The screening current has the highest value when the flux is half of the magnetic flux quantum, there is a phase shift between the wave functions equal to π , the interference is destructive, and the total current at the way out is minimal. In between the integer and half-integer values of magnetic flux quantum, the screening current takes the intermediate values, the dependence is linear. The direction of the screening current circulation changes at $\phi_0/2$. Therefore, the total current at the way out of the loop is oscillating with the magnetic field applied to the loop, the same as the voltage, which measurement enables the determination of the change of the magnetic field.

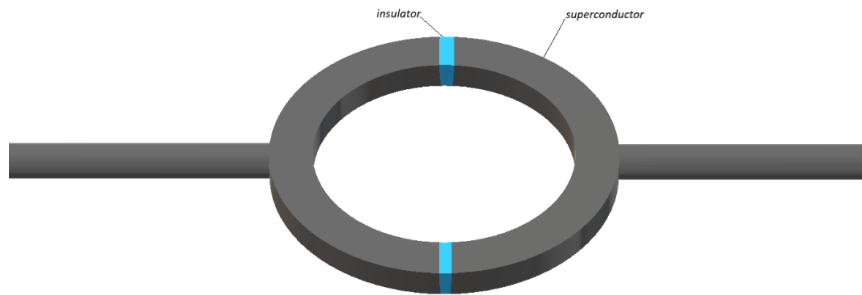


Figure 2.3.2 A scheme of SQUID.

The **SQUID** [16] in MPMS, is surrounded by the superconducting shield which separates the SQUID from the superconducting magnet. SQUID is connected with the detection coil, which is by induction coupled to the sample. In general, SQUID converts the current to voltage. The sample is put into a sample chamber. Outside the chamber, there is the magnet, and inside, there are the detection coils. The sample is moving through the detection coils. In the detection coils, the current is induced, by the magnetic moment of the sample. The detection coil is connected to the SQUID by the superconducting wires. All these elements are incorporated into one superconducting loop. The change of the current is proportional to the change in magnetic flux, and also to the change of the voltage at the output of the SQUID. This voltage oscillates with the flux. Summarizing, the magnetic moment is measured indirectly by measuring the voltage. To obtain a conversion from voltage to the magnetic moment, it is necessary to calibrate the system. It is usually performed by measuring the voltage for a sample with known magnetic susceptibility.

The **magnet** in MPMS [16] is a superconducting magnet in a configuration of the solenoid. It creates a closed superconducting loop. To charge the magnet, the current is let into the loop, where it is persistent due to the superconducting state. To change the field, the loop has to be opened and more current is injected or the current is reduced. The opening of the loop is performed by heating a part of the magnet and attaching it to the current source. When the proper amount of the current is in the loop, the loop is closed. The produced magnetic field is constant after some time, necessary for the field to relax. A certain threat is a situation when the magnet quenches. It happens when the loop is opened

and the current in the source is significantly different than the one in the loop. A part of a magnet loses the superconducting state and due to the resistance appearance, heat is produced, which in turn results in the enlargement of the magnet part which is not in the superconducting state. Such an event can cause a significant loss of helium, and in extreme cases, damage of the magnet. However, this effect can be also useful. It can be used in a controlled way to remove the remnant field from the magnet.

The scheme of the **detection coil** [16] is presented in Figure 2.3.3. It is built in a configuration of second-order gradiometer (3 coils) to avoid the detection of the magnetic field produced by the disturbing effect, such as the fluctuation of the magnetic field or the relaxation of the magnetic field. In general, the more coils, the better screening. The coils must have the same area to be immune to the field produced by the superconducting magnet. If the areas are not the same, in the circuit the current induced by the magnet can persist. Due to the fact, that it is impossible to produce identical coils, such remnant current will always be present. To remove it, a part of the detection coil is heated after every magnetic field change to come out from the superconducting state.

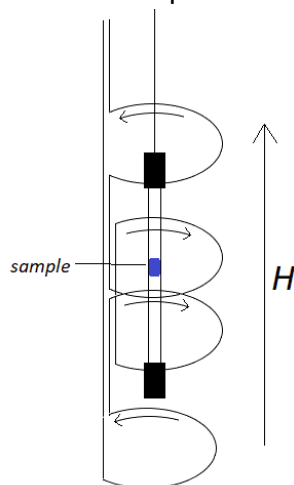


Figure 2.3.3 A scheme of second-derivative detection coil in MPMS. H – the strength of the applied field. Curved arrows - the direction of the current in the coils.

The **superconducting shield** [16] protects the SQUID from the magnetic field produced by the magnet, however, it has one more, very important task. While the magnetometer is cooled down, the ambient magnetic field is trapped and stabilized by the shield, to avoid its impact on the measurement.

The **sample** for measurement is put into the sample space on the long rod. To obtain a uniform temperature, the region in the sample space around the sample at a height of the detection coils is covered with copper.[16] There are mounted two thermometers by the sample, from which the average value is taken as measurement temperature. The rod is moved by the stepper motor. This enables stopping the sample at the specific position in the detection coils and measuring the voltage. The sample space and detection coil sizes limit the size of the sample. There is measured the change of the magnetic moment only, therefore, if the sample is longer than the detection coil size, no change will be observed,

as through the coil, the uniform object moves. This effect, however, has a positive consequence for mounting the sample for measurement. The sample is usually mounted in a long, plastic straw at the end of the rod. The straw does not give the contribution to the measured signal, as it is uniform. Apart from the size of the sample, the other limitation is the sample itself. It should be uniformly magnetized to avoid the distortion of the results. To obtain reliable results and reduce noise, the readings and scans should be repeated a few times and averaged. This can be set in the MultiVu software. Every final point, it is, a magnetization value at a specific temperature and field is obtained by the fit to the voltage versus position. The fitted function includes the value of the searched magnetic moment and calibration constants.

2.3.2. Samples preparation for measurements

For magnetic measurements, powder samples are packed into gelatin capsules (Figure 2.3.4). In the case of materials with anisotropic spins, the powder is additionally flooded with a small amount of the mineral oil, nujol, to avoid aligning of the crystallites in the field. The capsule is put into a plastic straw with a 5.25 mm diameter, and then, the straw is attached to the stick and put into a magnetometer.

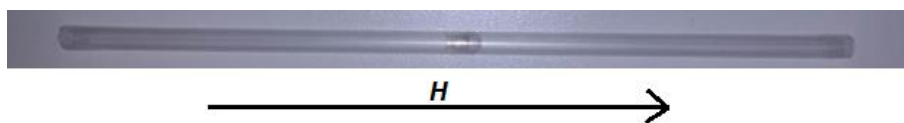


Figure 2.3.4 The powder sample was packed in a gelatin capsule and put into a plastic straw.

The **Co-1-c** sample is packed into a specially manufactured holder made of Delrin, enabling easy recognition of the direction of the measurements. That sample has a unique shape of a prism, which makes the directions' recognition hard. For **Co-2-c** and **Co-3-c** measurements, there are used also specially manufactured holders made of delrin. The holder is a round plate with a 5.25 mm diameter. The crystal is always placed on the largest plane, as it is the easiest way to fix the crystal to the holder. The crystal is immobilized with eicosane (wax). The first direction of the measurement is perpendicular to the largest plane of the crystal. The other two directions are chosen to be perpendicular to the first direction and each other. It is ensured by gluing the holder to the small tile made of PET foil with a length of the side of 5.25 mm. The second direction is a well-defined crystallographic direction. The crystal is placed on the tile in a way that the second direction is parallel to the edge of the tile and perpendicular to the first direction (Figure 2.3.5). The holder on the tile is put into the straw so that the second direction is parallel to the axis of the straw. The third direction is obtained by rotating the PET tile by 90°.

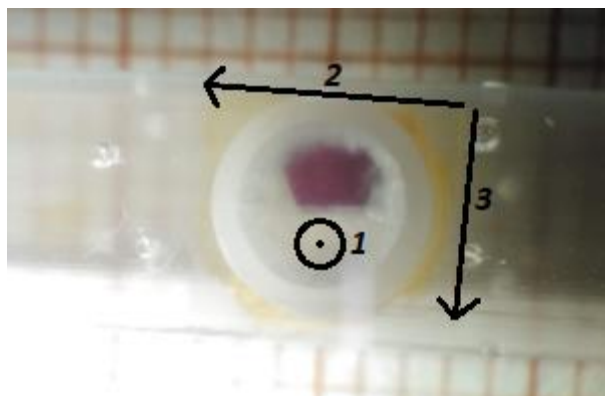


Figure 2.3.5 A photo of the single crystal sample of **3-Co** fixed to the holder made of delrin by eicosane. The holder is glued with Varnish to the PET tile and put into a plastic straw. The directions of measurements are marked in black.

2.3.3. Recalculation of the measured values and units

The measured quantity in the magnetometer is the magnetic moment in emu. Emu is cgs unit, meaning *electromagnetic* unit. In SI system 1 emu is $10^{-3}\text{A}\cdot\text{m}^2$ or 10^{-3}J/T .

Magnetization can be expressed in μ_B/mol :

$$M\left(\frac{\mu_B}{\text{mol}}\right) = \frac{m_{\text{measured}}(\text{emu}) - m_{\text{corrections}}(\text{emu})}{n(\text{mol}) \cdot N_A \cdot \mu_B}, \quad (2.3.3)$$

where n is the mole number, N_A is the Avogadro number ($6.02 \cdot 10^{23}/\text{mol}$), m is magnetization, and $\mu_B = 9.27 \cdot 10^{-21} \text{ erg/Gs}$.

Magnetic susceptibility can be expressed in cm^3/mol :

$$\chi\left(\frac{\text{cm}^3}{\text{mol}}\right) = \frac{m_{\text{measured}}(\text{emu}) - m_{\text{corrections}}(\text{emu})}{H(\text{Oe}) \cdot n(\text{mol})}. \quad (2.3.4)$$

$m_{\text{corrections}}$ is the diamagnetic correction.

2.3.4. Diamagnetic corrections

The diamagnetic contribution to the magnetization of the measured material comes mainly from the holder of the sample. In the case of this thesis, for powder samples, the diamagnetic contribution comes from capsule and nujol, and for a single crystal from delrin holder, eicosane, PET tile, Varnish glue. Apart from the holder contribution, there is always the diamagnetism of the sample. Below, there are presented procedures used to calculate these contributions. The diamagnetic correction is subtracted only from the dc magnetization, as ac magnetization is mathematically the derivative of the dc magnetization. The diamagnetic magnetization is subtracted from the dc magnetization, and it is constant. Therefore, in a derivative, it will disappear.

Gelatin capsule: There was performed a magnetization vs. field measurement for an empty capsule. On that basis, the universal formula was derived:

$$M_{\text{capsule}} = -0.407 \cdot 10^{-6} \cdot H \cdot m_{\text{capsule}}, \quad (2.3.5)$$

where M_{capsule} is the magnetization of the capsule in emu, $-0.407 \cdot 10^{-6}$ is the susceptibility of the capsule in cm^3/mg , H is the field in kOe, m_{capsule} is the mass of the capsule in mg.

Delrin holder: There was performed a magnetization vs. field measurement for an empty holder. On that basis, the universal formula was derived:

$$M_{holder} = -0.555 \cdot 10^{-6} \cdot H \cdot m_{holder}, \quad (2.3.6)$$

where M_{holder} is the magnetization of the holder in emu, $-0.555 \cdot 10^{-6}$ is the susceptibility of the holder in cm^3/mg , H is the field in kOe, m_{holder} is the mass of the holder in mg.

Constituent atoms: This contribution is usually lower than the contribution from the holder and can become negligible. The estimation is made on the basis of the tabularized magnetic susceptibilities of atoms, ions, compounds and bonds from [17]. The susceptibility contribution for $M^{II}(\text{NCS})_2(\text{ligand})_2$ compounds investigated for this thesis is approximately $-200 \cdot 10^{-6} \text{ emu/mol}$.

PET foil, eicosane, nujol: As the diamagnetic contribution of PET tile, eicosane and nujol is relatively low compared to the holder contribution, it is estimated as constituent atoms of the general formula of these materials: $-(\text{CH}_2)-$. The susceptibility contribution is around $-1.2 \cdot 10^{-5} \text{ emu/mol}$.

The **total diamagnetic correction** is the sum of the above-mentioned contributions. This correction is negative, therefore, subtracting it from magnetization, gives an increase of this value.

2.3.5. Demagnetization

Demagnetization effect [16] occurs for the sample with large magnetization (e.g. ferromagnets) and it depends on the shape of the sample. It decreases the value of the measured magnetic moment. It can be described by the additional field created in the sample, the demagnetization field, H_d . Then, inside the sample, the total field, H , is the sum of the applied external magnetic field, H_0 , and the demagnetization field:

$$H = H_0 + H_d. \quad (2.3.7)$$

The demagnetization field can be defined as:

$$H_d = -NM, \quad (2.3.8)$$

where N is the factor dependent on the shape of the sample. In cgs system of units, it takes the value from 0 to 4π . The values of the N factor for common shapes can be found in tables, e.g. [71]. For the dc magnetic susceptibility, the correction for demagnetization relies on recalculation of the susceptibility according to the equation [72]:

$$\frac{1}{\chi} = \frac{1}{\chi_A} - N, \quad (2.3.9)$$

where χ is the real susceptibility of the sample, χ_A is the measured susceptibility. Both susceptibilities are dimensionless (recalculated per volume). For ac magnetic susceptibility, the case is not so simple, as it is a complex number (see equation 2.3.10) and χ' mixes with χ'' . The formulas are [72]:

$$\chi' = \frac{\chi_A' - N(\chi_A'^2 + \chi_A''^2)}{(1 - N\chi_A')^2 + (N\chi_A'')^2}, \quad (2.3.10)$$

$$\chi'' = \frac{\chi_A''}{(1 - N\chi_A')^2 + (N\chi_A'')^2}. \quad (2.3.11)$$

2.3.6. Relaxation time determination

The relaxation times are determined indirectly from the frequency dependence of ac magnetic susceptibility. The ac magnetic susceptibility is in general:

$$\chi_{ac} = \chi' - i\chi'', \quad (2.3.12)$$

where χ' is the real and χ'' is the imaginary component of the susceptibility. The frequency dependence is expressed with the Cole-Cole model [2, 73, 74]:

$$\chi_{ac} = \chi_s + \frac{\chi_T - \chi_s}{1 + (i\omega\tau)^{1-\alpha}}, \quad (2.3.13)$$

where χ_s is the susceptibility in the limit of high frequencies (adiabatic limit) and χ_T is the susceptibility in the limit of low frequencies (isothermal limit). α describes the dispersion of the relaxation times. τ is the searched relaxation time. The individual formulas for frequency dependences of χ' and χ'' are:

$$\chi'(\omega) = \chi_s + (\chi_T - \chi_s) \frac{1 + (\omega\tau)^{1-\alpha} \sin\left(\frac{\pi\alpha}{2}\right)}{1 + 2(\omega\tau)^{1-\alpha} \sin\left(\frac{\pi\alpha}{2}\right) + (\omega\tau)^{2-2\alpha}}, \quad (2.3.14)$$

$$\chi''(\omega) = (\chi_T - \chi_s) \frac{(\omega\tau)^{1-\alpha} \cos\left(\frac{\pi\alpha}{2}\right)}{1 + 2(\omega\tau)^{1-\alpha} \sin\left(\frac{\pi\alpha}{2}\right) + (\omega\tau)^{2-2\alpha}}. \quad (2.3.15)$$

2.4. Calorimetry

2.4.1. Physical Properties Measurement System

Physical Properties Measurement System (PPMS) is a multifunctional equipment that enables measuring of specific heat, magnetic moment, magnetoresistance, and many other effects, depending on the installed options in the specific apparatus. In the framework of this thesis, the PPMS was used to measure the specific heat only. The PPMS Quantum Design, accessible for the author of this thesis (Figure 2.4.1), is equipped with a liquid helium cooling system. It enables measuring of heat capacity from 400 to 1.8 K. Due to an additional option, operating with helium-3 gas, it is possible to cool down the sample from 350 to 0.4 K. In PPMS, there is a superconducting magnet, similar to that in MPMS. The principle of operation is the same. In the accessible model of PPMS, the maximal magnetic field is ($\pm$)9 T.



Figure 2.4.1 Physical Properties Measurement System, Quantum Design, Institute of Physics, Jagiellonian University.

The basis of the specific heat measurement [75] is the following equation:

$$C_p = \left(\frac{dQ}{dT} \right)_p, \quad (2.4.1)$$

where C_p is the specific heat at the constant pressure, p . dQ is the amount of heat provided to the sample, dT is the change of the temperature caused by the heat. The heat is provided for some well-defined time to the sample and then, for the same amount of time, the sample is left for cooling. To limit the holder heat capacity, a sapphire sample platform is used (Figure 2.4.2). The sample is fixed on the platform with grease. The grease ensures good thermal contact between the platform and the sample. The platform is heated by the heater. To the platform, there is also a thermometer attached. The heater and the thermometer are connected to the power supply by small wires. The wires are also responsible for a thermal connection to the thermal bath – a puck that is also a shield for a sample. The puck is put into the sample chamber, in which the high vacuum is achieved. The vacuum causes that the thermal conductance between the sample and puck is almost totally through the wires.



Figure 2.4.2 The puck for specific heat measurement with He-4. Left: the whole puck with a shield. Right: The interior of the puck. In the center, there is a sample platform fixed on the 8 wires. Under the platform, there are a thermometer and a heater mounted.

In the case of specific heat measurement, the registered data are the temperature of the sample at specific times, called relaxation times. A well-defined heat amount is added to the sample for a specific time (heating period). After that, the power supply is cut off, and the cooling period starts. Then, the obtained temperatures vs. times curves are fitted with a model to obtain the heat capacity value. In this **thermal relaxation method**, [75, 76] it is assumed, that the specific heat of a sample is approximately constant in the narrow temperature range (temperatures from the T of the thermal bath to the T obtained by adding the heat). There are two models used by the PPMS software. The **simple model** is used mostly for addenda measurement and measurement where the thermal contact with the sample is very good. The time dependence of the platform temperature, T , in this model is entangled with the differential equation [75]:

$$C_{total} \frac{dT}{dt} = -K_w(T - T_b) + P(t), \quad (2.4.2)$$

where C_{total} is the total heat capacity of the measured system (sample with grease and a platform), K_w is the thermal conductance of the wires, T_b is the temperature of the puck (thermal bath), $P(t)$ is the power provided to the heater dependent on time (takes two values: P during the heating period, 0 during the cooling period). The solution of this equation is an exponential function, e.g. [76]:

$$T(t) = T_b + \Delta T \exp\left(-\frac{t}{\tau}\right), \quad (2.4.3)$$

with a parameter τ :

$$\tau = \frac{C_{total}}{K_w}, \quad (2.4.4)$$

which is a characteristic time constant, from which the value of specific heat is deduced, and ΔT :

$$\Delta T = \frac{P}{K_w}. \quad (2.4.5)$$

When the sample has poor thermal contact with the platform, there is used the **two-tau model**. In this model, there are distinguished the characteristic times for the platform and a sample. The differential equations are [75]:

$$C_{sample} \frac{dT_s}{dt} = -K_g(T_s(t) - T_p(t)), \quad (2.4.6)$$

$$C_{platform} \frac{dT_p}{dt} = P(t) - K_w(T_p(t) - T_b) + K_g(T_s(t) - T_p(t)), \quad (2.4.7)$$

where K_g is the thermal conductance between the platform and sample through grease. The solution comes down to the two characteristic times, τ_s (sample) and τ_p (platform), e.g. [76]:

$$T_p(t) = T_b + A \exp\left(-\frac{t}{\tau_s}\right) + B \exp\left(-\frac{t}{\tau_p}\right), \quad (2.4.8)$$

where A and B are constants. The time constants are [75]:

$$\tau_s = \frac{1}{\alpha + \beta'}, \quad (2.4.9)$$

$$\tau_p = \frac{1}{\alpha - \beta'}, \quad (2.4.10)$$

where α and β are:

$$\alpha = \frac{K_w}{2C_{platform}} + \frac{K_g}{2C_{platform}} + \frac{K_g}{2C_{sample}}, \quad (2.4.11)$$

$$\beta = \frac{\sqrt{K_g^2 C_{sample}^2 + 2K_g^2 C_{sample} C_{platform} + K_g^2 C_{platform}^2 + K_w^2 C_{sample}^2 + 2K_w^2 C_{sample} K_g - K_w C_{sample} K_g C_{platform}}}{2C_{platform} C_{sample}}. \quad (2.4.12)$$

This model is always fitted to the raw data for a sample, however, sometimes it is impossible to fit. In such a case, the value of specific heat determined from a simple model is taken. Another situation in which the simple model value is taken is when the error of the value from the two-tau model is larger.

The measurement procedure starts with a measurement of **addenda**. It is a measurement of a puck with grease which will later serve as a fixing and thermal medium for a sample. Measurement of addenda is necessary before every sample measurement, as it has to be later subtracted from the total heat capacity (heat capacity of puck, grease, and the sample). There is performed a few repetitions at one temperature, and then the results are averaged to obtain the most reliable value of specific heat.

The accessible sample sizes for measurement are dependent on the platform size. The specific heat is measured by using the relaxation method, therefore, the larger the sample, the longer the time of relaxation. The platform has 3 x 3 mm (Figure 2.4.2, right) and these are the limits of the sample size. The other limit is the relaxation time constant. For a large sample, the measurement can take a significant amount of time. The constant is usually larger in higher temperature, but the longest times are reached for peaks related to

ordering below 1 K. For such cases, sample masses of the order of 0.3 mg were more optimal.



Figure 2.4.3 The puck for specific heat measurements with He-3. Left: the whole puck. Right: the interior of the puck. In the center, there is a sample platform fixed on the 4 wires.

For the measurements with He-4, the puck (Figure 2.4.2) is directly put into the sample chamber. For measurements with He-3, a different puck (Figure 2.4.3) and a special insert is required (Figure 2.4.4).



Figure 2.4.4 Left: The insert for the He-3 option. Right: the enlargement of a part, where the puck is mounted.

2.4.2. Samples preparation for measurements

Depending on the sample form, the preparation method is different. For a single crystal sample, the sample is fixed to the platform as it is. The limitation is only the size of the crystal and its shape. The sample cannot be larger than the platform, the shape must enable good thermal contact with the platform. For example, when the sample is too large, fixing it to the platform can cause the grease to 'escape' under the platform, and then, the addenda changes. Also, if the sample is not all in the platform, the heat capacity value will be undervalued. If the sample is needle-shape, it cannot be fixed to the platform on the sharp edge, as such positioning does not ensure the proper thermal contact. A powder sample should be fixed to the platform in a way that does not contaminate the puck and enables determining the mass of the sample precisely. Therefore, pouring the powder directly on the grease on the platform is not necessarily a good method. For that reason, powders are pressed in the hydraulic press into a pastille. The pastilles have a 5 mm diameter. It is cut into a shape proper for a platform in a puck. The investigated materials could be pressed this way, as after the pressing, the pastille was not crumbling. The optimal mass of studied samples for measurement with He-4 is around 4 mg, for measurement with He-3 it is around 1 mg.

For the measurements in the magnetic field, the addenda was measured at the fields at which later, the sample is measured. The differences between addendas' heat capacity were negligible up to 10 kOe.

2.4.3. Recalculation of the measured values and units

The heat capacity of the sample is provided by the software, the addenda is already subtracted from the total specific heat. The values of heat capacity are usually provided in $\mu\text{J/K}$. The values have to be recalculated per mole. The values can be expressed in $\text{J}/(\text{K}\cdot\text{mol})$:

$$C_{mol} \left(\frac{\text{J}}{\text{mol}\cdot\text{K}} \right) = \frac{C_{sample} \left(\frac{\mu\text{J}}{\text{K}} \right) \cdot 10^{-6}}{n(\text{mol})}. \quad (2.4.13)$$

The magnetic contribution to the specific heat is obtained by subtraction of the Debye or/and Einstein model (see equation 1.1.19). The integral of C_{magn}/T over T at 0 Oe gives the entropy change, Δs , associated with the ordering. In theory, it is:

$$\Delta s \left(\frac{\text{J}}{\text{mol}\cdot\text{K}} \right) = R \ln(2S + 1), \quad (2.4.14)$$

where S is the spin.

2.5. Algorithms and Libraries for Physical Simulations (ALPS)

The **Algorithms and Libraries for Physical Simulations** (ALPS) [77-80] were used as support for the analysis of the data for some of the compounds. The ALPS package comprises the code implementing, among others, the Monte Carlo simulations. There are

implemented classic (e.g., *spinmc* program) and quantum (e.g. *loop* program) Monte Carlo simulations. It enables the calculation of magnetization, magnetic susceptibility, specific heat, etc., for the specified system.

The system is determined by building a model based on the crystal structure. There have to be determined the following bases: *unit cell* (determines the position of the spins in the structure and their pathways of exchange interaction), *lattice* (the model of crystal structure), and *latticegraph* (combination of lattice and unit cell, it also determines the size of the system (length, width, height) for which the simulation will be carried out). Apart from the model of the system, the other input parameters of simulation have to be chosen and set:

- ❖ physical model – can be chosen from the library (e.g., Ising, Heisenberg, etc.).
- ❖ depending on the physical model – proper parameters describing it (e.g., in 1D Ising model, the energy of interaction along a chain, J).
- ❖ the temperatures and fields at which the simulation should be performed.
- ❖ size of the system – determination of values for the parameters defined in the latticegraph.
- ❖ update – the method of updating for the Monte Carlo algorithms (*local* or *cluster*).
- ❖ sweeps – the number of steps of the Monte Carlo simulation.
- ❖ thermalization – the number of sweeps (should be enough to obtain an equilibrium state).

The parameters like the size of the system, sweeps, and thermalization are usually determined by performing trial simulations. The optimal numbers are when the simulation takes an acceptable amount of time, and the equilibrium state is achieved (the simulated value does not change for a larger system). The units in the simulations must be unified. The easiest way is to recalculate all physical values (temperature, field, energy, etc.) to K. For a simulation at the field, its value should be recalculated for the specific direction, otherwise, the simulation will be performed for the easy axis direction.

3. Magnetic properties of $\text{Mn}^{\text{II}}(\text{NCS})_2(3\text{-bromopyridine})_2$

In this chapter, there are presented the results of magnetic investigations of $[\text{Mn}(\text{NCS})_2(3\text{-bromopyridine})_2]_n$ (**Mn-1**). The results of the powder sample investigation presented in this thesis were published in [54]. The samples were provided and chemically characterized by the group of prof. Näther.

Symbols:

Mn-1 – $[\text{Mn}(\text{NCS})_2(3\text{-bromopyridine})_2]_n$

Mn-1-p – powder sample of **Mn-1**

3.1. Synthesis

A powder sample of **Mn-1**, **Mn-1-p**, was obtained by mixing the $\text{Mn}(\text{NCS})_2$ with 3-bromopyridine in 1:2 molar ratio in anhydrous *n*-butanol. The used amounts are: 0.5 mmol of $\text{Mn}(\text{NCS})_2$, 1 mmol of 3-bromopyridine, and 2 ml of *n*-butanol. The stirring lasted 2 days. To determine the crystal structure, small single crystals were synthesized. The procedure of synthesis was almost the same as for a powder sample, however, the solution was not mixed, but left for one day for crystallization.

3.2. Crystal structure

Mn-1 crystallizes in the monoclinic system $P2_1/n$. The unit cell parameters are presented in Table 3.2.1. There is only one crystallographically independent Mn^{II} position. The ion is octahedrally coordinated by four thiocyanate bridges and two 3-bromopyridine ligands (Figure 3.2.1). The Mn^{II} ions are connected into chains by the NCS bridges. The two N atoms and two S atoms from the NCS bridges and two N atoms from the pyridine rings are all in *trans* coordination. The *trans-trans-trans* coordination causes that the chain is linear (Figure 3.2.2).

Table 3.2.1 The unit cell parameters of **Mn-1**. [54]

Parameter	Value
<i>A</i>	9.6178(6) Å
<i>B</i>	5.7280(3) Å
<i>c</i>	14.6355(8) Å
α	90°
β	102.360(6)°
γ	90°

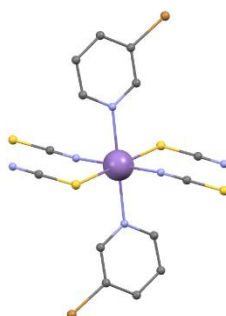


Figure 3.2.1 The view on the single Mn^{II} ion in **Mn-1**. Purple – Mn, grey – C, light blue – N, yellow – S, orange – Br, H – omitted.

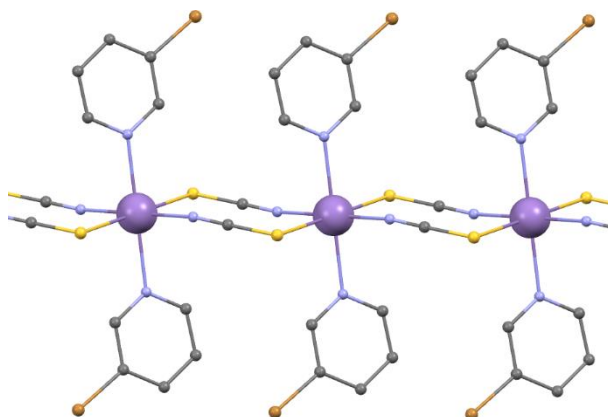


Figure 3.2.2 The view on the chain in **Mn-1**. The chains are along *c*. Purple – Mn, grey – C, light blue – N, yellow – S, orange – Br, H – omitted.

No hydrogen bonds are present between the chains.

3.3. Magnetic properties

The magnetization curve is presented in Figure 3.3.1. It was measured at 1.8 K. Throughout the whole field range, the magnetization increases with the field. At 50 kOe, the experimental points do not even approach saturation. Around 25 kOe, an inflection is very weakly visible. This can be a sign of the metamagnetic transition.

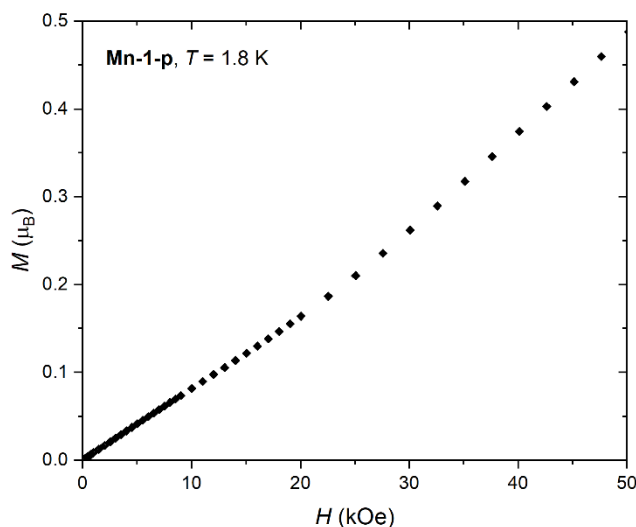


Figure 3.3.1 Field dependence of magnetization measured for **Mn-1-p** at 1.8 K.

To check, if **Mn-1** orders, there were measured zero-field and field cooled susceptibilities at 100 Oe (Figure 3.3.2). The zfc and fc curve overlap, no sharp peaks or irreversibility is observed which would suggest the magnetic ordering. Only a very wide maximum is observed. Around 4 K, the susceptibility increases once again. This can be caused by a small fraction of single, paramagnetic Mn^{II} ions.

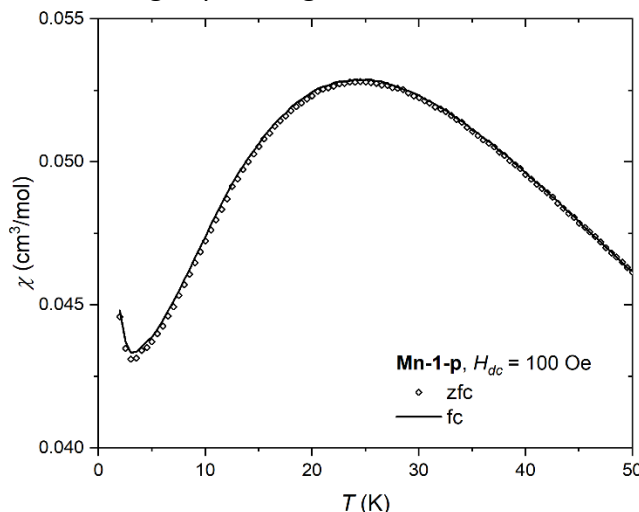


Figure 3.3.2 Zero-field and field cooled susceptibilities measured at 100 Oe for **Mn-1-p**.

For the broad maximum, the antiferromagnetic interaction is responsible, which is confirmed by the χT vs. T dependence (Figure 3.3.3). χT decreases with the decreasing temperature, in the whole range. The value at 300 K is reaching $4.06 \text{ cm}^3\text{K/mol}$, which is correct for Mn^{II} ions with spins equal to $5/2$, and g factor around 2. From the crystal structure analysis, the conclusion is that the exchange interaction is between the Mn^{II} ions along the thiocyanate bridges, it is, along the chains. The susceptibility of such spin chains can be modeled with the Fisher model, according to the equation 1.5.2, for $S = 5/2$ (Figure 3.3.3, Figure 3.3.4).

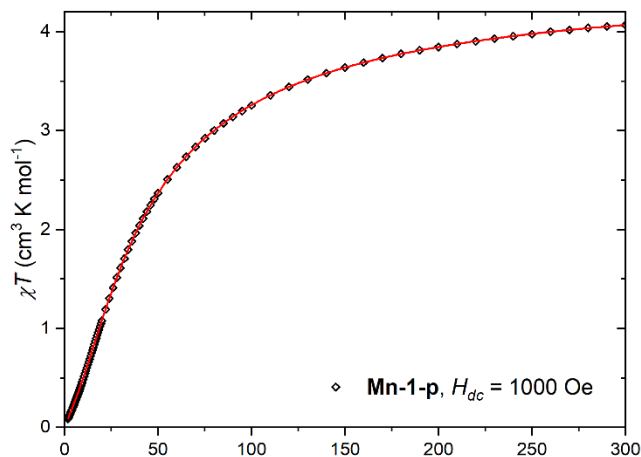


Figure 3.3.3 The magnetic susceptibility for **Mn-1-p** presented as χT vs. T . The solid line represents the fit of eq. 1.5.2.

The fit was performed in the range 15 – 300 K. The obtained values are $J/k_B = -5.76(5)$ K and $g = 2.04(5)$. This confirms the expectation about the antiferromagnetic type of exchange interaction along the chain. Below 10 K, the fit deviates from the experimental points

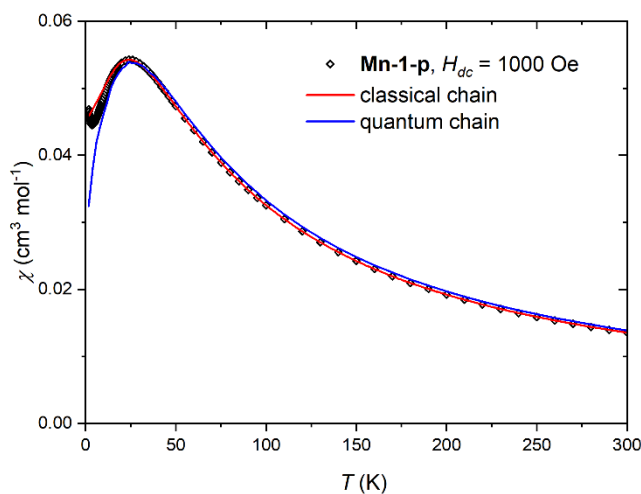


Figure 3.3.4 The temperature dependence of the magnetic susceptibility for **Mn-1-p**. The red line represents the fit of eq. 1.5.4, the blue line represents the result of the simulation.

The model used above was derived by Fisher for the classical Heisenberg chain. There were also performed simulations using the ALPS package. The simulation was performed for a quantum Heisenberg chain. The simulation was performed for a chain comprising 100 units in the temperature range from 300 to 1.8 K. The initial parameters were: spin: 5/2, $J/k_B = -5.76$ K, thermalization: 50000, sweeps: 400000, algorithm: loop, model: spin. To run the simulation, the *dirloop_sse* program was used. The result is presented in Figure 3.3.4. The quantum chain describes better the low-temperature part of the dependence. It starts to deviate also below 10 K, but in the opposite direction than the

classical model. On the basis of the simulation, there was estimated the fraction of the paramagnetic ions. There was taken the difference between the experimental and simulated value of the susceptibility at 1.8 K. For that temperature there was calculated the susceptibility for one mole of the Mn^{II} ions: $\chi = \frac{Ng^2\mu_B^2}{3k_B T} S(S + 1)$, for $S = 5/2$, and g taken from the classical chain fit: 2.04; $\chi = 2.53 \text{ cm}^3/\text{mol}$. Then, the difference was divided by the calculated χ value. The fraction is estimated for 0.58%.

The inflection on the magnetization curve cannot be associated with overcoming the antiferromagnetic interaction along the chain, because the estimated metamagnetic field for $S = 5/2$ and $J/k_B = -5.76 \text{ K}$, is 429 kOe. It is much higher than the experimentally observed value of 26 kOe. Therefore, its origin remains unknown.

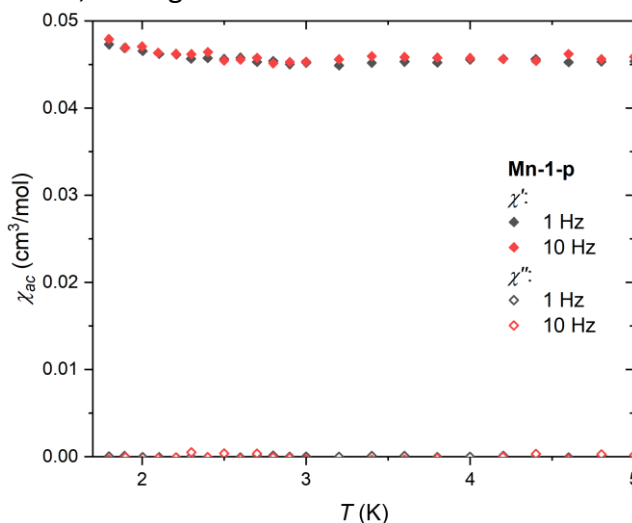


Figure 3.3.5 The ac magnetic susceptibility measured without the dc field for **Mn-1-p**.

The ac magnetic susceptibility for **Mn-1-p** measured at $H_{dc} = 0$ and $H_{ac} = 3 \text{ Oe}$ (Figure 3.3.5), shows zero imaginary component implicating the lack of the relaxation down to 1.8 K. None of the similar compounds shows the slow magnetic relaxation of single chains.[55]

3.4. Summary

$\text{Mn}(\text{NCS})_2(3\text{-bromopyridine})_2$ is a compound in which every Mn^{II} ion is coordinated by four NCS bridges and two 3-bromopyridine ligand. This coordination is *trans-trans-trans*, which makes the structural chains linear. The intrachain interaction is mediated through the NCS bridges and is antiferromagnetic. The magnetic relaxation of single chains is not observed. A compound with very similar properties is $\text{Mn}(\text{NCS})_2(4\text{-cyanopyridine})_2$. [55] However, this systems orders, in contrary to **Mn-1**.

4. Magnetic properties of $\text{Ni}^{\text{II}}(\text{NCS})_2(3\text{-ethylpyridine})_2$

In this chapter, there are presented the result of magnetic investigations of $[\text{Ni}(\text{NCS})_2(3\text{-ethylpyridine})_2]_n$. Two structures of this compound are known: the first one, containing only linear chains (**Ni-1**), and the second one containing linear and corrugated chains (**Ni-2**). The results of investigation presented in this thesis were published in [56]. The samples were provided and chemically characterized by the group of prof. Näther.

Symbols:

Ni-1 - $[\text{Ni}(\text{NCS})_2(3\text{-ethylpyridine})_2]_n$, linear chains.

Ni-2 - $[\text{Ni}(\text{NCS})_2(3\text{-ethylpyridine})_2]_n$, linear and corrugated chains.

Ni-1-p – powder sample of **Ni-1**.

Ni-2-p – powder sample of **Ni-2**.

4.1. Syntheses

The powder sample of **Ni-1 (Ni-1-p)** can be obtained by mixing the $\text{Ni}(\text{NCS})_2$ with 3-ethylpyridine in 1:2 molar ratio in the mixture of water and ethyl acetate (1:3 volume ratio). The amounts used for the synthesis of the sample are: 1 mmol of $\text{Ni}(\text{NCS})_2$, 2 mmol of 3-ethylpyridine, 0.5 ml of H_2O , and 1.5 ml of ethyl acetate. The mixing lasted 16 hours. The crystal structure of this form of the compound was obtained by performing SCXRD for a small single crystal. It was obtained differently than the powder. $\text{Ni}(\text{NCS})_2$ was dissolved in water (1 mmol in 0.5 ml). The solution was layered with 0.5 ml of ethyl acetate, in a way to avoid mixing the inorganic and organic parts. To the organic phase, the 3-ethylpyridine was added. The mixture was left at ease, to enable the slow diffusion of the substrates. The single crystals suitable for SCXRD were obtained after weeks.

The powder sample of **Ni-2 (Ni-2-p)** can be obtained by mixing the $\text{Ni}(\text{NCS})_2$ with 3-ethylpyridine in 1:2 molar ratio in ethyl acetate. The amounts used for the synthesis of the sample are: 1 mmol of $\text{Ni}(\text{NCS})_2$, 2 mmol of 3-ethylpyridine, and 2 ml of ethyl acetate. The mixing lasted 3 days. The crystal structure of this form of the compound was obtained by performing SCXRD for a small single crystal. It was obtained differently than the powder. $\text{Ni}(\text{NCS})_2$ and 3-ethylpyridine (1 mmol and 2 mmol) were mixed in 0.5 ml of water and 4 ml of acetate. The mixing lasted 4 days. Then, the residue was filtered. The filtrate was left at the ambient conditions and after weeks, the small single crystals suitable for SCXRD were obtained.

4.2. Crystal structure

The **Ni-1** form crystallizes in the triclinic system ($P\bar{1}$ space group). The unit cell parameters are presented in Table 4.2.1. There is only one crystallographically independent Ni^{II} position. In the unit cell, there are two Ni^{II} ions present. They are associated by the inversion (see the alignment of the pyridine rings, Figure 4.2.1). The Ni^{II} ions are octahedrally coordinated by four NCS bridges and two 3-ethylpyridine ligands. The NCS bridges connect the Ni^{II} ions into chains (Figure 4.2.1). Two of the NCS bridges are connected with the Ni^{II} ion by the nitrogen atoms, the other two by the sulfur atom. The 3-ethylpyridine ligands are connected to the Ni^{II} ion by the nitrogen atom in the pyridine ring. The positioning of the coordinating ligands in relation to each other decides the type of chain. In this case, the chain is linear, because the N and S atoms from thiocyanate groups, as well as the N atoms from pyridine rings, are all in *trans* coordination (*trans-trans-trans* coordination, Figure 4.2.2).

Table 4.2.1 The unit cell parameters of **Ni-1**. [56]

Parameter	Value
a	9.310 Å
b	10.516 Å
c	11.057 Å
α	68.06°
β	66.94°
γ	69.49°

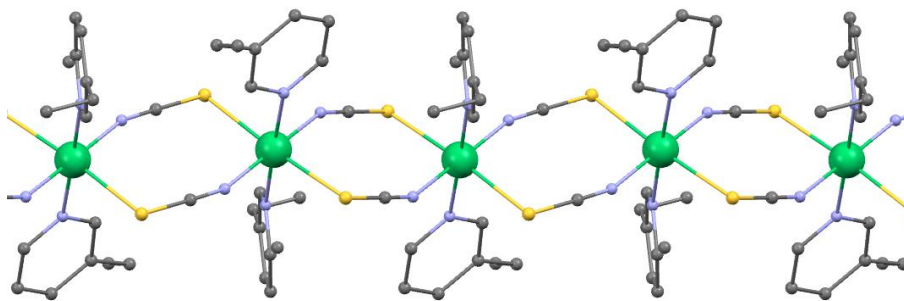


Figure 4.2.1 The view along b crystallographic axis for **Ni-1**. The chains are along c . Green – Ni, grey – C, light blue – N, yellow – S, H – omitted.

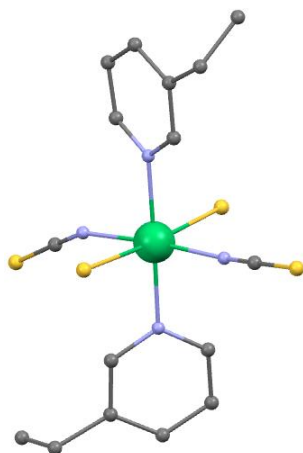


Figure 4.2.2 The view on the single Ni^{II} ion in **Ni-1**. Green – Ni, grey – C, light blue – N, yellow – S, H – omitted.

Ni-2 also crystallizes in $P\bar{1}$. The unit cell parameters are presented in table 4.2.2. The surrounding of the Ni^{II} is quantitatively the same, however, in some chains, the coordination is different. The **Ni-2** isomer consists of linear and corrugated chains, which are perpendicular to each other (Figure 4.2.3, Figure 4.2.4). In the linear chain, there are two crystallographically independent Ni^{II} positions, the surrounding atoms are in *trans-trans-trans* coordination (Figure 4.2.5, left). The chains are slightly different than in **Ni-1**. In the corrugated chain, there is only one position of Ni^{II}, however, the S atoms are in *cis* coordination, the same as the N atoms from pyridine rings. The N atoms from thiocyanate bridges are still in *trans* coordination (*cis-cis-trans* coordination, Figure 4.2.5, right).

Table 4.2.2. The unit cell parameters of **Ni-2**. [56]

Parameter	Value
<i>a</i>	10.103 Å
<i>b</i>	11.216 Å
<i>c</i>	18.545 Å
α	106.44°
β	94.39°
γ	111.05°

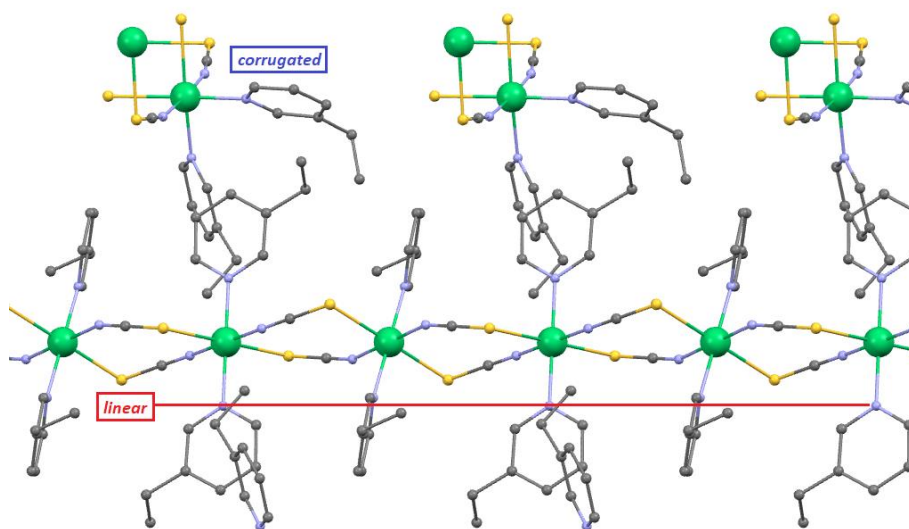


Figure 4.2.3 The view along a for **Ni-2**. The linear chains are along b . The solid line represents the direction of the chain. Green – Ni, grey – C, light blue – N, yellow – S, H – omitted.

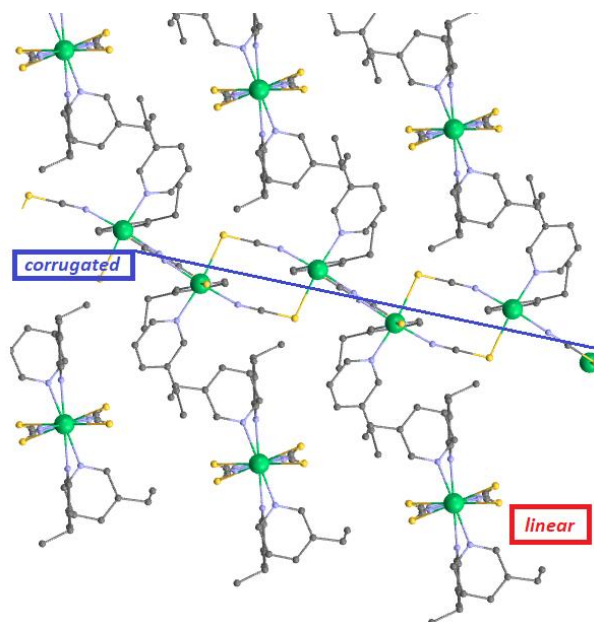


Figure 4.2.4 The view along b for **Ni-2**. The corrugated chains are approximately along a . The solid line represents the direction of the chain. Green – Ni, grey – C, light blue – N, yellow – S, H – omitted.

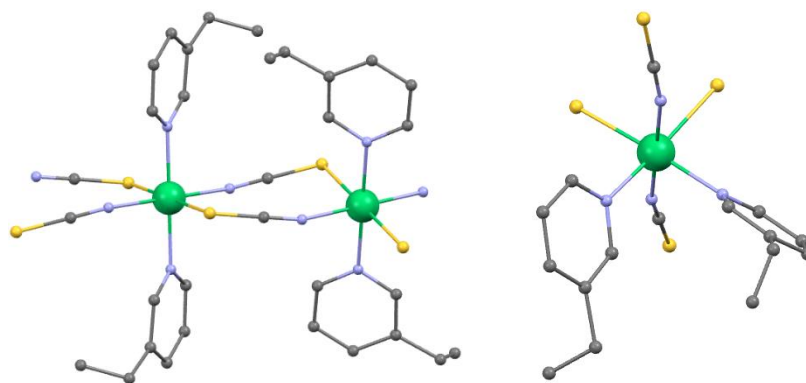


Figure 4.2.5 The view on the Ni^{II} ions in the linear (left) and corrugated (right) chain in **Ni-2**. Green – Ni, grey – C, light blue – N, yellow – S, H – omitted.

In both isomers, there are very weak interchain hydrogen bonds between the hydrogen from the ethyl group and the N atom from the thiocyanate bridges. For **Ni-1**, hydrogen bonding is also created with the S atom from the thiocyanate bridge. All the bonds are weak, as the characteristic angles are far from 180° (between 110 and 120°).

4.3. Magnetic properties

For both isomers, magnetic and calorimetric measurements were performed. The magnetization vs. field dependences were measured at 2 K, from 50 to 0 kOe (Figure 4.3.1). No metamagnetic transition or hysteresis is observed at this temperature, which suggests the paramagnetic state. However, the increase of magnetization from zero field is steep, which can indicate some kind of interaction in both systems. At 50 kOe, the magnetization still increases, it seems to be far from saturation. This is probably caused by the zero-field splitting effects of the Ni^{II} ions.

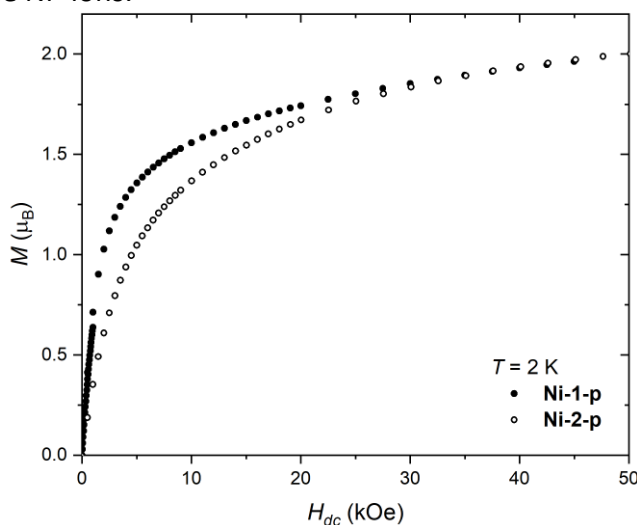


Figure 4.3.1 Field dependence of magnetization measured for **Ni-1-p** and **Ni-2-p** at 2 K.

Magnetic susceptibility was measured at 30, 100, and 1000 Oe. The zero-field and field cooled susceptibilities do not differ from each other, for both isomers (Figure 4.3.2). It confirms the paramagnetic state for both isomers down to 1.9 K.

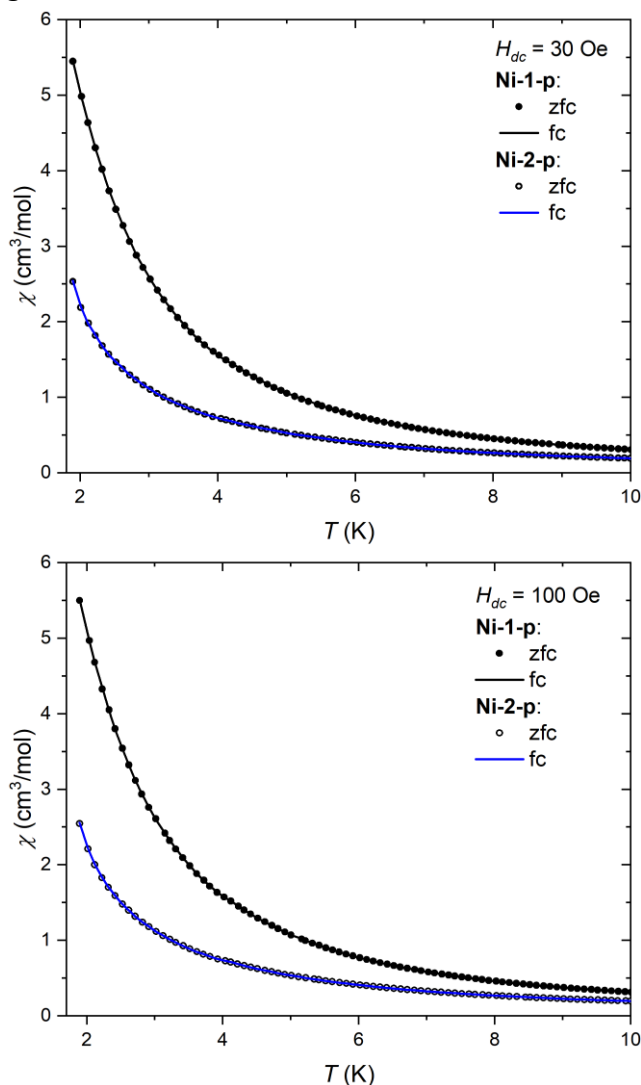


Figure 4.3.2 Zero-field and field cooled susceptibilities measured at 30 and 100 Oe for **Ni-1-p** and **Ni-2-p**.

The magnetic susceptibility and temperature product at 1000 Oe for both isomers (Figure 4.3.3) takes 1.20 cm³ K mol⁻¹ value at 300 K, which is characteristic for spins $S = 1$, with g equal to 2.18. The χT product in both cases increases with the decreasing temperature, which is the manifestation of the ferromagnetic interaction along the structural chains. For the **Ni-2** isomer, the increase is gentler, suggesting a lower exchange. At the low temperature, the χT product achieves a maximum for **Ni-1-p**, for **Ni-2-p** such effect is not observed down to 1.8 K. This is an effect of the zero-field splitting. The spin chains comprised of the Ni^{II} can be modeled with the equation 1.5.5.

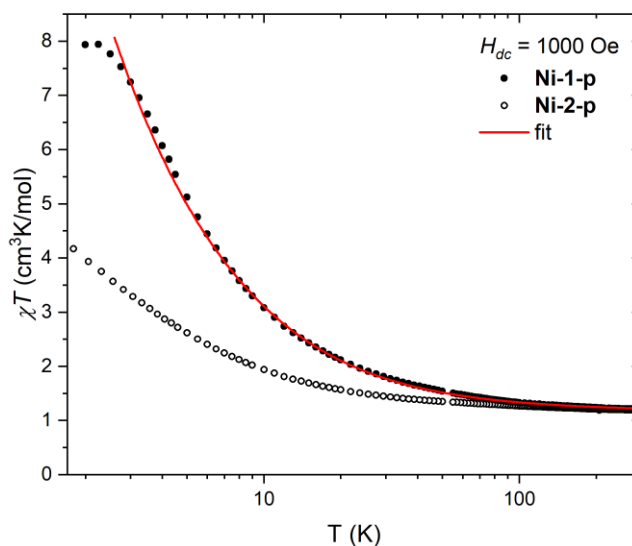


Figure 4.3.3 The magnetic susceptibility for **Ni-1-p** and **Ni-2-p** presented as χT vs. T . The solid line represents the fit of eq. 1.5.5.

The fit was performed only for **Ni-1-p**. It was performed from 10 to 300 K, as the used formula was obtained only for isotropic Heisenberg spins, the ZFS effects were not included, the same as the interchain interactions. Due to those reasons, the fit extrapolated below 10 K starts to deviate from the experimental points below 5 K. The exchange J/k_B is equal to 10.42(6) K, the g factor is 2.16(1). The value of J is one of the largest among similar linear chain compounds.[48] For **Ni-2-p**, the fit in the same range gives the averaged value of $J/k_B = 4.4$ K with $g = 2.18$, however, such fit cannot be treated as correct, due to the presence of two types of chains in the structure, and some average of their properties is observed in the measurements. The pure samples containing only one type of the chains present in **Ni-2-p** (linear or corrugated) were not possible to synthesize.

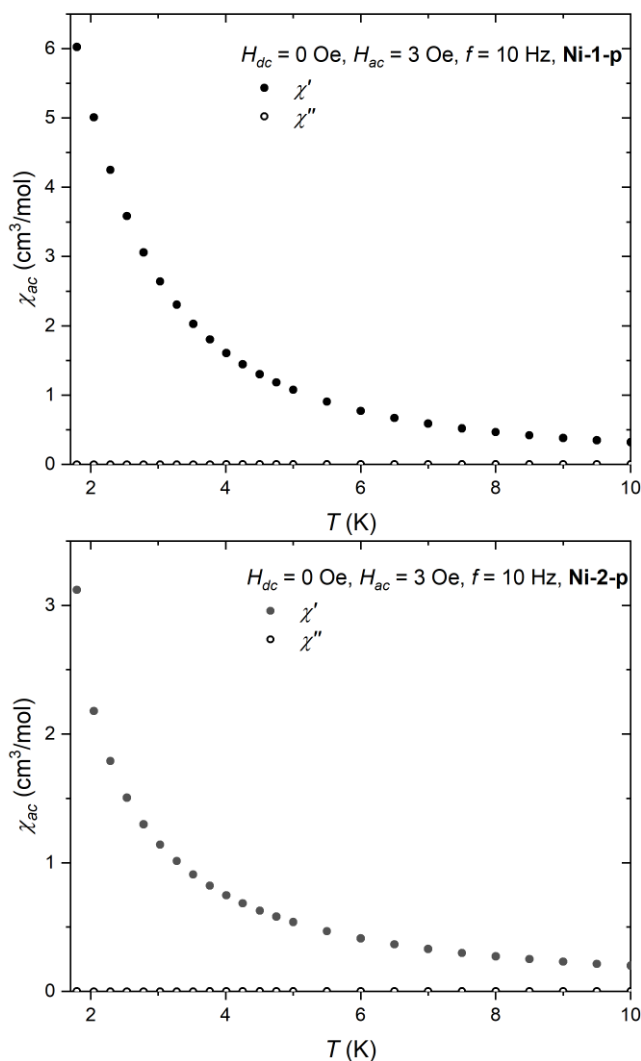


Figure 4.3.4 The ac magnetic susceptibility measured without the dc field for **Ni-1-p** and **Ni-2-p**.

The ac magnetic susceptibility for both isomers shows zero imaginary component implicating the lack of relaxation down to 1.8 K (Figure 4.3.4). None of the similar compounds shows the slow magnetic relaxation of single chains.[48]

To check, if the isomers order, specific heat measurements were performed (Figure 4.3.5). For both compounds, a sharp peak is visible, for **Ni-1-p** at 1.30 K, for **Ni-2-p** at 1.34 K. The relatively low temperature of ordering is consistent with weak intrachain interaction and very weak hydrogen bonds between the neighboring chains, which are the pathway for the interchain exchange interaction.

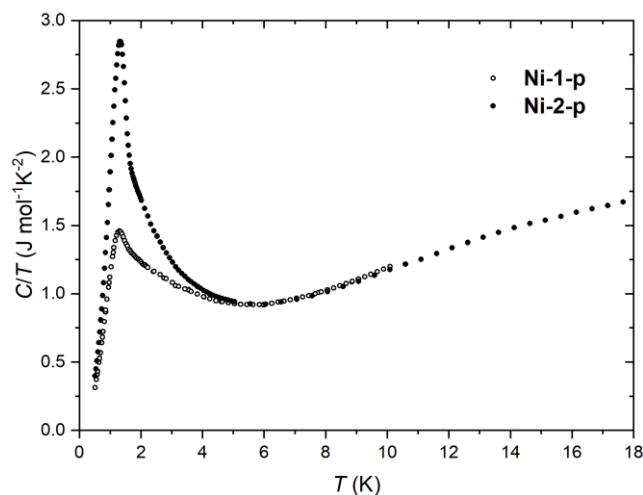


Figure 4.3.5 The temperature dependence of the specific heat for **Ni-1-p** and **Ni-2-p** 0 Oe.

4.4. Summary

In $\text{Ni}(\text{NCS})_2(3\text{-ethylpyridine})_2$ compounds, every Ni^{II} ion is coordinated by four NCS bridges and two 3-bromopyridine ligand. Depending on the coordination, the chain is linear (*trans-trans-trans*) or corrugated (*cis-cis-trans*). The intrachain interaction is mediated through the NCS bridges and is ferromagnetic for both types of chains. The exchange is better mediated for the linear chains. However, the exact value of the exchange constant is not easily derived for **Ni-2-p** from magnetic susceptibility, as the inseparable mixture of linear and corrugated chains is present in this isomer. The exact analysis of the investigated spin chains based on the Ni^{II} ion is in general hindered because of the strong ZFS effect in the low temperature, which is not easily modeled.[48]

5. Magnetic properties of $\text{Co}^{\text{II}}(\text{NCS})_2(\text{ligand})_2$ compounds

In this chapter, there are presented the results of magnetic investigations of $\text{Co}(\text{NCS})_2(\text{ligand})_2$ compounds: $\text{Co}(\text{NCS})_2(4-(3\text{-phenylpropyl})\text{pyridine})_2$ (**Co-1**), $\text{Co}(\text{NCS})_2(4\text{-methoxypyridine})_2$ (**Co-2**) and $\text{Co}(\text{NCS})_2(\text{aniline})_2$ (**Co-3**). The main research concerns the single crystals of these compounds. The investigations of powders, which were performed earlier, are used for comparison.

5.1. Magnetic properties of $\text{Co}^{\text{II}}(\text{NCS})_2(4-(3\text{-phenylpropyl})\text{pyridine})_2$

The magnetic investigations of $\text{Co}(\text{NCS})_2(4-(3\text{-phenylpropyl})\text{pyridine})_2$ (**Co-1**) started with a powder sample in 2014.[59] **Co-1** displays the properties of the ferromagnetic Ising chain and it orders ferromagnetically. In 2017 a single crystal was synthesized by the group of prof. Christian Näther, and after 4 years, in 2021, the research on that sample was published.[57] In this subchapter, the results of this research are presented.

Symbols:

Co-1 – $\text{Co}(\text{NCS})_2(4-(3\text{-phenylpropyl})\text{pyridine})_2$

Co-1-c – single crystal sample of **Co-1**

CoCd-1-p – powder sample of $\text{Co}_x\text{Cd}_{1-x}(\text{NCS})_2(4-(3\text{-phenylpropyl})\text{pyridine})_2$, $x = 0.013$

5.1.1. Synthesis

The synthesis of a single crystal suitable for magnetic measurements for $\text{Co}(\text{NCS})_2(\text{ligand})_2$ family takes a significantly longer time than the synthesis of a powder sample. **Co-1-c** was the first single crystal from this family obtained in a proper size, however, it was achieved by accident. $\text{Co}(\text{NCS})_2$ (0.25 mmol) and 4-(3-phenylpropyl)pyridine (0.50 mmol) in ethanol (1.5 ml) was mixed and left still for crystallization of small single crystals for SCXRD. A few syntheses with such a molar ratio (1:2) were prepared. The small crystals were indeed obtained after a week. Then, the syntheses were left with no interest. After months, it was discovered that in one of the vials, a large single crystal grew. It was 11 mm long and had dark pink color (Figure 5.1.1). Its monocrystalline character and crystal structure were confirmed by the SCXRD.

Such a large crystal could not be used for magnetic measurements, as it would not fit into the sample chamber. It was cut into smaller pieces, one of which was used for magnetic measurements. It has 5.73 mg and it was packed into a special holder in a way ensuring an easy identification of the direction of measurement (Figure 5.1.2).

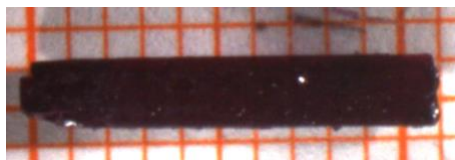


Figure 5.1.1 A photo of the single crystal of **Co-1-c**. The grid is 1 mm.

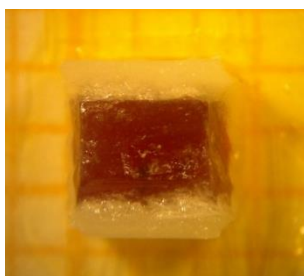


Figure 5.1.2 A photo of a part of the single crystal of **Co-1-c**, packed for magnetic measurements.

5.1.2. Crystal structure

The compound crystallizes in a monoclinic crystallographic system, the space group is $P2_1/n$. There are 4 formula units $\text{Co}(\text{NCS})_2(4-(3\text{-phenylpropyl})\text{pyridine})_2$ in the unit cell. The unit cell parameters are presented in Table 5.1.1.

Table 5.1.1 The unit cell parameters of $\text{Co}(\text{NCS})_2(4-(3\text{-phenylpropyl})\text{pyridine})_2$. [59]

Parameter	Value
a	11.2774(6) Å
b	16.0343(8) Å
c	15.8148(10) Å
α	90°
β	96.240(5)°
γ	90°

There are two crystallographically independent Co^{II} positions. The Co^{II} ions are connected by the thiocyanate bridges into chains. The independent Co^{II} ions are positioned alternatively in a single chain (Figure 5.1.3). There are two types of chains in the structure, and both of them are along the a crystallographic axis (Figure 5.1.4). They are related to each other by the 2-fold rotation symmetry.

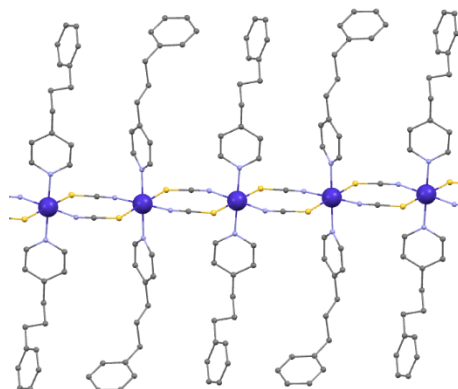


Figure 5.1.3 The view on the single chain in **Co-1**. Blue – Co, grey – C, light blue – N, yellow – S, H – omitted. The chains are along a .

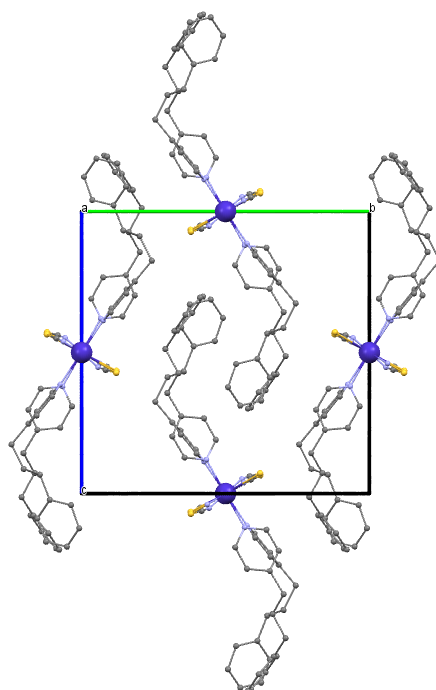


Figure 5.1.4 The view along a on the unit cell in **Co-1**. Blue – Co, grey – C, light blue – N, yellow – S, H – omitted.

The nitrogen and sulfur atoms' coordination around the Co ion is in all cases *trans* (*trans-trans-trans* coordination, Figure 5.1.5). This makes the chains linear. There are no hydrogen bonds present between the chains.

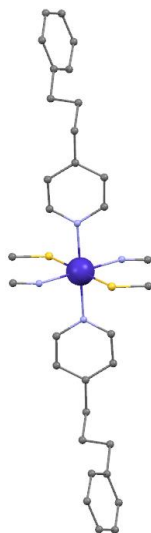


Figure 5.1.5 The view on one of the Co^{II} ion and its coordination in **Co-1**. Blue – Co, grey – C, light blue – N, yellow – S, H – omitted.

Directions of measurement were chosen to be perpendicular to each other and are:

$$X = [100],$$

$$Y \perp (01\bar{1}),$$

$$Z = X \times Y.$$

5.1.3. Specific heat

The specific heat measurement for **Co-1-c** was performed at 0 Oe. It is presented in Figure 5.1.6 as C/T vs. T . At 3.39 K, a sharp peak is visible, which indicates the magnetic ordering. In Figure 5.1.6, there are also presented the data for a previously investigated powder sample (**Co-1-p**).^[59] The high-temperature part of the data was used for a fit of the Debye, Einstein, and Ising model, as it overlaps with the points for a single crystal. For **Co-1-c**, the data above 20 K were measured in high intervals. The determined J_{Ising}/k_B value is 32.8(2) K. The other fitted parameters are $\Theta_D = 83.30(68)$ K, $\Theta_E = 149.6(7.0)$ K, $a_D = 3.44(8)$, $a_E = 7.4(1.4)$. The interaction between the chains was not included in this analysis. The compound is a ferromagnet (see section 5.1.4) and for ferromagnets, the T_c should not depend on the field.

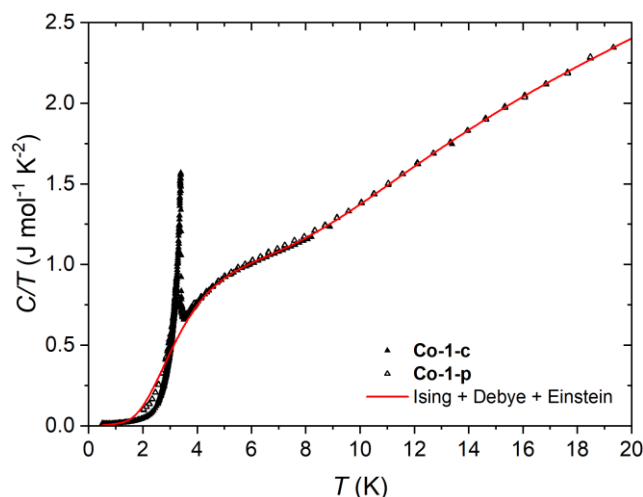


Figure 5.1.6 Specific heat presented as C/T vs. T , for **Co-1-c** and **Co-1-p**, at $H_{dc} = 0$ Oe. The red line represents the fit of the combination of Ising, Debye, and Einstein model.

The entropy change, determined from the integration of the C_{mag}/T vs. T dependence in the range from 40 to 2 K, is equal to $4.92 \text{ J mol}^{-1} \text{ K}^{-1}$, slightly lower than the theoretical value determining the ordering of the $\frac{1}{2}$ spins: $R \ln 2 = 5.72 \text{ J mol}^{-1} \text{ K}^{-1}$.

5.1.4. Magnetization curves

The magnetization curves were measured for 4 directions: **X**, **Y**, **Z**, and easy axis, at 1.8 K (Figure 5.1.7). In the measurement along the easy axis, the sample could move freely. In the field, the crystal positioned itself along the averaged axis (**ea**). The average for the measurement is over the two Co^{II} ions and the two types of chains. For all 4 curves, there is no metamagnetic transition visible, indicating the ferromagnetic type of ordering (ferromagnetic type of interaction between the chains).

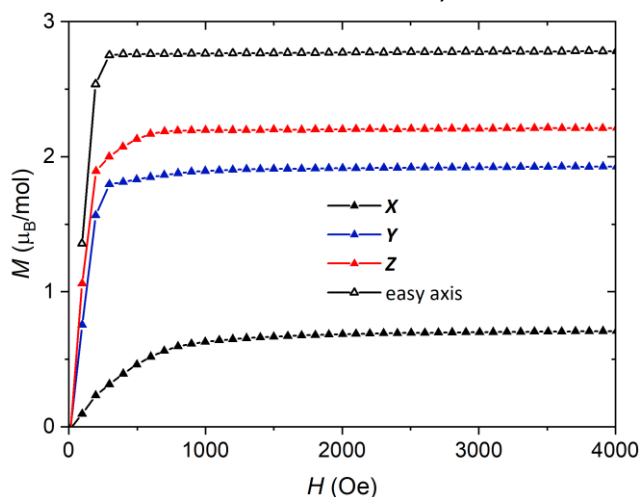


Figure 5.1.7 Field dependences of magnetization measured for **Co-1-c** at 1.8 K for 4 directions. The lines are to guide the eye.

The magnetization increases with the field at the beginning of the curve. This is an effect of demagnetization, the curve should instantly get to the saturation value after

turning on the field. The demagnetization effect is very important for ferromagnets. Therefore, the magnetic susceptibility was corrected for that effect before it was analyzed.

5.1.5. Easy axis determination

The values of saturation of magnetization were used to determine the easy axis direction experimentally. The experimental confirmation of the easy axis direction is a very important point of these investigations, as it is impossible to determine it for a powder sample. Before the **Co-1-c** sample, the easy axis was known only from *ab initio* calculations. It is close to the Co-N_{pyridine} bond. The *ab initio* calculations provide not only the direction of the easy axis, but also, the *g* factors values and the energy gaps between the ground and the first excited states (Table 5.1.2). The easy axes directions as well as the mentioned values are slightly different for the two Co ions, as the crystal field is for them slightly different. The *ab initio* calculations were performed by dr Michael Böhme from Jena University.

Table 5.1.2 The values of *g* factors and the energy gaps (between the ground and first excited state) for the two Co^{II} ions in **Co-1** derived from the *ab initio* calculations.[57]

g_x	g_y	g_z	E (K)
1.883	2.836	7.285	232
1.952	3.192	6.926	202

To the calculation of the easy axis of **Co-1-c**, the values of magnetization at 4 kOe were taken. The calculations were performed using the Mathematica software. To recalculate the crystallographic system to the Cartesian system, the following equation was used:

$$\begin{pmatrix} x_c \\ y_c \\ z_c \end{pmatrix} = \begin{pmatrix} a & 0 & a \cos \beta \\ 0 & b & 0 \\ 0 & 0 & c \sin \beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad (5.1.1)$$

where x_c , y_c , and z_c represent the coordinates of the vector in the Cartesian system, a , b , c , and β are the unit cell parameters, the matrix is the conversion matrix for the monoclinic system, and x , y , z represents the crystallographic coordinates. To simplify the calculations, it is assumed that there is one easy axis in one chain (the independence of the two Co ions is neglected). Therefore, the magnetic easy axis vectors for two types of chains in the Cartesian system are:

$$\mathbf{m}_1 = \begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}; \quad \mathbf{m}_2 = \begin{pmatrix} -m_x \\ m_y \\ -m_z \end{pmatrix}. \quad (5.1.2)$$

On that basis, there are created 4 equations:

$$M_X = \frac{1}{2}(|\mathbf{m}_1 \cdot \mathbf{X}| + |\mathbf{m}_2 \cdot \mathbf{X}|), \quad (5.1.3)$$

$$M_Y = \frac{1}{2}(|\mathbf{m}_1 \cdot \mathbf{Y}| + |\mathbf{m}_2 \cdot \mathbf{Y}|), \quad (5.1.4)$$

$$M_Z = \frac{1}{2}(|\mathbf{m}_1 \cdot \mathbf{Z}| + |\mathbf{m}_2 \cdot \mathbf{Z}|), \quad (5.1.5)$$

$$M_{ea} = \frac{1}{2}(|\mathbf{m}_1 + \mathbf{m}_2|) \text{ or } M_{ea} = \frac{1}{2}(|\mathbf{m}_1 - \mathbf{m}_2|) \quad (5.1.6)$$

where M_X , M_Y , M_Z , and M_{ea} are the theoretical values of magnetization saturation. The values from the experiment (at 4 kOe) are: $M_{X-exp} = 0.708 \mu_B$, $M_{Y-exp} = 1.926 \mu_B$, $M_{Z-exp} = 2.212 \mu_B$, $M_{ea-exp} = 2.780 \mu_B$. These equations are incorporated into one equation on *chi-square* function:

$$\chi^2 = (M_X - M_{X-exp})^2 + (M_Y - M_{Y-exp})^2 + (M_Z - M_{Z-exp})^2 + (M_{ea} - M_{ea-exp})^2. \quad (5.1.7)$$

The equation was minimized, and the following $\mathbf{m}_1$ easy axis was obtained: (0.66, 1.79, 2.80) μ_B . The easy axis from the *ab initio* calculations is: (0.34, 1.92, 2.96) μ_B . The angle between the averaged over two Co^{II} ions easy axis determined experimentally and theoretically is 5.8°. The angle between the easy axis determined experimentally and the averaged direction of the Co-N_{ligand} bond is 7.5°. The angle between the easy axis determined theoretically and the averaged direction of the Co-N_{ligand} bond is 2.2°. This confirms the agreement of theory and experiment.

5.1.6. Magnetic susceptibility

The dc and ac magnetic susceptibility were corrected for demagnetization. As the demagnetization factor, $4\pi/3$ was taken for all directions, because the sample has approximately a shape of a prism. In Figure 5.1.8 and Figure 5.1.9, there are compared the measured susceptibilities and the susceptibilities corrected for demagnetization.

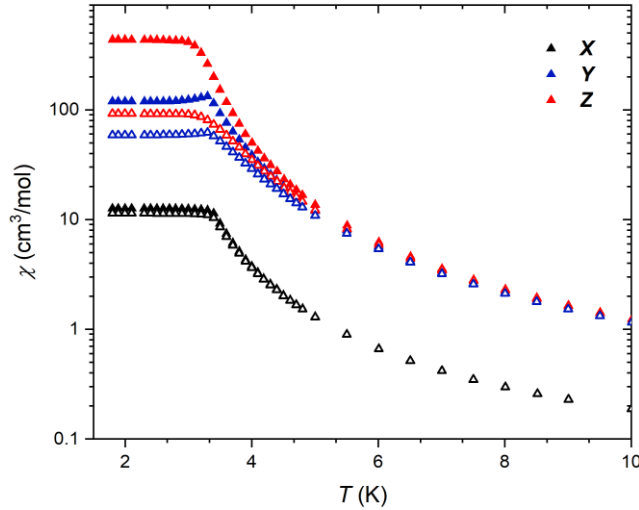


Figure 5.1.8 The magnetic susceptibility measured for **Co-1-c** at 100 Oe for 3 directions. Empty points – data from measurement. Full points – data corrected for demagnetization.

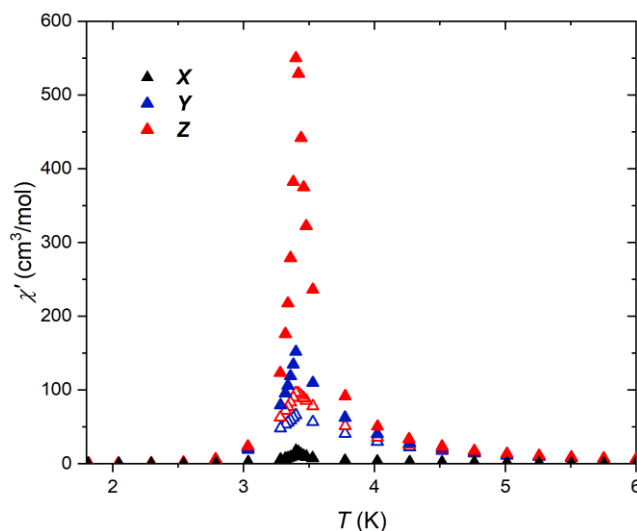


Figure 5.1.9 The ac magnetic susceptibility measured for **Co-1-c** at $H_{dc} = 0$ Oe and $H_{ac} = 3$ Oe for 3 directions, $f = 10$ Hz. Empty points – data from measurement. Full points – data corrected for demagnetization.

The magnetic susceptibility was averaged over the three perpendicular directions, to obtain data comparable with data obtained for a previously investigated powder sample.[59] The averaged magnetic susceptibility was analyzed with the Ising model with interchain interaction (equation 1.5.7 – 1.5.10) in the temperature range from 15 to 3.5 K (Figure 5.1.10). The fitted values are J , zJ' and g_z . g_x and g_y were included in the analysis as $g_{\perp}$ and it was fixed at 2.5, which is reasonable for Co^{II} ion in the distorted octahedron.[15] Also, taking into consideration the averaged values obtained from *ab initio* calculations (Table 5.1.2), the $g_{\perp} = \sqrt{\frac{g_x^2 + g_y^2}{2}} \approx 2.5$. The J_{Ising}/k_B value is 31.7(1) K, zJ'/k_B is 0.10(1) K and g_z is 7.28(3). This means the ferromagnetic interaction along the chains and the ferromagnetic interaction between them, and therefore, the ferromagnetic ground state of this compound. g_z factor is consistent with the value obtained from *ab initio* calculations. Below T_c , the data deviates from the fit, as the system orders. At T_c , the model diverges to infinity for a ferromagnet.

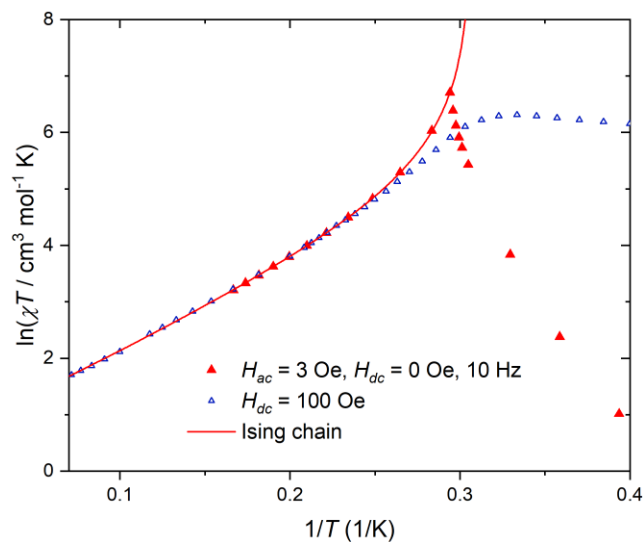


Figure 5.1.10 The magnetic susceptibility for **Co-1-c** analyzed with the Ising model.

5.1.7. Magnetic relaxation

The ac magnetic susceptibility was measured at 0 Oe, and its temperature dependence is presented in Figure 5.1.11. In χ' , a peak around 3.4 K is visible, consistent with a peak in specific heat responsible for magnetic ordering. The χ'' component is not zero below the T_c , indicating the presence of magnetic relaxation at zero field. The relaxation is further investigated by measuring the frequency dependence of the ac magnetic susceptibility at different temperatures at 0 Oe. For a ferromagnet, the magnetic relaxation of single chains takes the longest time at zero field. Therefore, only measurements without the field were performed. The direction **Y** was chosen, as the preliminary results showed the independence of the relaxation time on the direction of the measurement.

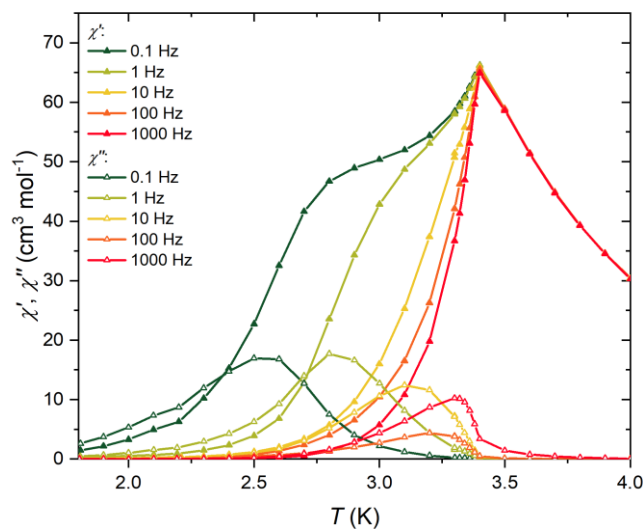


Figure 5.1.11 Ac magnetic susceptibility measured for **Co-1-c** at $H_{dc} = 0$ Oe and $H_{ac} = 3$ Oe along **Y**, for 5 different frequencies.

The frequency dependence of the ac magnetic susceptibility is usually presented as the Argand plot, it is, χ'' vs. χ' . The frequency dependence is no longer visible, however, it is easier to recognize the presence of other relaxation processes in such representation. In Figure 5.1.12, there is presented an Argand plot of the ac magnetic susceptibility for **Co-1-c**. There are clearly visible two semicircles at all temperatures, indicating the presence of two relaxation processes. The experimental data were analyzed within the double-mode Cole-Cole model. The relaxation times determined from this analysis are presented in Figure 5.1.13.

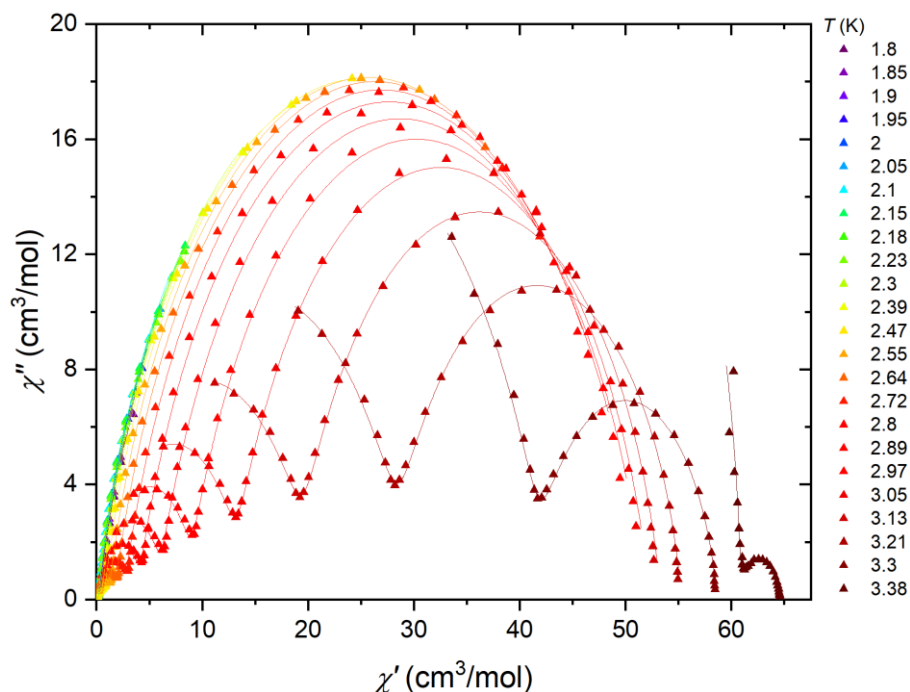


Figure 5.1.12 The Argand plot of the ac magnetic susceptibility measured for **Co-1-c** at $H_{dc} = 0$ Oe and $H_{ac} = 3$ Oe along **Y**. The lines represent the fits of the double-mode Cole-Cole model.

The relaxation times are significantly different for the two processes. The processes are called here **A-Co-1** and **B-Co-1**. Process **A-Co-1** is the slower process, process **B-Co-1** is the faster process. Both processes demonstrate Arrhenius-like behavior. For process **A-Co-1**, the two linear regimes can be distinguished, indicating the presence of *crossover*, this in turn indicates that the **A-Co-1** process is the **single chain relaxation** process. The second process has only one linear regime and is not interpreted as a single chain relaxation.

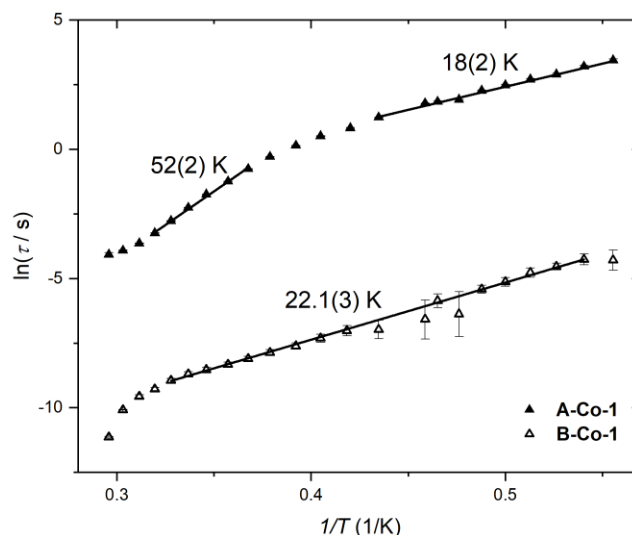


Figure 5.1.13 The relaxation times for **Co-1-c** along **Y**, $H_{dc} = 0$ Oe. The lines represent the fits of Arrhenius law.

The analysis of the single chain relaxation (process **A-Co-1**) is not as obvious as it would arise from the conventional approach presented in chapter 1.3. First of all, the energy barriers determined from the fit of the Arrhenius law were compared to the energy gap between the ground and first excited states of doublets. This gap was determined theoretically from the *ab initio* calculations, and they are 202 and 232 K for the two crystallographically independent Co^{II} ions. This energy gap should correspond to the effective energy barrier for the Orbach process and therefore, for the energy of anisotropy (Δ_A) in the single chain relaxation model. From the Arrhenius law, the energy barriers are 52 and 18 K for infinite and finite regimes, respectively. From that comparison, it is obvious that the Orbach process is an impossible pathway for the relaxation of single spins. Also, from the recalculation of the energy barriers using the equations:

$$\Delta_{\tau 1} = 2\Delta_{\xi} + \Delta_A = 52 \text{ K}, \quad (5.1.8)$$

$$\Delta_{\tau 2} = \Delta_{\xi} + \Delta_A = 18 \text{ K}, \quad (5.1.9)$$

the Δ_A value is negative. All of this leads to the conclusion that the conventional model cannot be used.

To check, if the Orbach process indeed does not contribute to the relaxation of single spins in **Co-1-c**, there was performed an indirect analysis for the isotypic compound, $\text{Co}_x\text{Cd}_{1-x}(\text{NCS})_2(4-(3\text{-phenylpropyl})\text{pyridine})_2$, $x = 0.013$ (**CoCd-1-p**). This compound imitates the behavior of single spins due to the magnetic dilution with Cd^{II} ions, which are diamagnetic. The dilution is high enough to remove the magnetic interactions between the Co^{II} ions in the chains and between the chains. The samples were in powder form. There were few batches investigated, a batch with $x = 0.013$ was chosen for further investigations. Such low content of the magnetic ions results in high noise in magnetic measurements. The chosen batch does not contain any impurities, there is no sign of magnetic ordering (Figure 5.1.14, Figure 5.1.15). The frequency dependences of the ac magnetic susceptibility were measured at different fields and temperatures and were analyzed with the single-mode Cole-Cole

model (Figures 5.1.16 – 5.1.22). Only one process is observed. The relaxation times are presented in Figure 5.1.23 and Figure 5.1.24.

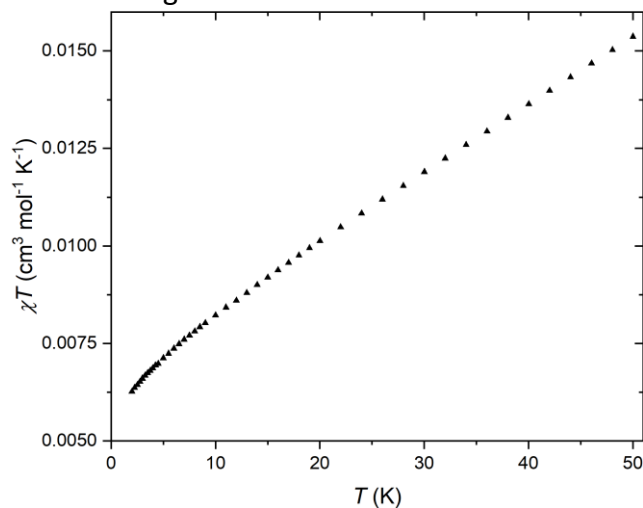


Figure 5.1.14 The magnetic susceptibility measured for **CoCd-1-p** at 1000 Oe presented as χT vs. T . Co molecules content in the sample is 1.3%.

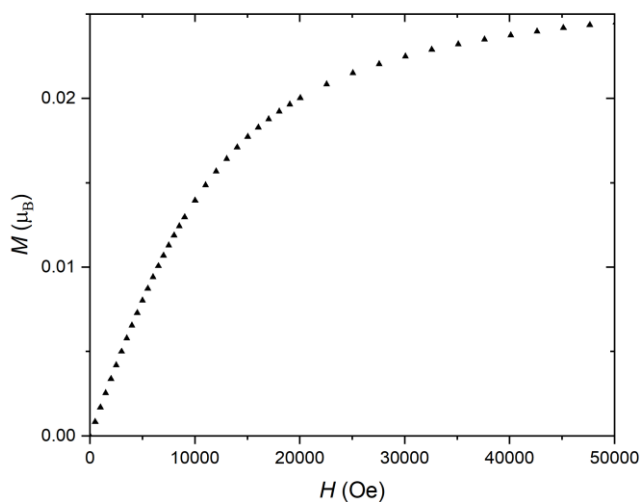


Figure 5.1.15 Field dependence of magnetization measured for **CoCd-1-p** at 2 K. Co molecules content in the sample is 1.3%.

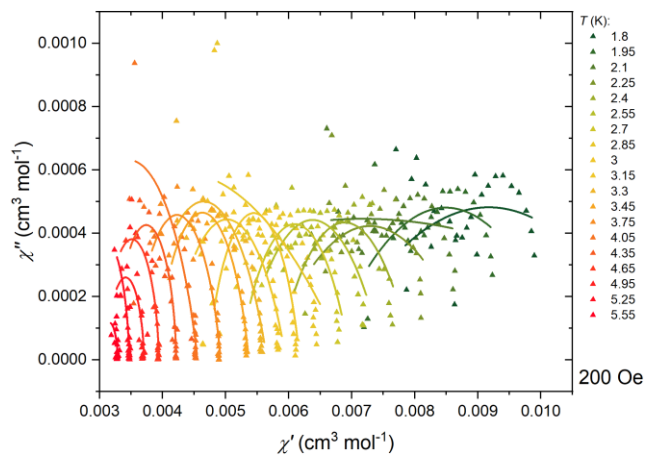


Figure 5.1.16 The ac magnetic susceptibility measured for **CoCd-1-p** at 200 Oe. The lines are the fits of the single-mode Cole-Cole model. Co molecules content in the sample is 1.3%.

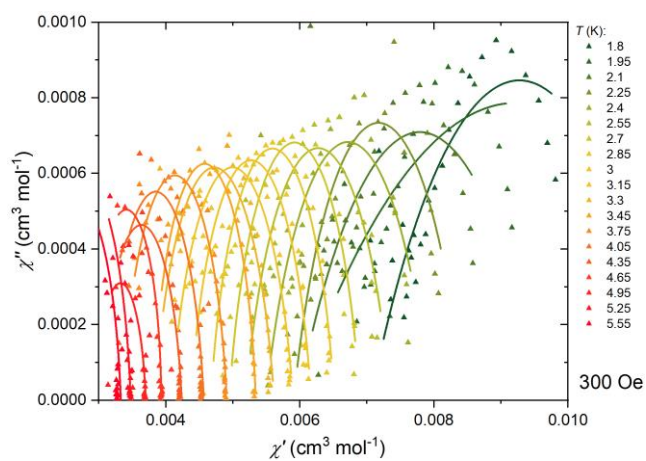


Figure 5.1.17 The ac magnetic susceptibility measured for **CoCd-1-p** at 300 Oe. The lines are the fits of the single-mode Cole-Cole model. Co molecules content in the sample is 1.3%.

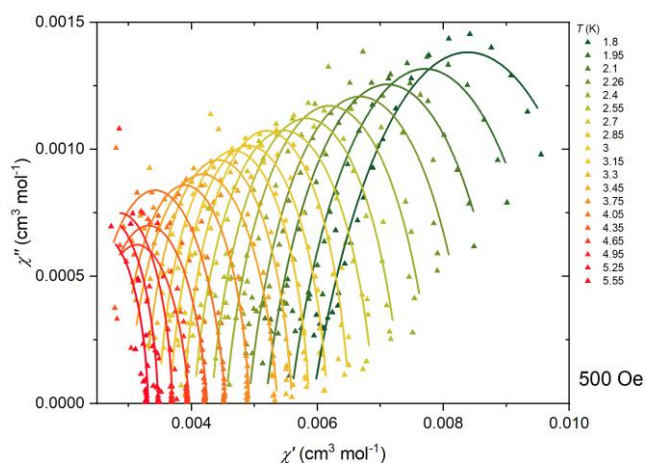


Figure 5.1.18 The ac magnetic susceptibility measured for **CoCd-1-p** at 500 Oe. The lines are the fits of the single-mode Cole-Cole model. Co molecules content in the sample is 1.3%.

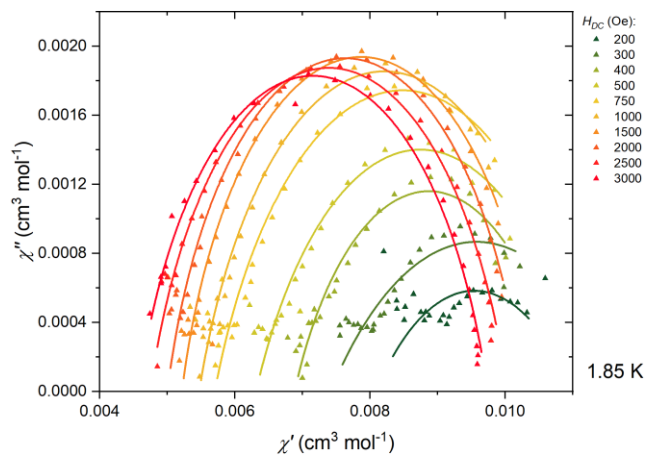


Figure 5.1.19 The ac magnetic susceptibility measured for **CoCd-1-p** at 1.85 K. The lines are the fits of the single-mode Cole-Cole model. Co molecules content in the sample is 1.3%.

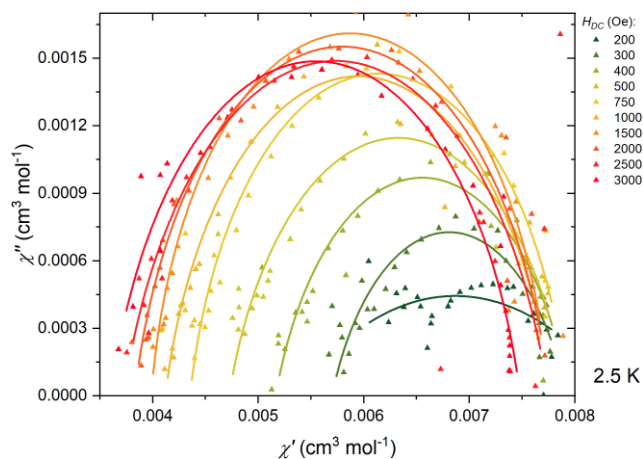


Figure 5.1.20 The ac magnetic susceptibility measured for **CoCd-1-p** at 2.5 K. The lines are the fits of the single-mode Cole-Cole model. Co molecules content in the sample is 1.3%.

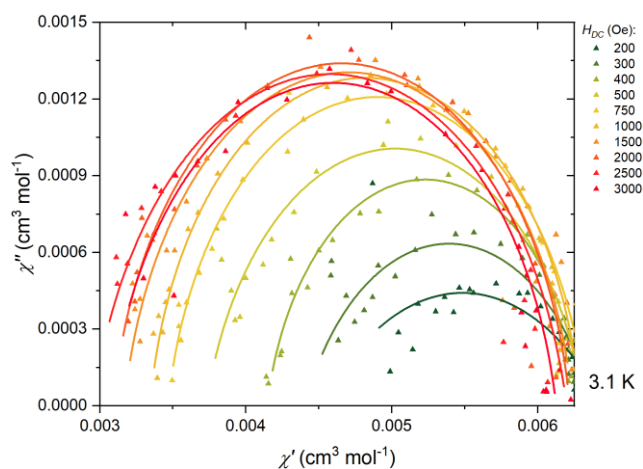


Figure 5.1.21 The ac magnetic susceptibility measured for **CoCd-1-p** at 3.1 K. The lines are the fits of the single-mode Cole-Cole model. Co molecules content in the sample is 1.3%.

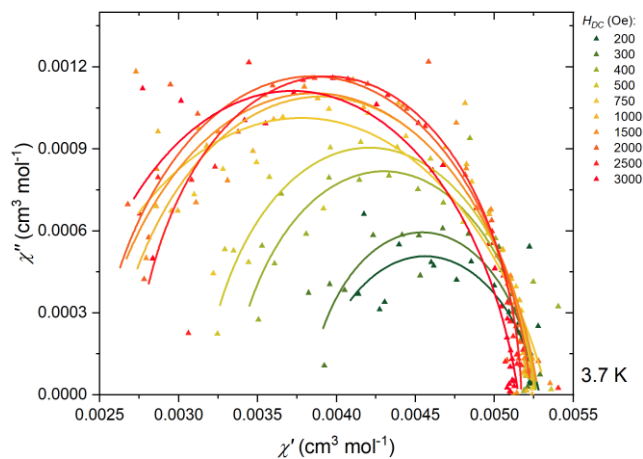


Figure 5.1.22 The ac magnetic susceptibility measured for **CoCd-1-p** at 3.7 K. The lines are the fits of the single-mode Cole-Cole model. Co molecules content in the sample is 1.3%.

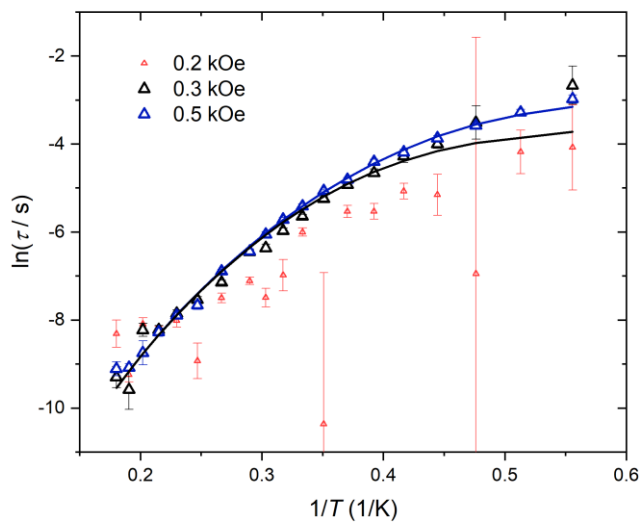


Figure 5.1.23 Temperature dependence of the relaxation time for an isotypic **CoCd-1-p** compound for different fields. Co molecules content in the sample is 1.3%.

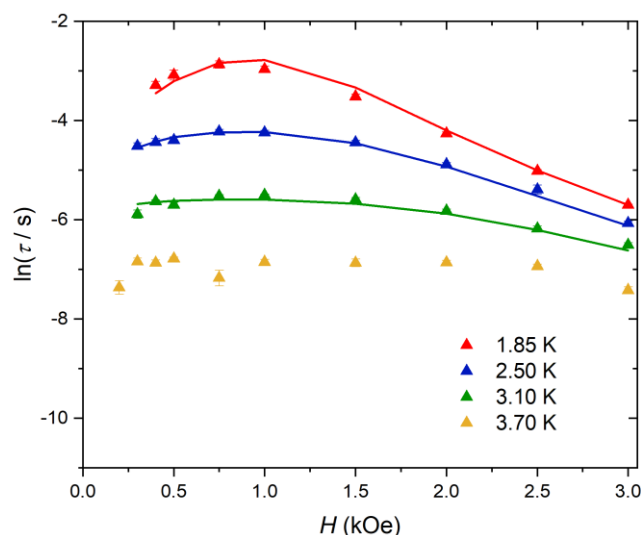


Figure 5.1.24 Field dependence of the relaxation time for an isotypic **CoCd-1-p** compound for different temperatures. Co molecules content in the sample is 1.3%.

At the low fields, the relaxation time becomes impossible to measure with high certainty. This is due to the fact, that the amplitude of this process becomes too low, it is, a small number of single spins relaxes. At zero field, the signal and the relaxation time are too low, and it is impossible to fit the Cole-Cole model to the ac magnetic susceptibility. The temperature dependences at the low temperature start to flatten and deviate from the linear course of the $\ln(\tau)$ vs. $1/T$ dependence. In the field dependence, there is visible a peak at the lowest temperature. This confirms the presence of other relaxation pathways. For sure, there are present qtm (dominating in the low fields) and direct process (dominating in the high fields). The Raman process is not excluded, as the curvature of the temperature dependence can be caused by it. To the temperature dependence at 0.3 and 0.5 kOe, and the field dependence at 1.85, 2.50, and 3.10 K, equation 1.3.6 was simultaneously fitted. The Orbach process was indeed impossible to fit with reasonable parameters. The obtained values of the parameters are: $n = 6.79(12)$, $C = 0.120(18) \text{ s}^{-1} \text{ K}^{-n}$ (Raman), $A = 1.951(50) \text{ s}^{-1} \text{ K}^{-1} \text{ kOe}^{-4}$ (direct). For qtm, it was impossible to fit both constants with properly high certainty, due to the lack of the experimental point at 0 Oe (the point at 0 Oe determines the value of B_1). Therefore, it was only a ratio of B_1 to B_2 determined: 5(2), for the field in kOe. The 1 in the denominator can be neglected – the measurement at 0 Oe is impossible to measure due to the very short relaxation time, therefore B_1 is very large. In such an approximate ratio, the other parameters of the fit remain the same, with an accuracy of their uncertainties.

The single spin contribution was taken at zero field and used in the analysis of the single chain relaxation. The single spin in the presented system can interact through the exchange interactions, but also through the dipole-dipole interaction. At 0 K, assuming the lack of the interchain exchange interactions, the dipole-dipole interactions and the anisotropy of spin, result in the ferromagnetic state. The magnetic relaxation starts with the single spin flip. The spin which can flip is a spin, for which the ac magnetic field in the

measurement is larger than the field resulting from the interchain dipolar interaction, but only along the easy axis. The field perpendicular to the easy axis is also important. The spins that relax, experience the perpendicular field also close to 0. Therefore, the spins that start the relaxation are located at the border of the 3D domains, in the middle of the chain, not in the 1D domain. This was obtained from the micromagnetic Monte Carlo simulations performed by M. Rams.[57]

However, the single spins relaxation in a chain must not necessarily be the same as for the non-interacting single spins, as the phonon spectra can be different. It means that the values obtained from the analysis of **CoCd-1-p** relaxation times can be different, but the determined pathways are the same. For that reason, the values characterizing the single spin and chain relaxations were included in one model.

The procedure is based on the fit of both temperature regimes simultaneously. To do that, the equations included in [81] were used. The original equation for the conventional approach is:

$$\tau_{SCM} = \tau_0 \exp\left(\frac{2\Delta_\xi + \Delta_A}{k_B T}\right) \cdot f\left(\frac{L}{\xi}\right), \quad (5.1.10)$$

where τ_0 is the preexponential factor including the preexponential factor from the Orbach process and a constant for the infinite size regime. The function f describes the *finite size effects*, and is defined:

$$f(x) = \left(1 + \frac{\omega^2}{x^2}\right)^{-1}, \quad (5.1.11)$$

$$\omega \tanh\left(\frac{\omega}{2}\right) = x. \quad (5.1.12)$$

The correlation length is:

$$\xi = \frac{a}{2} \exp\left(\frac{\Delta_\xi}{k_B T}\right), \quad (5.1.13)$$

where a is the length of one unit in a chain. The length of the chain, L :

$$N = \frac{L}{a}, \quad (5.1.14)$$

where N is the number of Co-units in the chain. Equation 5.1.9, was modified to replace the single spin contribution of the Orbach process in the following way:

$$\tau_{SCM} = \frac{1}{2} \left(\frac{1}{C T^n + B_1}\right) \exp\left(\frac{2\Delta_\xi}{k_B T}\right) \cdot f\left(\frac{L}{\xi}\right). \quad (5.1.15)$$

The $\frac{1}{2}$ factor is the constant in the relaxation time of the infinite size regime. For a finite size regime, the factor is $N/2$. [46] The single spin contribution includes only the Raman and qtm processes, as at $H_{dc} = 0$, the direct process vanishes. From the qtm, only constant B_1 remains. Equation 5.1.14 was fitted to the SCM relaxation time of **Co-1-c**, from 3.2 to 1.8 K. The fitted values are: $\Delta_\xi/k_B = 15.4(6)$ K, $n = 12.7(6)$, $C = 0.09(5) \text{ s}^{-1} \text{ K}^{-n}$, $B_1 = 30(15) \cdot 10^3 \text{ s}^{-1}$. The L and a were included through the crossover temperature, T^* , which is related to ξ , L , and a by:

$$L = 2\xi = a \exp\left(\frac{\Delta_\xi}{k_B T^*}\right). \quad (5.1.16)$$

The fit is presented in Figure 5.1.25. The value of Δ_ξ is close to the value obtained from the specific heat analysis with the Ising model ($\Delta_\xi/k_B = J_{\text{Ising}}/2k_B = 15.9$ K). The parameters of the single spin relaxation are significantly different, that those obtained from investigations of

CoCd-1-p. It means that the assumption that the relaxation of a single spin in a chain occurs differently than for non-interacting spins is correct. The reason for that can be a different phonon spectrum in **Co-1-c** than in **CoCd-1-p**. The values have large uncertainties. This is due to the narrow temperature range used for fitting. Also, the n power in the Raman process is very high, rather too high as for Co^{II} compounds.[82] This can mean, that in the presented approach, there are still some effects not included. Despite that, the model finally correctly describes the energy barriers of the SCM relaxation, which is the most important achievement in this case.

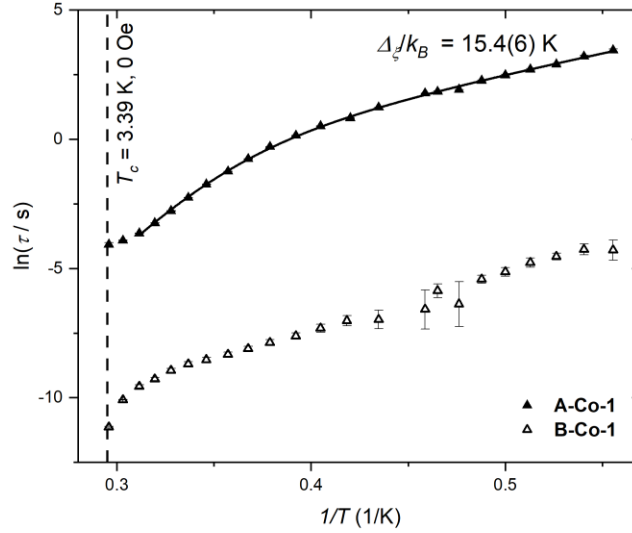


Figure 5.1.25 The relaxation times for **Co-1-c**, Υ , $H_{dc} = 0$ Oe. The line represents the fit of equation 5.1.14.

The crossover temperature was estimated to be 2.6 K, from the experimental points. This gives the 450 units in the chain. This can be surprising, as the measured sample is a single crystal. Such a sample should have very long chains. In this case, the chains are around 250 nm long, which in comparison with the size of the crystals, is very low. However, in such a crystal, there can be still some point defects or small cracks. Important are also the defects in the magnetic structure. The deciding impact of the defects is discussed in detail in the chapter considering the $\text{Co}(\text{NCS})_2(4\text{-methoxypyridine})_2$ compound.

The second relaxation process (**B-Co-1**) has an energy barrier determined from the Arrhenius law of 22.1 K. There is only one linear regime in the $\ln(\tau)$ vs. $1/T$ representation, indicating the lack of characteristic for SCM crossover. For that reason, this cannot be directly assigned to the single chain relaxation. However, knowing from the analysis of the **A-Co-1** process, that the chains are relatively short in the sample at 0 Oe, it is possible that the second process is the relaxation of the short fragments of chains as single molecule magnets by the Orbach process. Such cases were reported in the literature.[83] This process is a coherent rotation of fragments of chains, which are single domains. The energy barrier of such a process, according to Stoner and Wohlfarth is:

$$\Delta E = ND(1 - h)^2, \quad (5.1.17)$$

where D is the anisotropy constant of the easy axis, and h is:

$$h = \frac{\mu_B B}{2D}, \quad (5.1.18)$$

where B is the induction of the magnetic field for an easy axis. The E parameter is here neglected. Therefore, the energy barrier depends on the anisotropy, but also it is proportional to the length of the chain. For zero field, the energy should be simply ND . The relaxation time in such case satisfies the Arrhenius law of thermal activation. In the case of process **B-Co-1**, the determined energy barrier is very low in comparison to D predicted from *ab initio*: 101 and 116 K (E is neglected), therefore, such a mechanism is probably not possible in this case.

The other very important issue for the process **B-Co-1** is the fact that it dominates the relaxation at the temperatures close to the T_c , which is visible for the temperature dependence of the amplitude (Figure 5.1.26). At lower temperatures, process **A-Co-1** dominates. The dominance of process **B-Co-1** at higher temperatures suggests that for this process, spin waves may be responsible, as their population increases with temperature.[84]

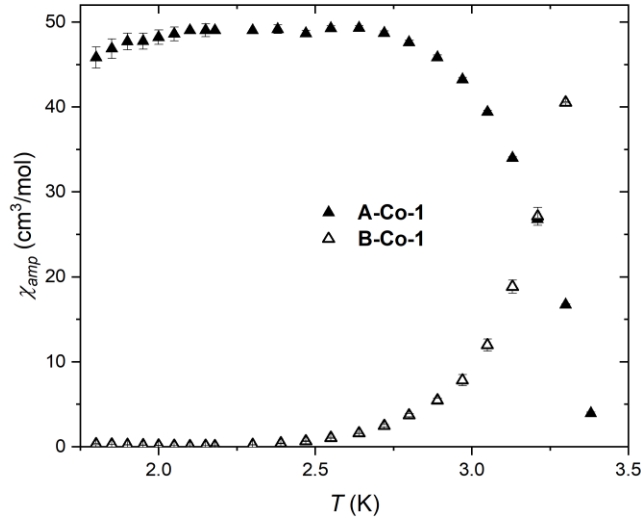


Figure 5.1.26 The amplitude, χ' , for the **A-Co-1** and **B-Co-1** processes for **Co-1-c**.

The α parameters for process **A-Co-1** are around 0.2, and for process **B-Co-1** even smaller (Figure 5.1.27). This confirms a narrow distribution of the relaxation times, and therefore a narrow distribution of the chain sizes, as expected for a single crystal.

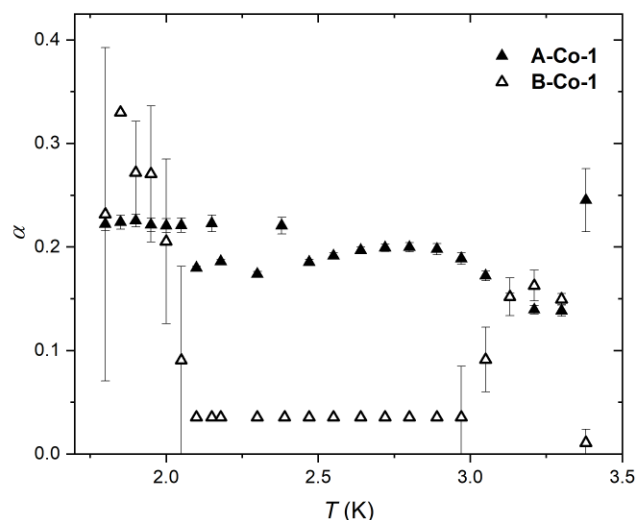


Figure 5.1.27 The α parameter for **A-Co-1** and **B-Co-1** processes for **Co-1-c**.

5.1.8. Summary

$\text{Co}(\text{NCS})_2(4-(3\text{-phenylpropyl})\text{pyridine})_2$ is a compound in which every Co^{II} ion is coordinated by four NCS bridges and two 4-(3-phenylpropyl)pyridine. This coordination is *trans-trans-trans*, which makes the structural chains linear. The intrachain interaction is mediated through the NCS bridges and is ferromagnetic. The 4-(3-phenylpropyl)pyridine ligand is large and the hydrogen bonds are not present between the neighboring chains. The interchain interaction is of dipolar origin, ferromagnetic, and significantly weaker than the intrachain interaction – the zJ'/J ratio is 0.0032. The coexistence of the ferromagnetic intrachain and ferromagnetic interchain interactions causes the ferromagnetic ordering at 3.39 K.

The single crystal of $\text{Co}(\text{NCS})_2(4-(3\text{-phenylpropyl})\text{pyridine})_2$ was the first single crystal from the investigated family large enough for the magnetic measurements. The investigations of it revealed significantly different magnetic relaxations than for the previously investigated powder sample.[59] For a powder sample, only one relaxation process was visible, but it could not be assigned to the single chain relaxation. The energy barrier of that process estimated with the Arrhenius law is over 100 K, which was previously never encountered for any of the compounds from this family – the usual value is around 30 K. Therefore, the relaxation was interpreted as cluster spin-glass behavior. For a single crystal, two relaxation processes are observed: process **A-Co-1**, which is recognized as a single chain relaxation due to the well-visible crossover of the relaxation times, and process **B-Co-1**, assigned here to the spin wave excitations. The relaxation times of process **A-Co-1** were analyzed using the modified approach, in which the Orbach contribution to the single spin relaxation was replaced with Raman, direct and qtm processes. The single spin processes were derived from the supporting investigations of the magnetically diluted compound, $\text{Co}_x\text{Cd}_{1-x}(\text{NCS})_2(4-(3\text{-phenylpropyl})\text{pyridine})_2$, $x = 0.013$. The compound is

isotypic to $\text{Co}(\text{NCS})_2(4-(3\text{-phenylpropyl})\text{pyridine})_2$ and behaves as a Single Ion Magnet. The Orbach process was excluded as a single spin relaxation pathway as the energy level scheme obtained from *ab initio* calculations does not correspond to the energy barriers obtained from the analysis of the relaxation times for diluted compound. The new approach to the relaxation of single chains enabled determining the energy of a domain wall correctly.

The other achievement of this research is the experimental confirmation of the easy axis direction. Previously, for other compounds, the easy axis was known only from *ab initio* calculations. Such experimental determination finally confirms the theoretical studies.

5.2. Magnetic properties of $\text{Co}^{\text{II}}(\text{NCS})_2(4\text{-methoxypyridine})_2$

The magnetic investigations of $\text{Co}(\text{NCS})_2(4\text{-methoxypyridine})_2$ (**Co-2**) started with a synthesis of a powder sample in 2017, the research was published in 2020.[60] **Co-2** displays the properties of the ferromagnetic Ising chain and it orders antiferromagnetically. A little bit earlier, in 2019, a group from Graz University published an article about the investigations of the same compound.[85] However, in this article, there was a mistake in the crystal structure determination, and also, the analysis of the magnetic relaxation was not broad. For that reason, our group decided to continue the research on that compound. After publishing very extensive research on the powder (magnetic investigations, *ab initio* calculations, Monte Carlo simulations, EPR measurements),[60] a single crystal sample of this compound was synthesized by the author of the thesis. At the very beginning, it seemed, that these investigations will not provide much new information, however, after preliminary magnetic investigations, strange effects in magnetic relaxation were observed. The results of the research concerning the single crystal sample of this compound were published in 2022,[58] and are presented in this chapter.

Symbols:

Co-2 – $\text{Co}(\text{NCS})_2(4\text{-methoxypyridine})_2$

Co-2-c – single crystal sample of **Co-2**

Co-2-g1 – mildly ground crystals of **Co-2**

Co-2-g2 – hard ground crystals of **Co-2**

Co-2-p – previously investigated powder sample of **Co-2** [60]

5.2.1. Synthesis

The synthesis of a single crystal of **Co-2**, **Co-2-c**, was performed by mixing the $\text{Co}(\text{NCS})_2$ (0.25 mmol) and 4-methoxypyridine (0.25 mmol) in 2 ml ethanol. Almost immediately, a small amount of a powder started to create. The suspension was stirred for 14 days and then filtered off, to remove any potential impurities or the non-dissolved powder product. The filtrate was then left for slow evaporation in a vial. The vial was closed, but in the cap, small holes were made to enable the evaporation. After the whole solvent

evaporated, some small crystals were obtained. The crystals were too small for magnetic investigations. The larger crystals were obtained by recrystallizing the product of evaporation. The recrystallization was performed by dissolving it in 3 ml of ethanol. The solution was then left for evaporation for around 3 weeks. The process was repeated 4 times. As a result of the last recrystallization, there was obtained a crystal (around 30 mg), however, it was not a single crystal, as it had visible growths on it. For that reason, the crystal was cut into a few parts. One of the parts was chosen for investigation (Figure 5.2.1). The single crystal is 0.84 mg. The monocrystalline character of the sample was confirmed by the SCXRD. The crystal faces were indexed (Figure 5.2.2).

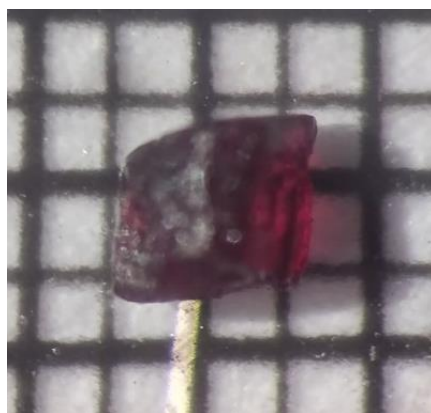


Figure 5.2.1 A photo of a single crystal of **Co-2** used for magnetic investigations. The grid is 0.5 mm.

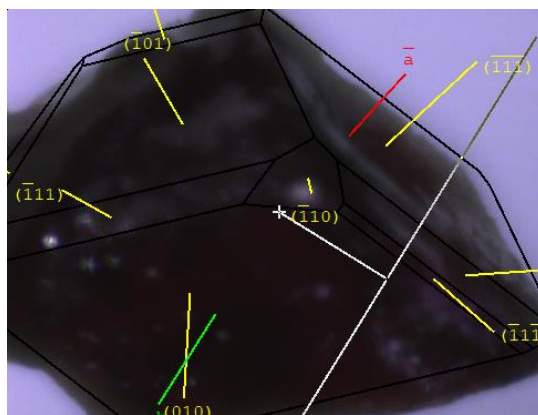


Figure 5.2.2 A photo of a single crystal of **Co-2** with the crystal faces indexed.

5.2.2. Crystal structure

The compound crystallizes in a triclinic crystallographic system, the space group is $P\bar{1}$. There are 2 formula units $\text{Co}(\text{NCS})_2(4\text{-methoxypyridine})_2$ in the unit cell. The unit cell parameters determined for a single crystal sample are presented in Table 5.2.1. The measurement was performed for a whole sample.

Table 5.2.1 The unit cell parameters of $\text{Co}(\text{NCS})_2(4\text{-methoxypyridine})_2$, determined for **Co-2-c**.

Parameter	Value
a	8.9577(5) Å
b	10.3859(7) Å
c	10.8543(7) Å
α	66.188(2)°
β	67.991(2)°
γ	82.987(2)°

There are two crystallographically independent Co^{II} positions. The Co^{II} ions are connected by the thiocyanate bridges into chains. The independent Co^{II} ions are positioned alternatively in a single chain (Figure 5.2.3). There is one type of chain in the structure, they are along the $[10\bar{1}]$ (Figure 5.2.4).

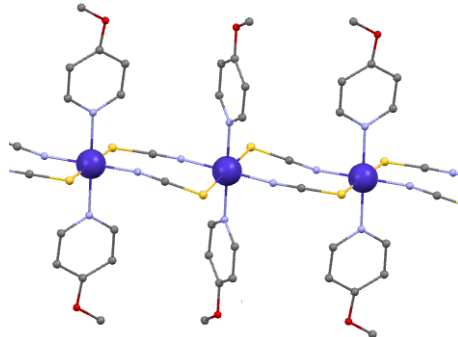


Figure 5.2.3 A view on the chain in the crystal structure of **Co-2**. Blue – Co, grey – C, light blue – N, yellow – S, red – O, H – omitted.

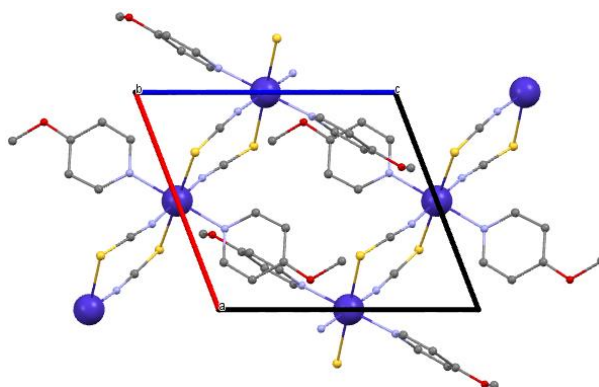


Figure 5.2.4 The view along the c crystallographic axes in the structure of **Co-2**. Blue – Co, grey – C, light blue – N, yellow – S, red – O, H – omitted.

The nitrogen and sulfur atoms' coordination around the Co ion is in all cases *trans* (*trans-trans-trans* coordination, Figure 5.2.5). This makes the chains linear. There are hydrogen bonds between the chains (Figure 5.2.6). The bonds are created between the hydrogen atom of the methoxy group and the sulfur atom of the NCS bridge in the neighboring chain, and also between the hydrogen atom of the methoxy group and the

oxygen atom of the neighboring chain. The angles in both cases are around 151° , indicating the interaction is relatively strong.

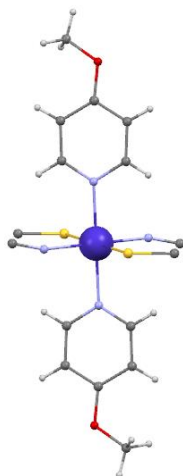


Figure 5.2.5 The view on one of the Co^{II} ion and its coordination in **Co-2**. Blue – Co, grey – C, light blue – N, yellow – S, red – O.

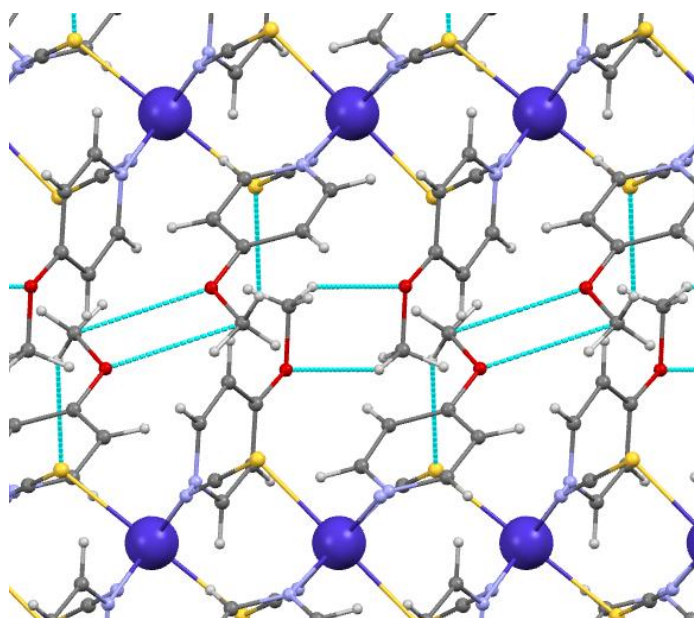


Figure 5.2.6 The view on the hydrogen bonds in **Co-2**. Blue – Co, grey – C, light blue – N, yellow – S, red – O. The hydrogen bonds are marked with cyan lines.

The choice of the directions of the measurement was dictated by the easiest fixing of the sample for magnetic measurements and at the same time, ensuring their perpendicularity. The way of fixing the sample is presented in section 2.3.2. The directions of the measurements are:

$\mathbf{X} \perp (010)$,

$\mathbf{Y} = [100]$,

$\mathbf{Z} = \mathbf{X} \times \mathbf{Y}$.

5.2.3. Magnetization curves

The magnetization curves were measured for 3 directions of **Co-2-c** (*X*, *Y*, *Z*) at 1.8 K and are presented in Figure 5.2.7. For all 3 curves, there is a metamagnetic transition visible, indicating the antiferromagnetic interactions in the system. The transitions begin at different critical fields in different directions.

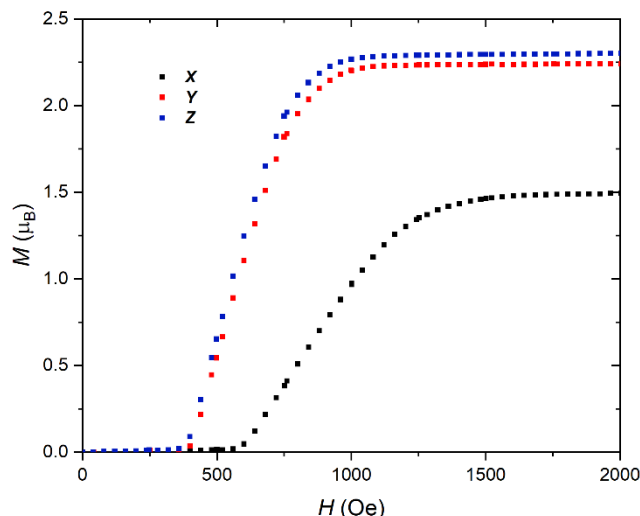


Figure 5.2.7 The field dependence of the magnetization for 3 directions of **Co-2-c**.

The magnetization does not saturate, even in the high fields (Figure 5.2.8). To estimate the value of the energy needed to overcome the interchain interaction for one Co^{II} spin, the value of the magnetization above the metamagnetic transition was extrapolated to zero field. Then, the magnetization was multiplied by the value of the critical field (Table 5.2.2). The energy is similar in all three cases, confirming the independence of this energy value on the direction.

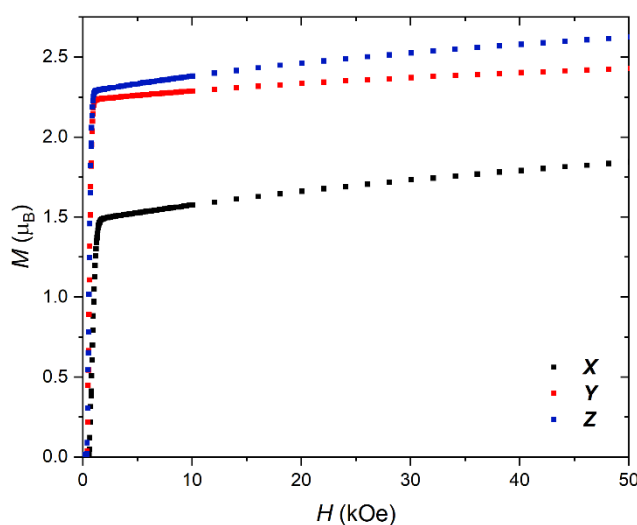


Figure 5.2.8 The field dependence of the magnetization for 3 directions of **Co-2-c**, up to 50 kOe.

Table 5.2.2 The values of the critical field, the magnetization of saturation at 0 Oe, and their product for **Co-2-c**.

Direction:	<i>X</i>	<i>Y</i>	<i>Z</i>
H_c (Oe)	597	407	385
M (μ_B)	1.43	2.22	2.28
$H_c \cdot M$ (Oe $\cdot\mu_B$)	853	903	878

5.2.4. Specific heat

The magnetic ordering was confirmed by the specific heat measurement for **Co-2-c** (Figure 5.2.9) at zero field, for direction *X*. A sharp peak is observed at $T_c = 3.94$ K. To the specific heat in the range from 4.5 to 40 K, a combination of Debye, Einstein, and Ising models was fitted. The fitted parameters are: $\Theta_D = 74.16(46)$ K, $a_D = 2.04(2)$, $\Theta_E = 159.2(1.1)$ K, $a_E = 5.16(5)$, $J_{\text{Ising}}/k_B = 29.9(6)$ K. The interactions between the chains are not included in this analysis.

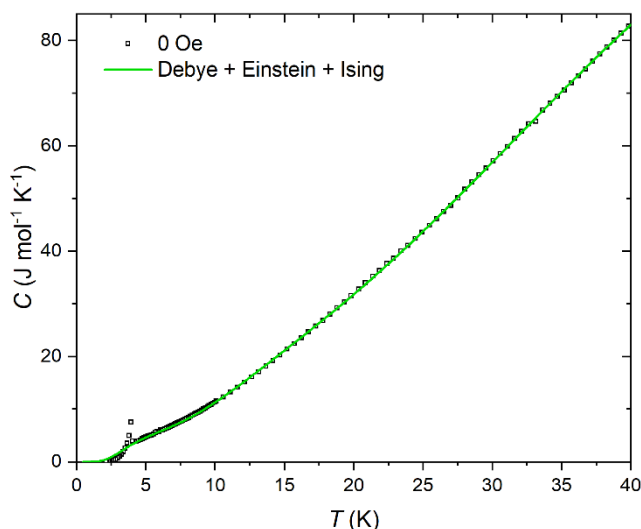


Figure 5.2.9 The temperature dependence of the specific heat measured for **Co-2-c** without the field. The line represents the fit of the combination of Debye, Einstein, and Ising models.

Knowing that the ground state is antiferromagnetic, there were also performed measurements at different magnetic fields. The phonon contribution, estimated based on the fit of the Debye and Einstein models, was subtracted from all the measurements to obtain the magnetic contribution to the specific heat. This magnetic contribution for zero field with the fit of the Ising model is presented in Figure 5.2.10, for different fields in Figure 5.2.11.

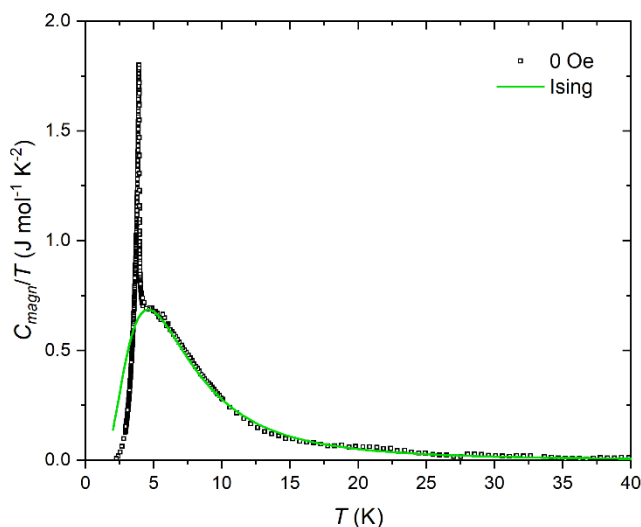


Figure 5.2.10 The temperature dependence of the magnetic contribution to the specific heat measured for **Co-2-c** without the field. The line represents the fit of the Ising model.

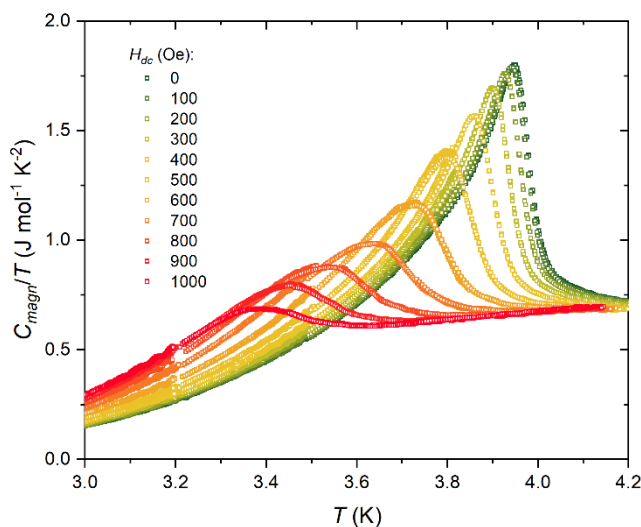


Figure 5.2.11 The temperature dependence of the magnetic contribution to the specific heat measured for **Co-2-c** for different fields.

The entropy change, determined from the integration of the C_{magn}/T vs. T dependence in the range from 40 to 2 K at zero field, is equal to $5.59 \text{ J mol}^{-1} \text{ K}^{-1}$, close to the theoretical value determining the ordering of the $\frac{1}{2}$ spins: $R \ln 2 = 5.72 \text{ J mol}^{-1} \text{ K}^{-1}$. On the basis of the measurements at different fields, there was prepared a phase diagram (Figure 5.2.12). On the left side of the diagram, there is an antiferromagnetic phase.

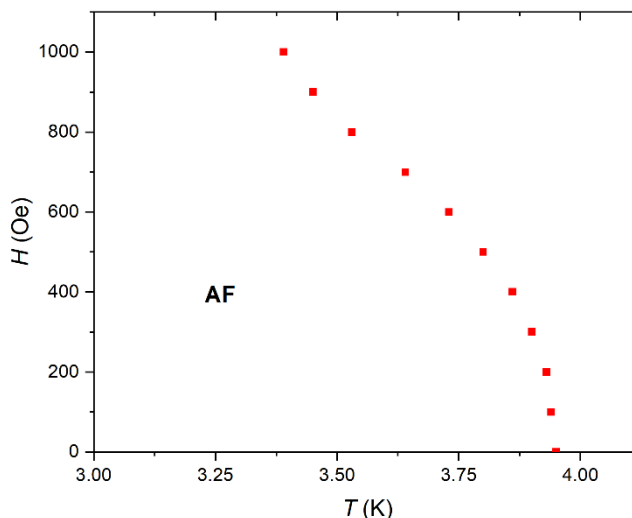


Figure 5.2.12 A phase diagram for **Co-2-c**, determined from the specific heat measurements.

5.2.5. Easy axis determination

The values of saturation of magnetization at zero field were used to determine the easy axis direction experimentally. From the *ab initio* calculations, it is known, that the easy axis is close to the Co-N_{pyridine} bond.[60] The *g* factors values and the energy gaps between the ground and the first excited state are presented in Table 5.2.3. The easy axes directions as well as the mentioned values are slightly different for the two Co ions, as the crystal field is for them slightly different. The *ab initio* calculations were performed by dr Michael Böhme from Jena University.

Table 5.2.3 The values of *g* factors and the energy gaps (between the ground and first excited state) for the two Co^{II} ions in **Co-2**, derived from the *ab initio* calculations.[60]

g_x	g_y	g_z	E (K)
1.840	3.017	7.004	187
2.017	3.734	6.568	223

The calculations were performed using the Mathematica software. To recalculate the crystallographic system to the Cartesian system, the following equation was used:

$$\begin{pmatrix} x_c \\ y_c \\ z_c \end{pmatrix} = \begin{pmatrix} a & b \cos \gamma & c \cos \beta \\ 0 & b \sin \gamma & c \frac{\cos \alpha - \cos \beta \cdot \cos \gamma}{\sin \gamma} \\ 0 & 0 & \frac{c \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}}{\sin \gamma} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad (5.2.1)$$

where x_c , y_c , and z_c represent the coordinates of the vector in the Cartesian system, a , b , c , and θ are the unit cell parameters, the matrix is the conversion matrix for the triclinic system, and x , y , z represents the crystallographic coordinates. To simplify the calculations, it is assumed that there is one easy axis in a chain (the independence of the two Co^{II} is neglected). Therefore, the magnetic easy axis vector in the Cartesian system is:

$$\mathbf{m}_1 = \begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}; \quad (5.2.2)$$

On that basis, there were created 3 equations:

$$M_X = |\mathbf{m}_1 \cdot \mathbf{X}|, \quad (5.2.3)$$

$$M_Y = |\mathbf{m}_1 \cdot \mathbf{Y}|, \quad (5.2.4)$$

$$M_Z = |\mathbf{m}_1 \cdot \mathbf{Z}|. \quad (5.2.5)$$

where M_X , M_Y , and M_Z are the values of magnetization saturation from the experiment at zero field (Table 5.2.2). This system of 3 equations was solved and 4 solutions for $\mathbf{m}_1$ were obtained: (2.22, -0.44, 2.65) μ_B , (2.22, 0.44, -2.65) μ_B , (2.22, 2.21, 1.54) μ_B and (-2.22, 2.21, 1.54) μ_B . The first one was assumed to be correct, as it is the closest solution to the easy axis determined from *ab initio* calculations: (2.33, -1.14, 2.19) μ_B . The angle between the averaged over two Co^{II} ions easy axis determined experimentally and theoretically, is 14.1°. The angle between the easy axis determined experimentally and the averaged direction of the Co-N_{ligand} bond is 16.5°. The angle between the easy axis determined theoretically and the averaged direction of the Co-N_{ligand} bond is 2.5°. The difference between the theoretical and experimental easy axis can be caused by the small error in the positioning of the sample for the measurement. However, the difference is low enough to consider the experiment and theory results in agreement.

5.2.6. Magnetic susceptibility

In Figure 5.2.13, there are presented the zero field and field-cooled susceptibilities measured at 30 and 100 Oe. In Figure 5.2.14, there are presented the ac magnetic susceptibilities at $H_{dc} = 0$ Oe and $H_{ac} = 3$ Oe. Both ac and dc magnetic susceptibilities increase with the decreasing temperature down to around 4 K. Below that temperature, the susceptibility starts to decrease fast, achieving almost 0 close to 1.8 K. This confirms the antiferromagnetic ground state of the compound.

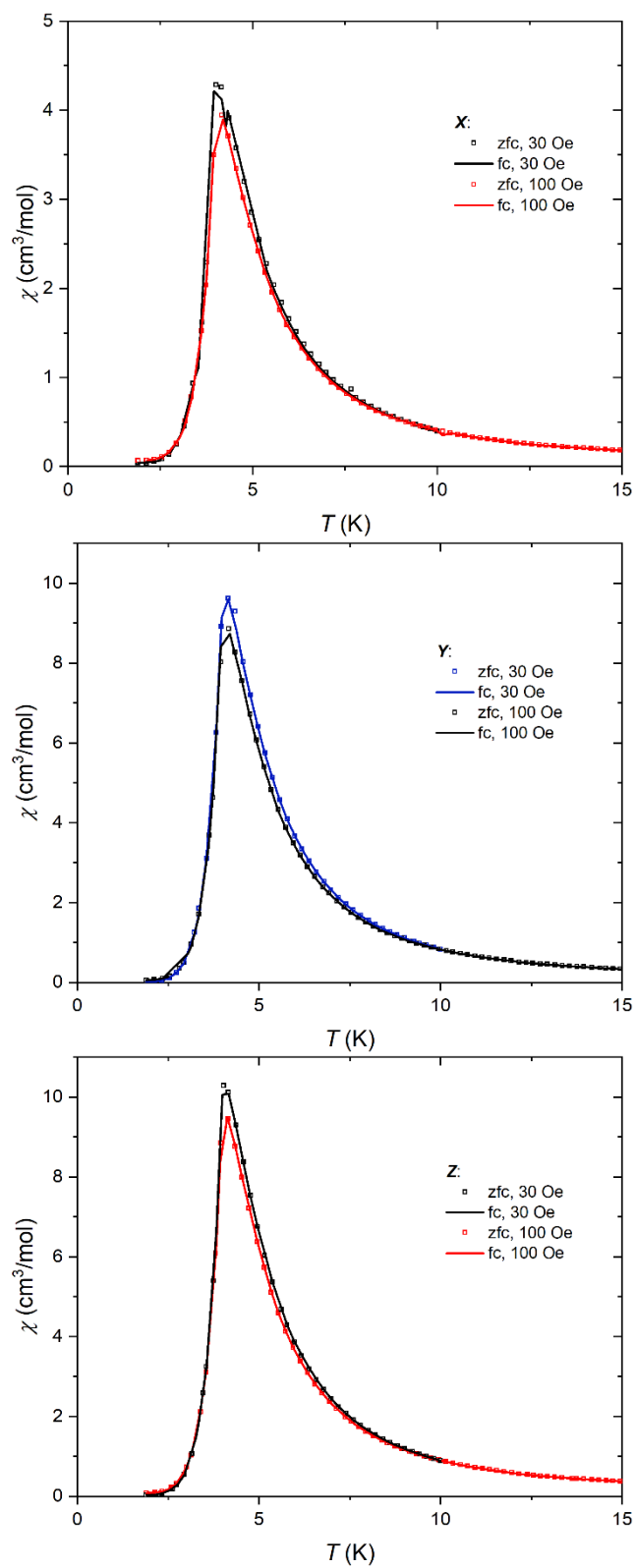


Figure 5.2.13 Zero field and field cooled susceptibilities measured for **Co-2-c** along **X**, **Y**, and **Z**.

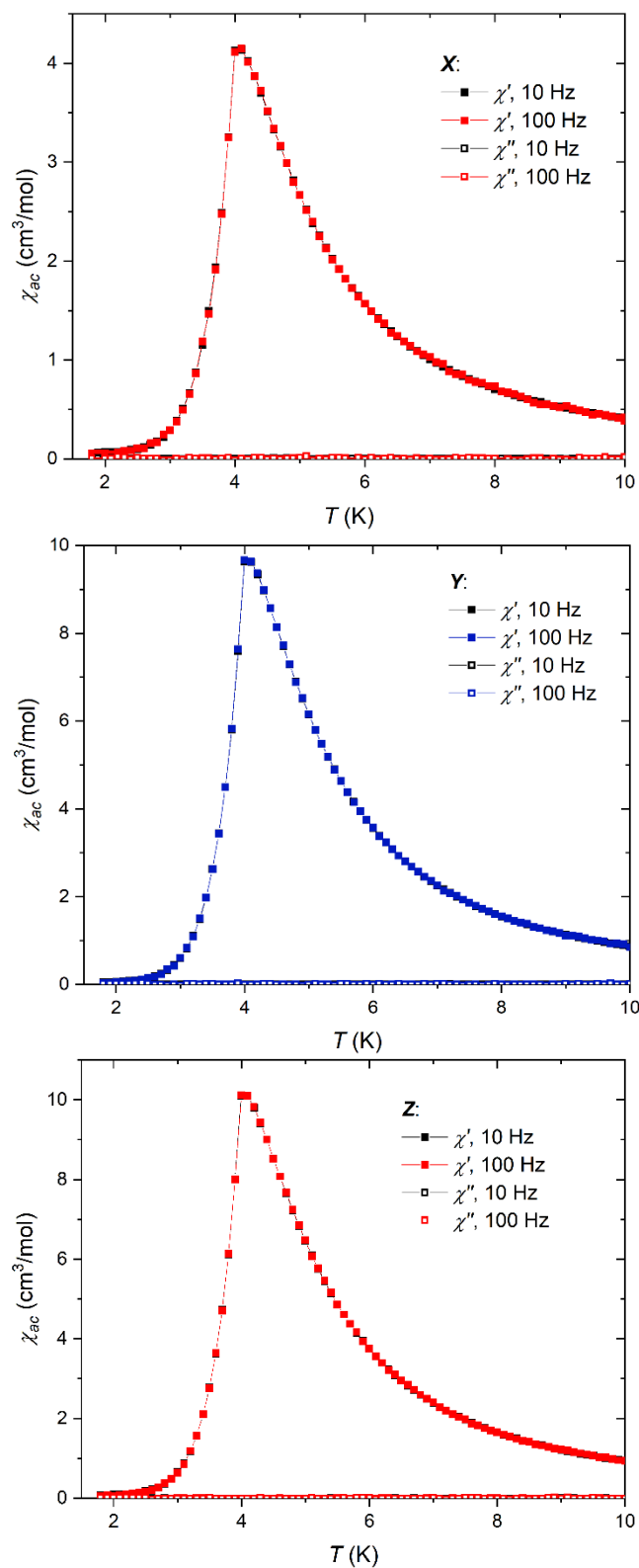


Figure 5.2.14 The ac magnetic susceptibility measured for **Co-2-c** at $H_{dc} = 0$ Oe and $H_{ac} = 3$ Oe, along X, Y, and Z.

To the high-temperature part of the susceptibilities for 3 directions of **Co-2-c**, the Ising model was fitted simultaneously using the equations 1.5.11 – 1.5.17 (Figure 5.2.15). The fit was performed in the range from 5 to 50 K. The obtained parameters of the fit are: $J_{\text{Ising}}/k_B = 34.0(3)$ K, $zJ/k_B' = -0.377(5)$ K, $g_z = 6.33(6)$, $g_x = 2.9(2)$, $g_y = 4.6(2)$, $\chi_0 = 0.0057(7)$ cm³/mol, α_3 is 2.81(3) rad. The negative value of zJ' confirms, the antiferromagnetic type of interactions between the chains. The J_{Ising}/k_B value is positive and close to the one obtained from the specific heat analysis. The g_x and g_y factors have large uncertainties and are slightly larger than the values obtained from *ab initio*, but the g_z is lower. However, all the g factors were possible to fit. The deviation at the lowest temperatures is caused by the ordering.

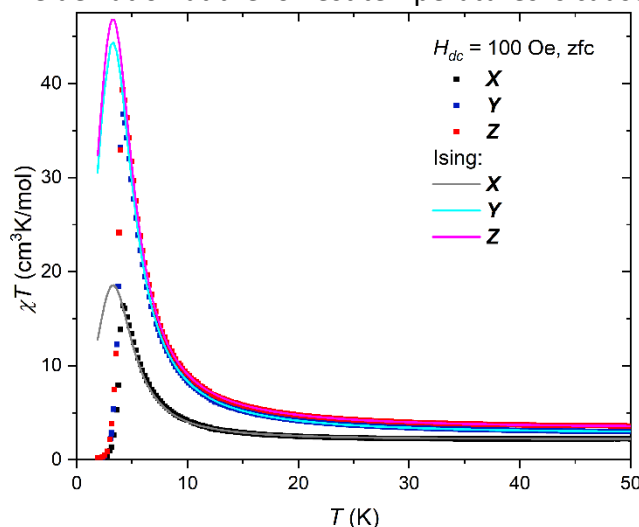


Figure 5.2.15 The ac magnetic susceptibility presented as χT vs. T for **Co-2-c**. The lines represent the simultaneous fit of the Ising model.

5.2.7. Magnetic relaxation

At the zero field, in the ac magnetic susceptibility, there is no imaginary component visible (Figure 5.2.14). This indicates the lack of magnetic relaxation at zero field, contrary to the ferromagnetic **Co-1-c**. The ac magnetic susceptibility was therefore measured at the fields corresponding to the metamagnetic transition, because the highest signal should be observed in the fields, at which the magnetization curve is the steepest, which is indeed at the fields corresponding to the metamagnetic transition. This was confirmed experimentally for the powder sample.[60] For a powder sample, the relaxations were measured from 0 to 800 Oe. The relaxations were possible to measure at the fields below the critical field, even though in that range the signal was very small. This was assigned to the presence of defects in the structure and confirmed experimentally by measuring pristine and ground powder samples. As a result, a higher amplitude was obtained for a ground sample. For a single crystal sample, the signal at the fields below the metamagnetic transition is so small, that the reliable analysis of the ac magnetic susceptibility with the Cole-Cole model would not be possible. For that reason, for **Co-2-c**, the relaxations were measured only at the fields corresponding to the metamagnetic transition. The

temperature range of the measurements was from 1.8 to 4.5 K. The frequency range was from 0.1 to 1500 Hz. The measurements were performed for directions **X** (800 Oe (Figure 5.2.16), 1100 Oe (Figure 5.2.17)) and **Z** (600 Oe (Figure 5.2.18)). The ac magnetic susceptibility was analyzed with the Cole-Cole model, single or double-mode, depending on the temperature. At temperatures close to the critical temperature, the Argand plots have the two semicircles shape, indicating the presence of two relaxation processes simultaneously. The relaxation times obtained from these fits are presented in Figure 5.2.19, in the Arrhenius plot.

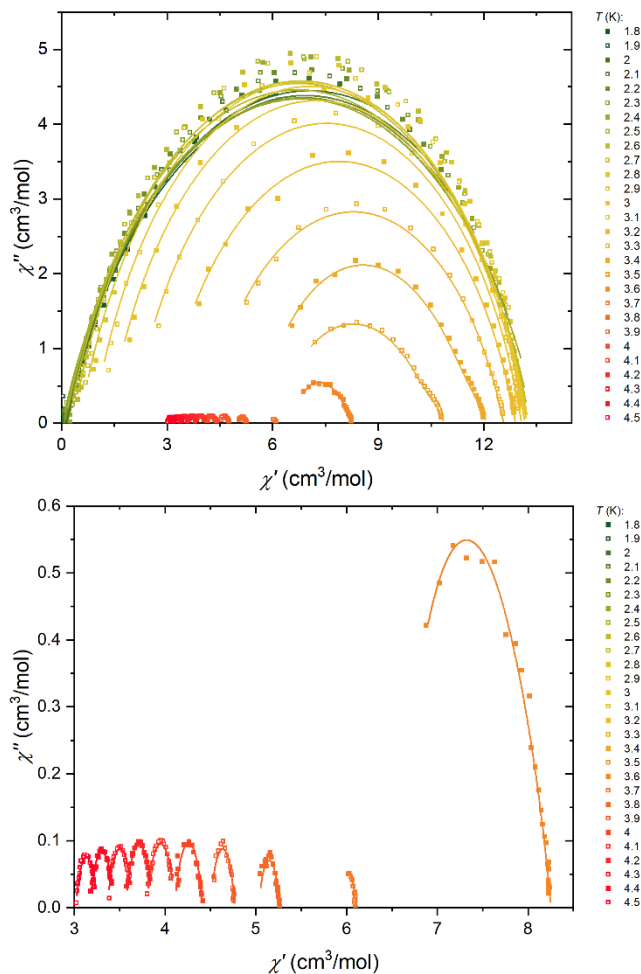


Figure 5.2.16 The ac magnetic susceptibility measured for **Co-2-c** at 800 Oe, along direction **X**. The lines are the fits of the single or double-mode Cole-Cole model. Top: the whole χ' and χ'' range. Bottom: Enlargement of the curves at the highest temperatures.

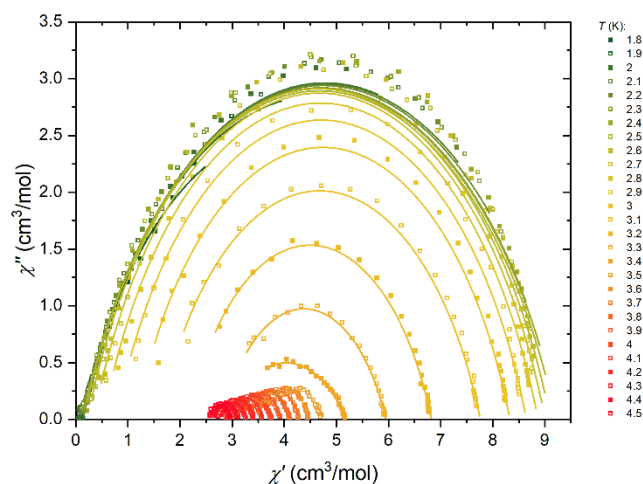


Figure 5.2.17 The ac magnetic susceptibility measured for **Co-2-c** at 1100 Oe, along direction **X**. The lines are the fits of the single or double-mode Cole-Cole model.

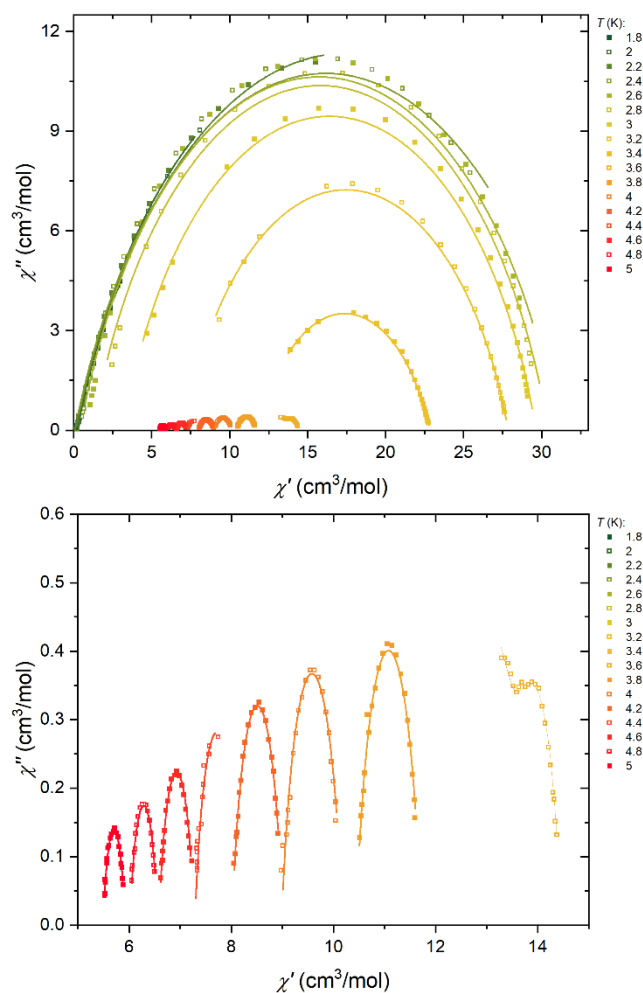


Figure 5.2.18 The ac magnetic susceptibility measured for **Co-2-c** at 600 Oe, along direction **Z**. The lines are the fits of the single or double-mode Cole-Cole model. Top: the whole χ' and χ'' range. Bottom: Enlargement of the curves at the highest temperatures.

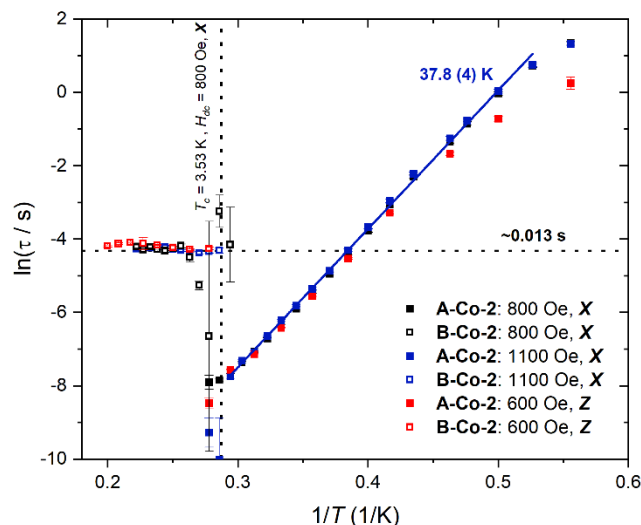


Figure 5.2.19 The temperature dependence of the relaxation times for **Co-2-c** presented in the Arrhenius plot.

The relaxation times obtained for a single crystal, do not display a uniform dependence. At the temperature below the ordering temperature (3.53 K at 800 Oe for **X**), the linear dependence is visible in the Arrhenius plot. This process, called here **A-Co-2**, was assigned to the single chain relaxation, despite the lack of the characteristic crossover. Above the ordering temperature, the other process emerges, **B-Co-2**, which has unusual characteristics – it is temperature, field, and direction independent. Its relaxation time is 0.013 s.

The single chain relaxation process was also observed for a previously investigated powder sample, **Co-2-p**, however, some significant differences between these two samples are observed (Figure 5.2.20). First of all, the relaxation time of a single chain for a powder is faster by around 70 times at 2.8 K. Apart from that, the energy barrier estimated by fitting the Arrhenius law is around 8 K lower than for a powder.

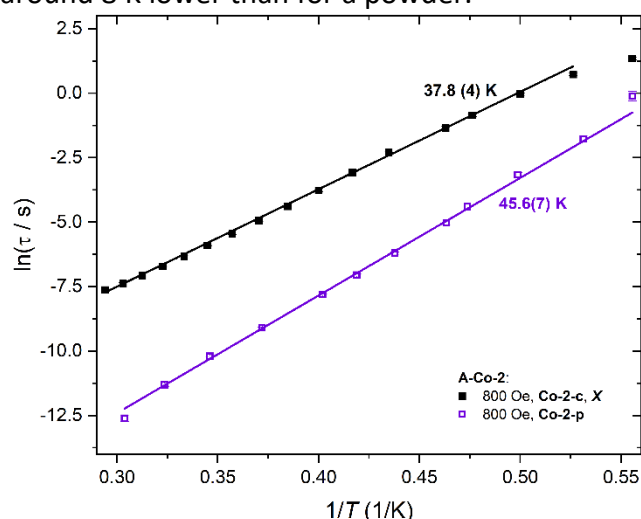


Figure 5.2.20 The temperature dependence of the relaxation times of the single chain relaxation presented in the Arrhenius plot for **Co-2-c** (800 Oe, **X**) and **Co-2-p**.

The change in the relaxation times can be caused by the form of the sample itself. The single crystal sample has in general worse thermal contact with the thermal bath than the powder sample, and for that reason, a lower number of phonons can be delivered to the sample, which can affect the relaxation of a chain significantly. This is called a phonon bottle-neck effect,[86] and it can be observed in the ac magnetic measurements as the change of the relaxation time depending on the amplitude of the ac magnetic field. It was checked experimentally for a single crystal sample for direction Y at 3 and 3.3 K (Figure 5.2.21 and Figure 5.2.22). For both measurements, the peak in the frequency dependence of χ'' does not change its position significantly. Therefore, the phonon bottle-neck effect is excluded as the cause of the change in relaxation times.

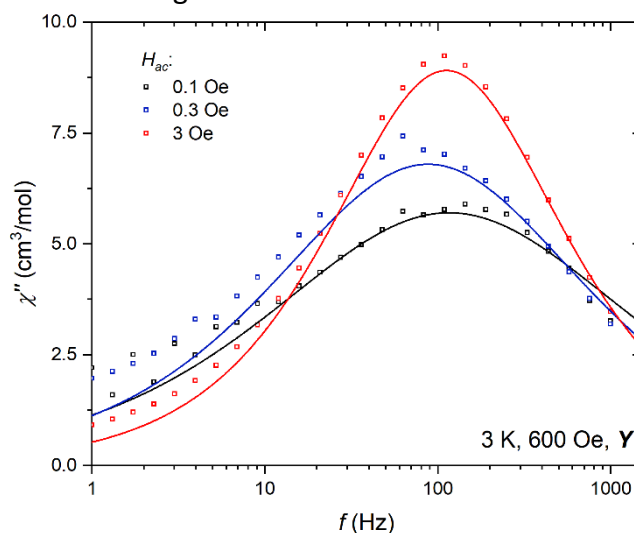


Figure 5.2.21 The imaginary component of the ac magnetic susceptibility measured for **Co-2-c**, along direction Y , at 3 K, $H_{dc} = 600$ Oe and different H_{ac} . The lines are the fits of the single-mode Cole-Cole model.

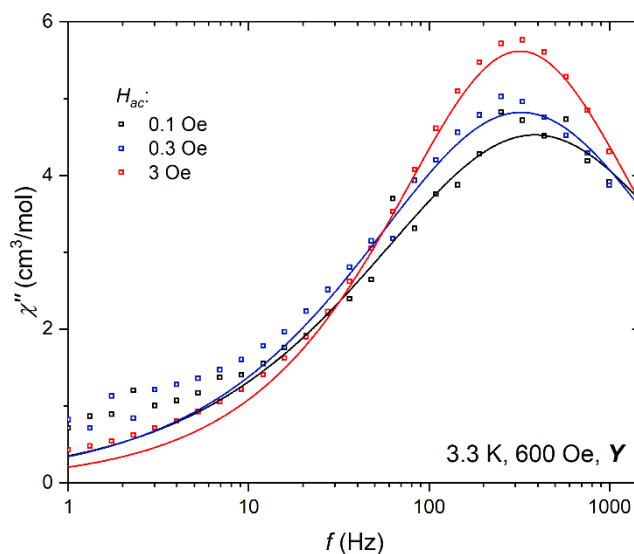


Figure 5.2.22 The imaginary component of the ac magnetic susceptibility measured for **Co-2-c**, along direction **Y**, at 3.3 K, $H_{dc} = 600$ Oe and different H_{ac} . The lines are the fits of the single-mode Cole-Cole model.

The change in the relaxation time is observed for the whole accessible temperature regime. The point at the 1.8 K for a single crystal is slightly tilted from the linearity of the Arrhenius fit, however, this does not indicate the presence of crossover, it is rather caused by the poor data quality at this temperature. This leads to the conclusion, that the observed relaxation times are within one regime: finite or infinite. This is a finite chain regime, as in this regime, the relaxation time depends on the length of the chain.[46] Such an assumption is reasonable taking into consideration, that in a powder sample, more defects exist and therefore, the chains are shorter. A similar dependency was observed for $[\text{Co}(\text{hfac})_2\text{NITPhOMe}]$ compound.[87] In the research concerning this compound, there were synthesized single crystals of a pure compound and a compound magnetically diluted with Zn^{II} ions. The purpose of the dilution was to shorten the chains – a Zn^{II} ion is an obstacle to the exchange interaction along the chains. In the experimental studies, for a pure compound, the crossover was observed, and for the diluted compounds, the change of the crossover temperature was observed in comparison to the pure compound. Apart from that, it was observed that the higher the dilution, the lower the relaxation times in the finite size regime, it is, the shorter the chain, the faster the relaxation in the finite size regime. For the infinite size regime, the time was not changing between the samples. However, this system was not magnetically ordered. In the **Co-2** system, the magnetic ordering occurs, and only below the T_c , the single chain relaxation is observed.

To confirm that the relaxation time difference is indeed caused by the different lengths of the chains in a powder and a single crystal, and to exclude at the same time a possible mistake in the analysis, the single crystal leftovers from the large crystal from synthesis was crushed on a powder. The synthesis of diluted single crystals would be too time-consuming. The original sample was not destroyed. The grinding of the sample was

done twice. The first sample, **Co-2-g1**, was ground mildly, to obtain a powder with relatively large crystallites. The second sample, **Co-2-g2**, was a harder ground sample **Co-2-g1**, to obtain small crystallites. The sizes were determined by using a Zeiss Axio Observer Z1 inverted microscope with a DIC adapter. From the photos taken in this microscope (Figure 5.2.23 and Figure 5.2.24), the sizes of individual crystals were obtained and then, they were averaged over their volume. The averaged sizes are 150(5) μm for **Co-2-g1** and 1.6(3) μm for **Co-2-g2**. Apart from the sizes, the purity of the powder was checked by EA and PXRD on the **Co-2-g1** sample. The results of EA are consistent with the theoretical content (Table 5.2.4) The PXRD pattern is presented in Figure 5.2.25. The pattern is the same as the pattern measured for a powder previously investigated and the theoretical pattern calculated from the crystal structure.[60] Additionally, the magnetization curve was measured for both samples, to confirm that the metamagnetic transition did not shift in relation to **Co-2-p** (Figure 5.2.26).

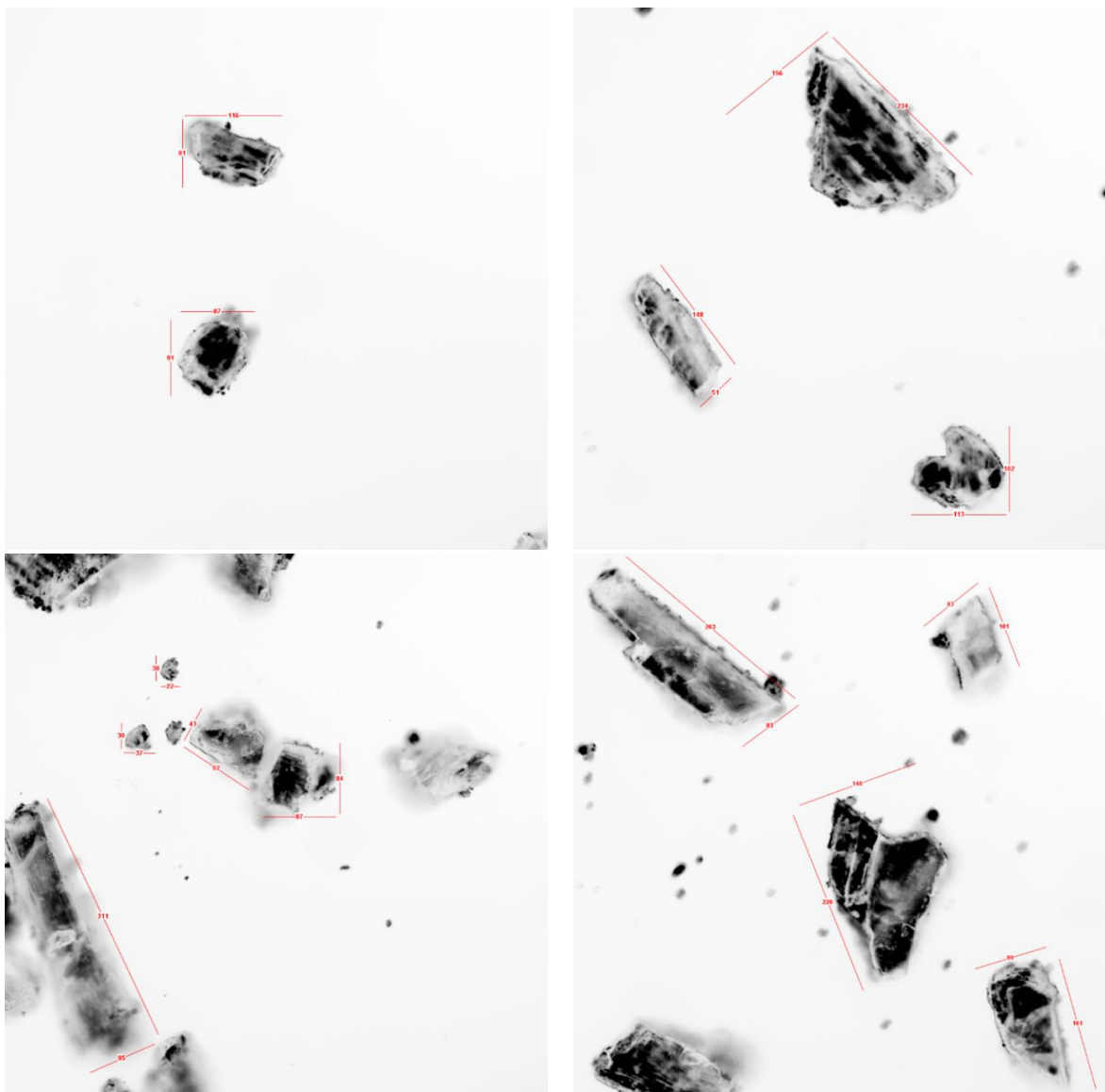


Figure 5.2.23 The photos of crystallites in the **Co-2-g1** sample ($648 \times 648 \mu\text{m}$). The red lines are the measured distances, the red numbers are their lengths (μm).

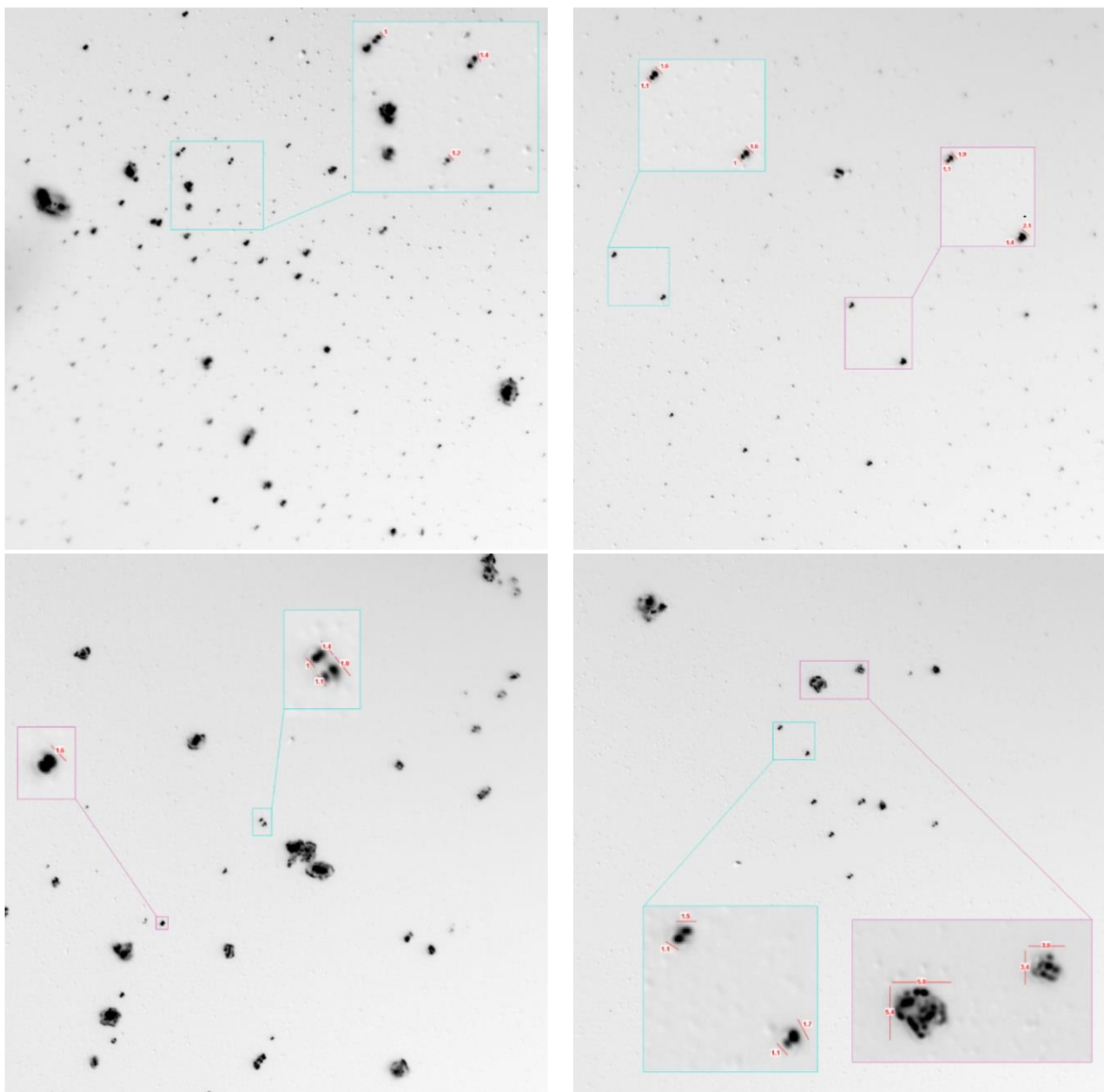


Figure 5.2.24 The photos of crystallites in the **Co-2-g2** sample (161 × 161 μm). The red lines are the measured distances, the red numbers are their lengths (μm). The frames represent the enlarged areas.

Table 5.2.4 The results of the elemental analysis for **Co-2-g1**, compared with the theoretical values.

$\text{CoC}_{14}\text{H}_{14}\text{N}_4\text{O}_2\text{S}_2$	C	N	H	S
Elemental Analysis	42.73	14.12	3.62	16.57
Theoretical	42.69	14.23	3.59	16.29

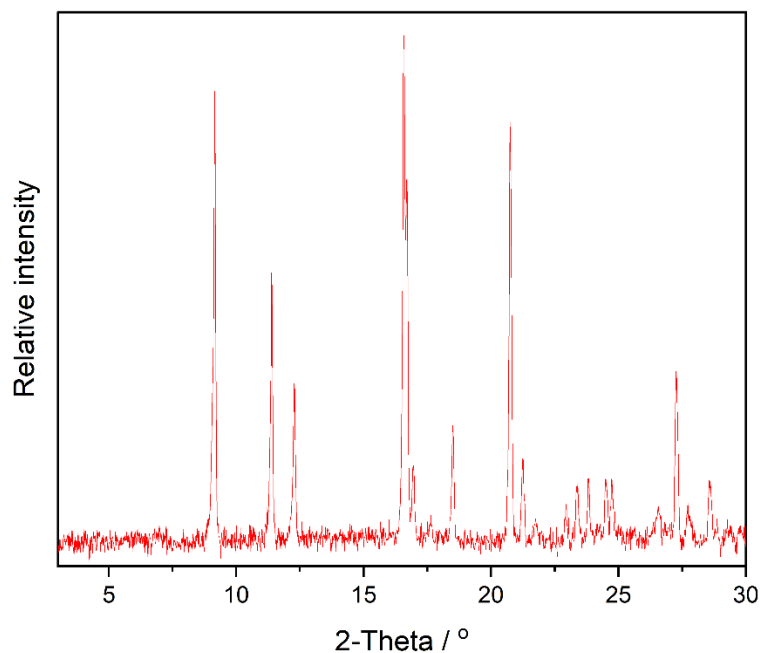


Figure 5.2.25 The powder X-Ray diffraction pattern obtained for **Co-2-g1**.

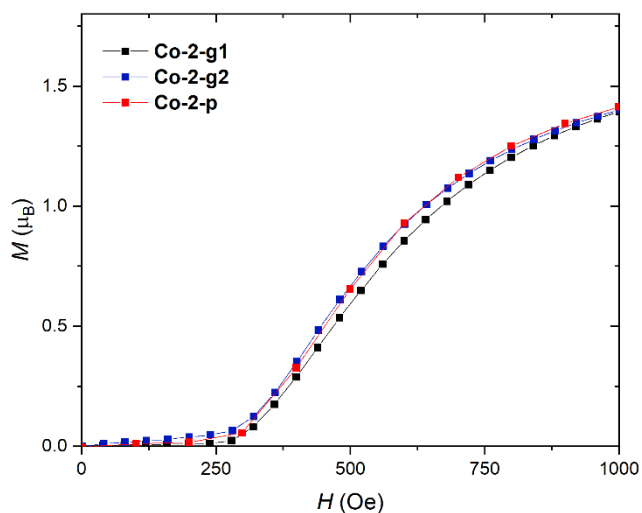


Figure 5.2.26 The magnetization curves measured for **Co-2-g1** and **Co-2-g2** samples and compared to the data for a previously investigated powder sample, **Co-2-p**, published in [60].

The ac magnetic susceptibility for these two samples was measured at 800 Oe (Figure 5.2.27 and Figure 5.2.28). The data were analyzed with the Cole-Cole model. The curves seem to be distorted, especially for the **Co-2-g2** sample. This can be caused by the high distribution of the chain sizes, and therefore, the high distribution of the relaxation times.

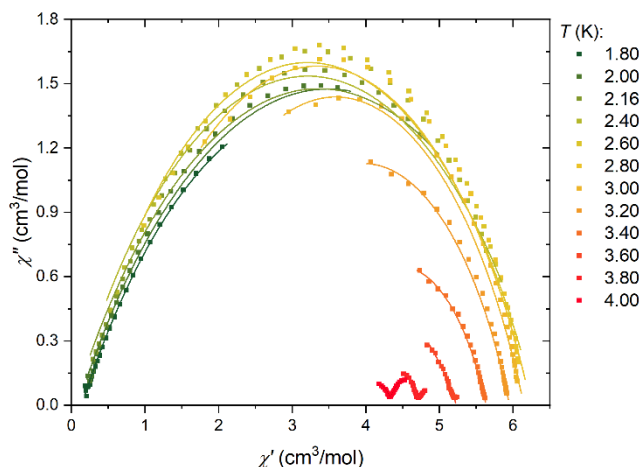


Figure 5.2.27 The ac magnetic susceptibility measured for the **Co-2-g1** at 800 Oe, presented as an Argand plot. The lines are the fits of the single or double-mode Cole-Cole model.

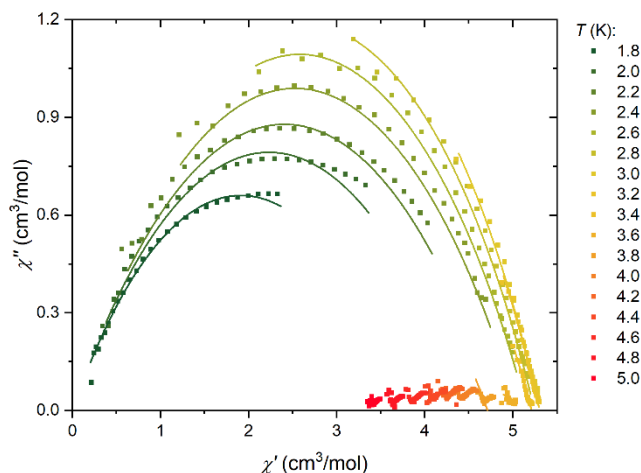


Figure 5.2.28 The ac magnetic susceptibility measured for the **Co-2-g2** sample at 800 Oe, presented as an Argand plot. The lines are the fits of the single or double-mode Cole-Cole model.

The relaxation times determined for ground samples are presented in Figure 5.2.29, together with data for single crystal and previously investigated powder sample. The relaxation times lower gradually, and for the **Co-2-g2** sample, the times are almost the same as for **Co-2-p**. This confirms that the faster relaxation is directly connected to the shorter chains in the finite chains regime.

The question is, why only finite size regime relaxation is observed, and why there is no crossover visible, especially, when the effect was observed for a single crystal of **Co-1-c**. The single chain relaxation is visible only below the critical temperature, therefore, the lowest temperature at which the crossover can appear is around 3.5 K for 800 Oe. The number of units in such a chain is:

$$N = \frac{2\xi(T)}{a} = \exp\left(\frac{\Delta_\xi}{k_B T^*}\right). \quad (5.2.6)$$

For $T^* = 3.5$ K, N is equal to 110 units. This seems far too low for a single crystal. The answer lies in the ordering. For ordered chains, the correlation length spreads to infinity.[88, 89]

This means that the chains in the ordered system should always display the magnetic chain relaxation in the finite size regime, and the crossover should never be observed. However, it is possible, that the correlation length is not infinite, but long enough to shift the crossover beyond the accessible range of the temperature at which, the single chain relaxation is observed. This may be the case, taking into consideration the fact, that the interchain interaction in this and similar systems from the investigated family are weak. For that reason, the observation of the crossover for some of the systems cannot be excluded. For **Co-1**, zJ' is 0.1 K, for **Co-2** it is around 4 times larger, -0.377 K. Therefore, it is probable, that for **Co-1-c**, the correlation length is significantly shorter than for **Co-2-c**, and for that reason for **Co-1-c**, the crossover is visible. However, this conclusion still needs conformation for more systems, not only from $\text{Co}(\text{NCS})_2(\text{ligand})_2$ family.

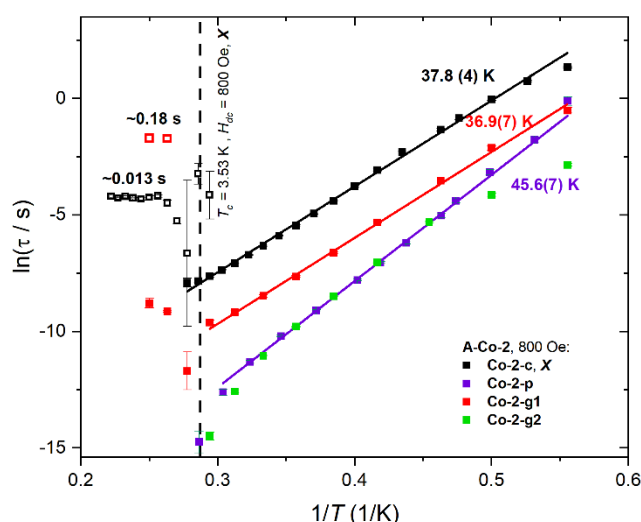


Figure 5.2.29 The Arrhenius plot of the relaxation times for **Co-2-c**, **Co-2-p**, **Co-2-g1**, and **Co-2-g2**. The lines represent the fits of the Arrhenius law.

The fits of the Arrhenius law give the energy barrier values, which for **Co-2-g1** is almost the same as for the single crystal. This energy barrier does not have a physical meaning and serves here only as an estimation if the lowering of the relaxation times is equal in the whole accessible temperature range. The 8 K difference for **Co-2-p** and **Co-2-g2** can be caused by the distortion of the ac magnetic susceptibility. For powders, it is usually the case, due to the high distribution of the crystallites in the sample, and therefore, the chain sizes. Basing on the results for **Co-1-c**, it can be assumed, that the single spin relaxation pathways are similar, and should be Raman, direct and qtm process. However, a similar analysis of the relaxation time as for **A-Co-1** is impossible to perform, because the crossover is not visible, the temperature range is too narrow, and the dependency is close to linear.

Process **B-Co-2** for **Co-2-c** has a significantly different characteristic than process **B-Co-1** for **Co-1-c**. It is temperature, field, and direction independent. It emerges only above the critical temperature, however, it cannot be excluded, that the process is present in the

whole temperature range, but it is not visible, because its amplitude is not high, and it can vanish in the single chain relaxation process. The amplitude of the chain relaxation is several times larger than the amplitude of process **B-Co-2** (Figure 5.2.30).

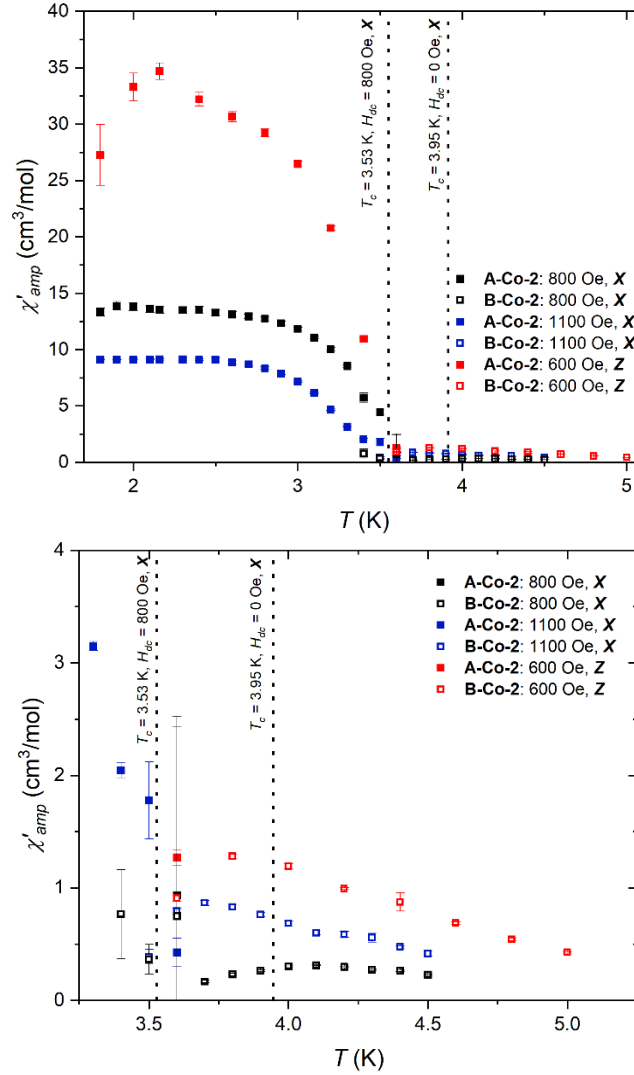


Figure 5.2.30 The temperature dependence of the amplitude of the relaxation processes for **Co-2-c**. Top: whole temperature regime. Bottom: only the highest temperatures.

The α parameters do not differ significantly for processes **A-Co-2** and **B-Co-2** (Figure 5.2.31). Also, the process **B-Co-2** vanishes for powder samples. For **Co-2-g1** it is still slightly visible, however, its analysis is not certain due to large noise. For **Co-2-g2** and **Co-2-p**, it is no longer visible. This also indicates some kind of dependency on the chain lengths, but it is impossible to determine, as the resolution of data is not sufficient. For certain, the effect is not an impurity or any technical effect. It is possible, that this process origin is the relaxation of short fragments of chains like SMMs. The temperature independency suggests qtm, which is not contrary to the field independence. The qtm process can be treated approximately as field independent in the narrow range of fields. The other possibility is

that this is a coherent rotation of 1D domains, for which the energy barrier is very small.[90] However, for now, there is no experimental way to confirm any of the hypotheses.

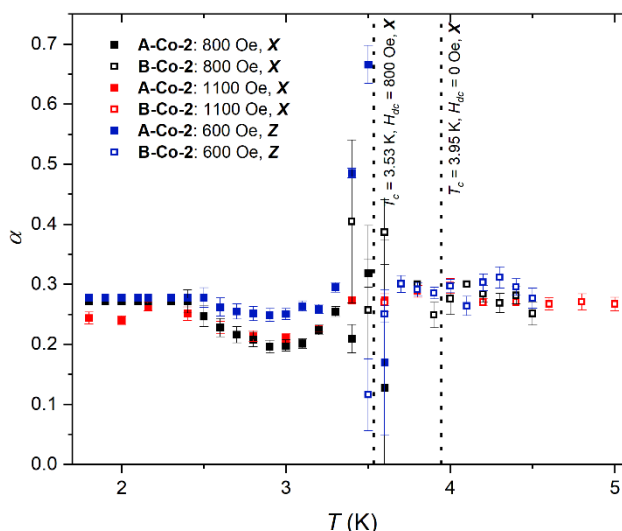


Figure 5.2.31 The temperature dependence of the α parameters of the relaxation process for **Co-2-c**.

5.2.8. Summary

$\text{Co}(\text{NCS})_2(4\text{-methoxypyridine})_2$ is a compound in which every Co^{II} ion is coordinated by four NCS bridges and two 4-methoxypyridine ligands. This coordination is *trans-trans*, which makes the structural chains linear. The intrachain interaction is mediated through the NCS bridges and is ferromagnetic. The hydrogen bonds are a pathway of interchain exchange interactions that is antiferromagnetic and significantly weaker than the intrachain interaction – the $|zJ'/J|$ ratio is 0.011. The coexistence of the ferromagnetic intrachain and antiferromagnetic interchain interactions causes the antiferromagnetic ordering at 3.94 K.

The investigation of the single crystal of $\text{Co}(\text{NCS})_2(4\text{-methoxypyridine})_2$ was performed to get more information about the magnetic relaxations in this system. There are observed two relaxation processes for a single crystal: process **A-Co-2**, which is a single chain relaxation at the fields corresponding to the metamagnetic transition, and process **B-Co-2**, assigned here to the relaxation of short fragments of chains as single molecules by qtm or coherent rotation of 1D domains with low energy barrier. For the previously investigated powder sample, there are also observed two relaxation processes: the same as for the single crystal process of single chain relaxation, **A-Co-2**, and the other single chain relaxation, but at the fields below H_c , called here process **C-Co-2**. For a powder sample, the origin of the **A-Co-2** and **C-Co-2** processes were elucidated by combining the magnetic measurements and Monte Carlo simulation results.[60] From the simulation, process **A-Co-2** starts at the borders of the 3D magnetic domains during the metamagnetic transition, and process **C-Co-2** starts at the defects of the magnetic structure. These defects

can overlap the crystal structure defects. This was confirmed experimentally, by grinding the initial powder sample and performing for it the ac magnetic measurements. The amplitude of the ac magnetic susceptibility at zero field was larger than for the initial powder sample. This important result is also confirmed by the single crystal investigations. For a single crystal, process **C-Co-2** is indeed not observed due to the low number of defects.

Despite the process **A-Co-2** is observed for the single crystal and the powder, there is a significant difference for it between the samples: the relaxation is faster for the powder. The explanation is that in the powder sample, the chains are shorter than in a single crystal. Also, the relaxation time differences are observed in the whole accessible range of temperature, which means, the observed relaxation is only in the finite size regime. The reason for that is the fact that in the ordered systems, the correlation length diverges to infinity,[88] which means that the length of the chains will be always shorter from it.

Apart from the analysis of the relaxation, it was possible to confirm the easy axis direction for the single crystal, for the second time for the compound from $\text{Co}(\text{NCS})_2(\text{ligand})_2$ family.

5.3. Magnetic properties of $\text{Co}^{\text{II}}(\text{NCS})_2(\text{aniline})_2$

The magnetic investigations of $\text{Co}(\text{NCS})_2(\text{aniline})_2$ (**Co-3**) started with a powder sample in 2018, the research was published in 2020.[51] It concerned also two other compounds, with ligands morpholine and ethylenethiourea. All of them are slightly different compounds from **Co-1** and **Co-2**, as the ligand is non-pyridine-based. This was recognized as the reason for the lack of single chain relaxation for the compounds from $\text{Co}(\text{NCS})_2(\text{ligand})_2$ family. This was one of the grounds for the synthesis of a single crystal. The other reason was the strange magnetic behavior. **Co-3** displays the properties of the ferromagnetic Ising chain. The investigations of the powder sample revealed the antiferromagnetic ordering, however, below the metamagnetic transition, a hysteresis is observed. For a powder, it was impossible to determine, in which direction which interactions are present, there were only made predictions based on the crystal structure and the knowledge gained for other compounds. The **Co-3** single crystal was the third single crystal from the $\text{Co}(\text{NCS})_2(\text{ligand})_2$ family, the second synthesized by the author of the thesis. The research concerning the single crystal of **Co-3** is in preparation. It is planned to publish in 2023.

Symbols:

Co-3 – $\text{Co}(\text{NCS})_2(\text{aniline})_2$

Co-3-c – single crystal sample of **Co-3**

Co-3-g – mildly ground crystals of **Co-3**

Co-3-p – previously investigated powder sample of **Co-3** [61]

5.3.1. Synthesis

The synthesis of a single crystal of **Co-3**, **Co-3-c**, was performed by dissolving the $\text{Co}(\text{NCS})_2$ (0.25 mmol) in 3 ml ethanol, then the mixture was stirred for a week, and then filtered to remove the potential non-dissolved impurities. After that, the 0.125 mmol of aniline was added to the filtrate, stirred for a few minutes, and then left for slow evaporation for 4 weeks. After that time the small crystals were obtained. In the hope to grow larger ones, the remaining product was recrystallized in 2 ml of ethanol at 70°C . After another 8 days, the large single crystal was obtained (Figure 5.3.1). It has a shape of a very thin plate. It is 0.81 mg. The monocrystalline character of the crystal and the crystal structure was confirmed by the SCXRD. The crystal faces were indexed (Figure 5.3.2).

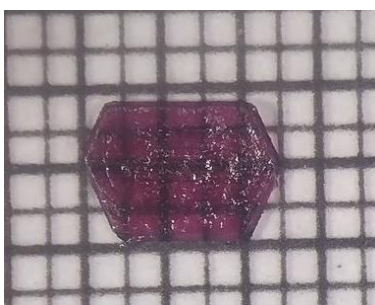


Figure 5.3.1 A photo of the single crystal of **Co-3**. The grid is 0.5 mm.

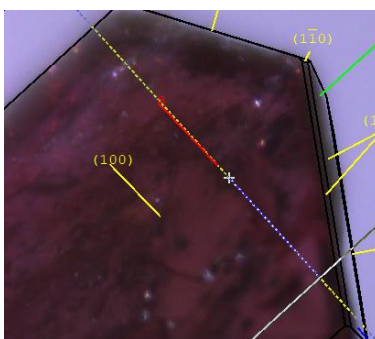


Figure 5.3.2 A photo of a single crystal of **Co-3** with the crystal faces indexed.

5.3.2. Crystal structure

The compound crystallizes in a monoclinic crystallographic system, the space group is $P2_1/c$. There are 2 formula units $\text{Co}(\text{NCS})_2(\text{aniline})_2$ in the unit cell. The unit cell parameters determined for a single crystal sample are presented in Table 5.3.1.

Table 5.3.1 The unit cell parameters of $\text{Co}(\text{NCS})_2(\text{aniline})_2$ determined for **Co-3-c**.

Parameter	Value
a	11.0713(6) Å
b	5.6519(2) Å
c	12.6753(7) Å
α	90°
β	101.368(2)°
γ	90°

There is only one crystallographically independent Co^{II} position, contrary to **Co-1** and **Co-2**. The Co^{II} ions are connected by the thiocyanate bridges into chains (Figure 5.3.3). There are two types of chains in the structure, they are related to each other by the 2-fold rotation symmetry. They are along the b crystallographic axis (Figure 5.3.4).

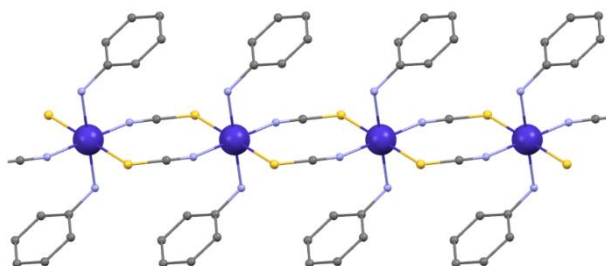


Figure 5.3.3 The view on the single chain in the structure of **Co-3**. Blue – Co, grey – C, light blue – N, yellow – S, H – omitted.

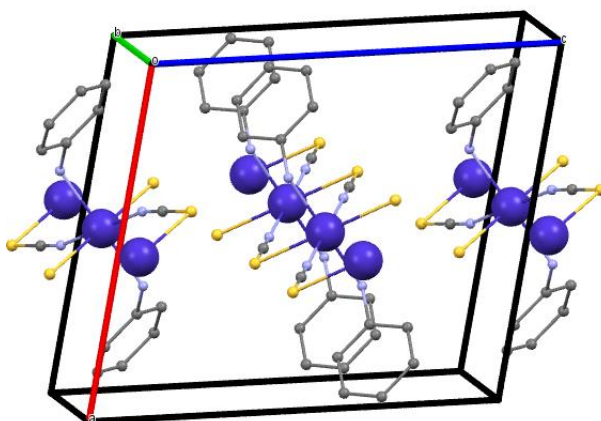


Figure 5.3.4 The view on the unit cell of **Co-3**. Blue – Co, grey – C, light blue – N, yellow – S, H – omitted.

The nitrogen and sulfur atoms' coordination around the Co ion is in all cases *trans* (*trans-trans-trans* coordination, Figure 5.3.5). This makes the chains linear. In the structure, there are present hydrogen bonds, between the hydrogens of the N atom of aniline and S from the NCS bridge of the neighboring chain. The angles are 162°, indicating the interaction

is relatively strong. These bonds lead to the creation of crystallographic *bc* planes (Figure 5.3.6).

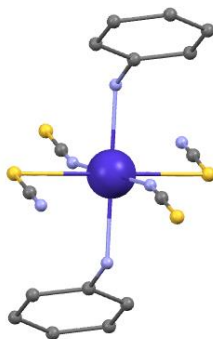


Figure 5.3.5 The view on one of the Co^{II} ion and its coordination in **Co-3**. Blue – Co, grey – C, light blue – N, yellow – S, red – O, H – omitted.

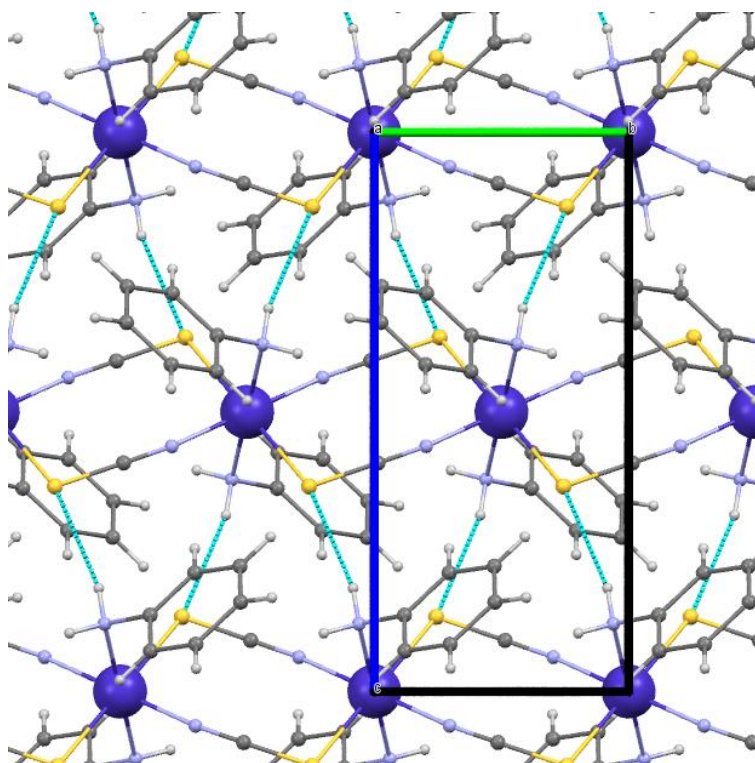


Figure 5.3.6 The view on the *bc* planes in the **Co-3** structure. Blue – Co, grey – C, light blue – N, yellow – S. The hydrogen bonds are marked with cyan lines.

The choice of the directions of the measurement was dictated by the easiest fixing the sample for magnetic measurements and at the same time, to ensure their perpendicularity. The way of fixing of the sample is presented in section 2.3.2. The directions of the measurements are:

$$\mathbf{X} \perp (100),$$

$$\mathbf{Y} = [010],$$

$$\mathbf{Z} = \mathbf{X} \times \mathbf{Y}.$$

5.3.3. Magnetization curves

The magnetization curves were measured for three directions of **Co-3-c**, at 1.8, 3.0 and 5.5 K. First of all, for directions **X** and **Z**, in the magnetization curves, the metamagnetic transition around 6 kOe is visible, and below the transition, there is a remnant hysteresis (Figure 5.3.7). For direction **Y**, the sample behaves as a ferromagnet, a wide hysteresis with the coercive field around 3 kOe is visible. This confirms the interpretation for a powder sample, that there is some kind of ferromagnetic interaction in this system.[61] In all cases, the hysteresis closes with increasing temperature (Figures. 5.3.8 – 5.3.10). For **Y** at 3 K, the hysteresis becomes very narrow (Figure 5.3.9). Also, another metamagnetic transition emerges with a significantly lower H_c than for **X** and **Z**. The value of the critical field and magnetization of saturation extrapolated to $H = 0$ is presented in Table 5.3.2.

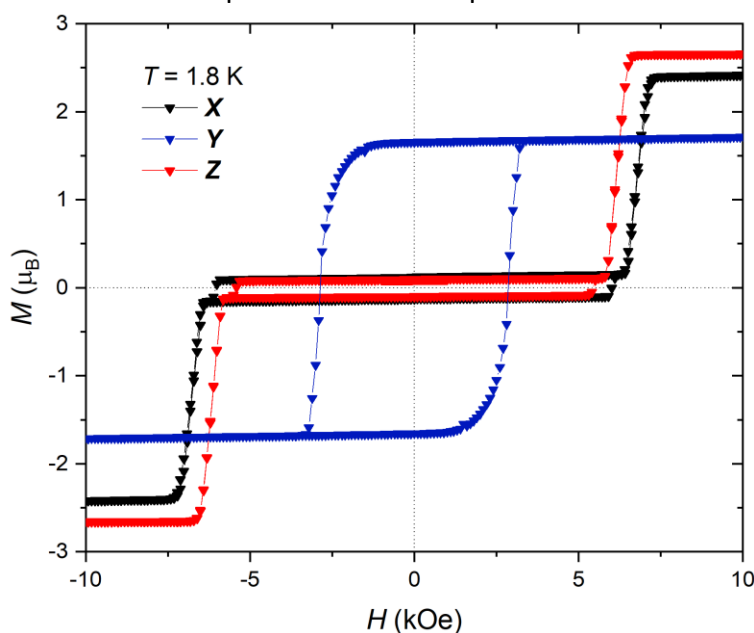


Figure 5.3.7 The field dependence of magnetization for **Co-3-c** measured along 3 directions at 1.8 K.

Table 5.3.2 The values of the critical field and the magnetization of saturation at 0 Oe for **Co-3-c**.

Direction:	X	Y	Z
H_c (Oe)	6456	-	5813
M (μ_B)	2.35	1.66	2.64

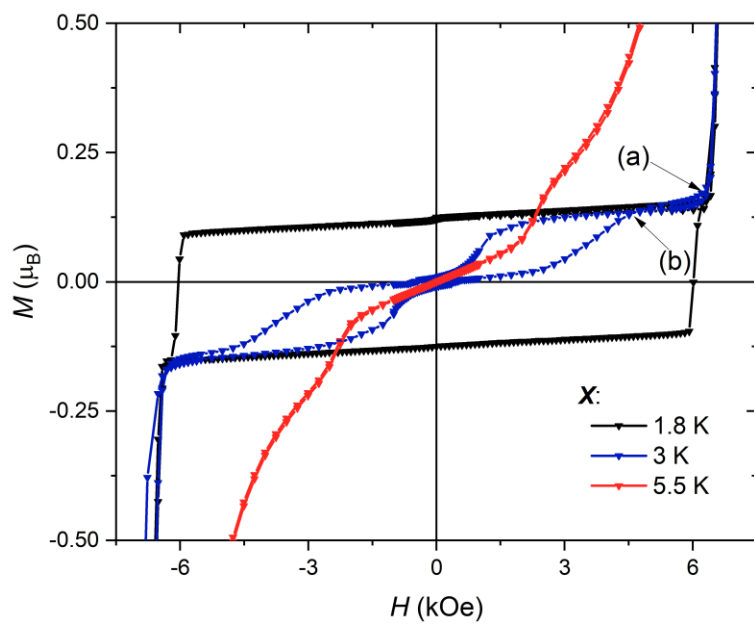


Figure 5.3.8 The field dependence of magnetization measured for **Co-3-c** along **X** at different temperatures.

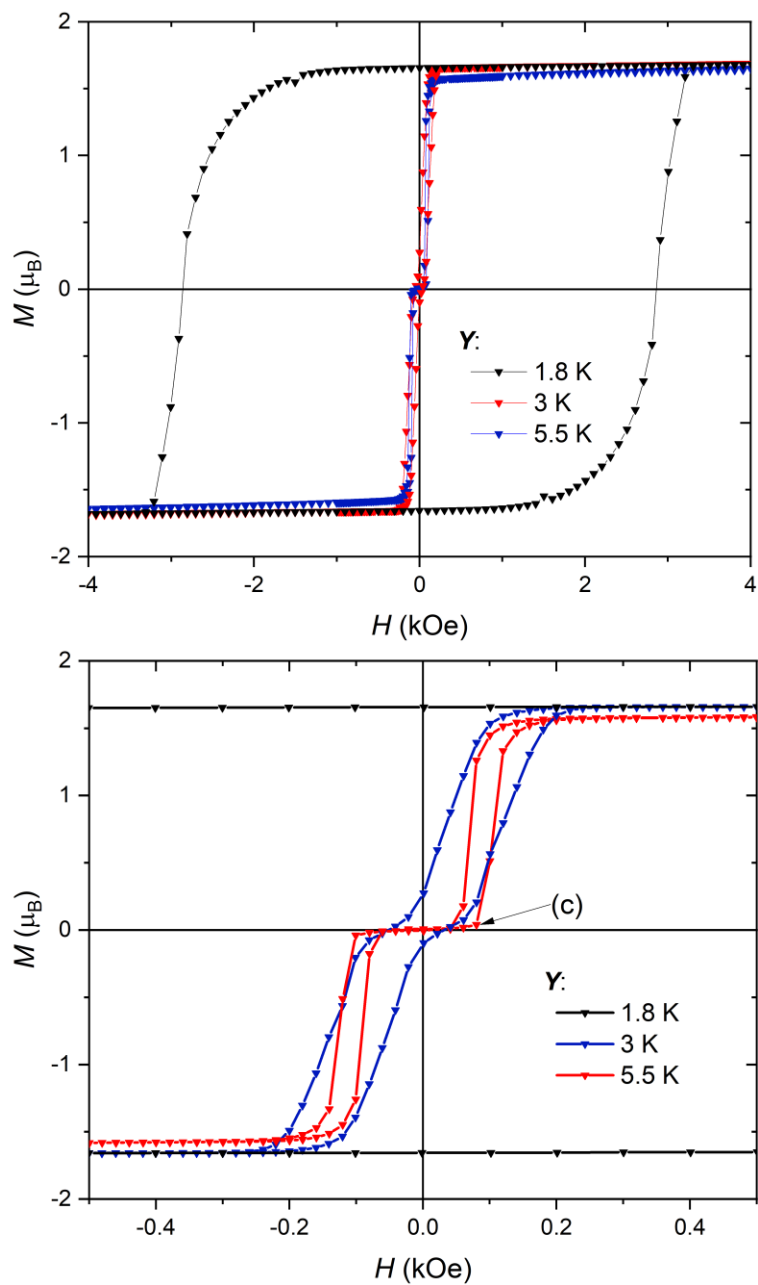


Figure 5.3.9 The field dependence of magnetization measured for **Co-3-c** along **Y** at different temperatures. Top: field range from -4 to 4 kOe. Bottom: field range from -0.5 to 0.5 kOe.

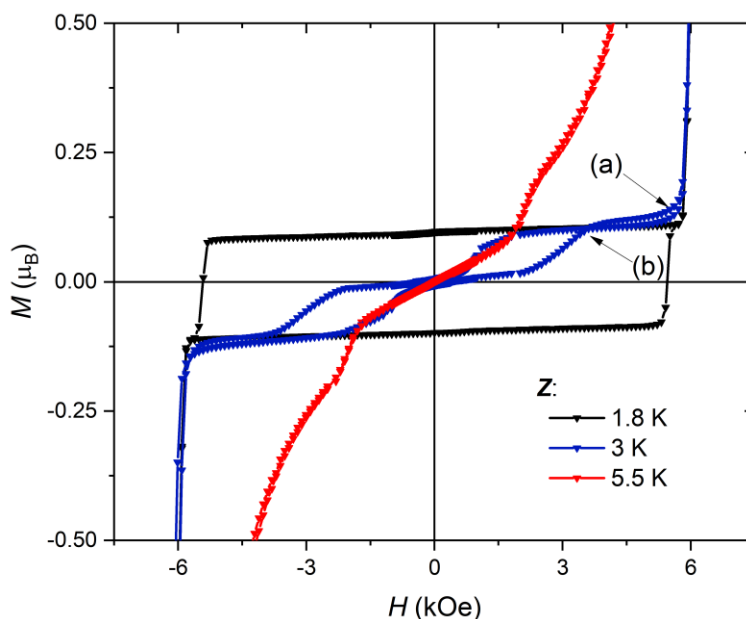


Figure 5.3.10 The field dependence of magnetization measured for **Co-3-c** along **Z** at different temperatures.

In total, there are three metamagnetic transitions visible: (a), (b), (c) (marked in Figures 5.3.8, 5.3.9 and 5.3.10). To investigate these transitions, the magnetization curves were measured at additional temperatures for **X** and **Y**. The results are presented in Figures 5.3.11 – 5.3.13.

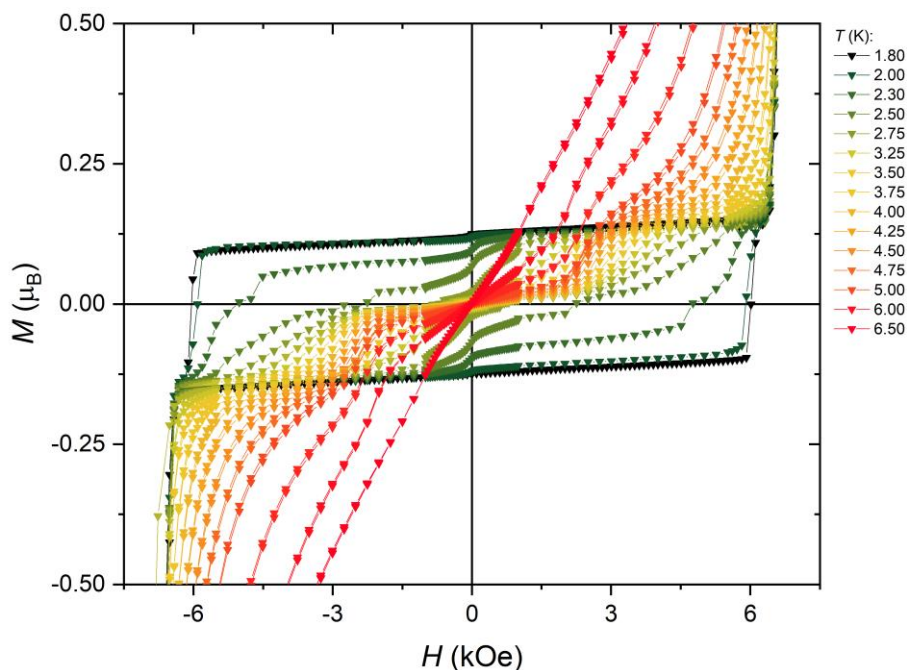


Figure 5.3.11 The field dependence of magnetization measured for **Co-3-c** along **X** at different temperatures.

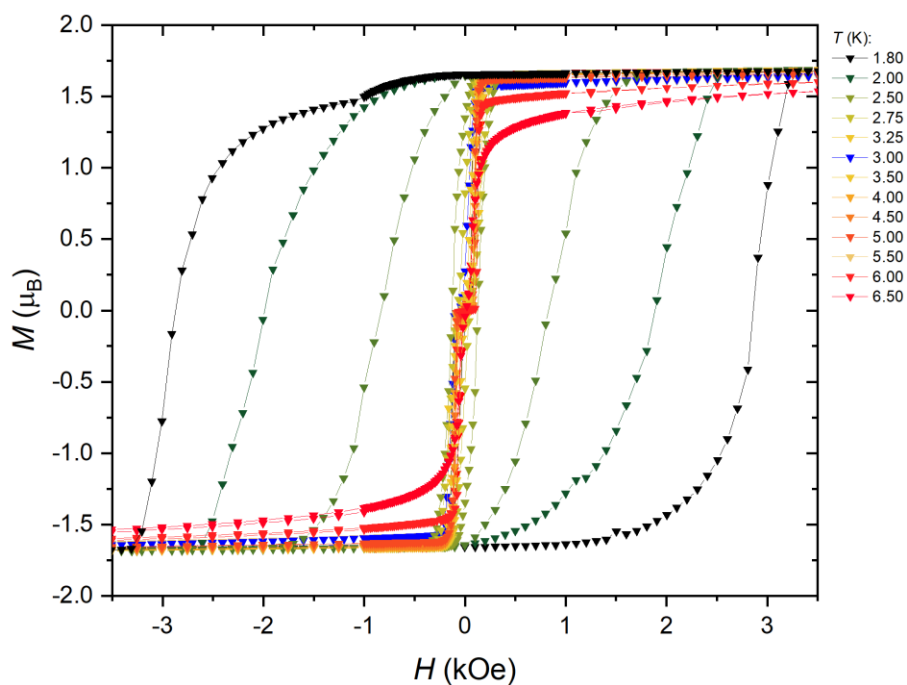


Figure 5.3.12 The field dependence of magnetization measured for **Co-3-c** along **Y** at different temperatures.

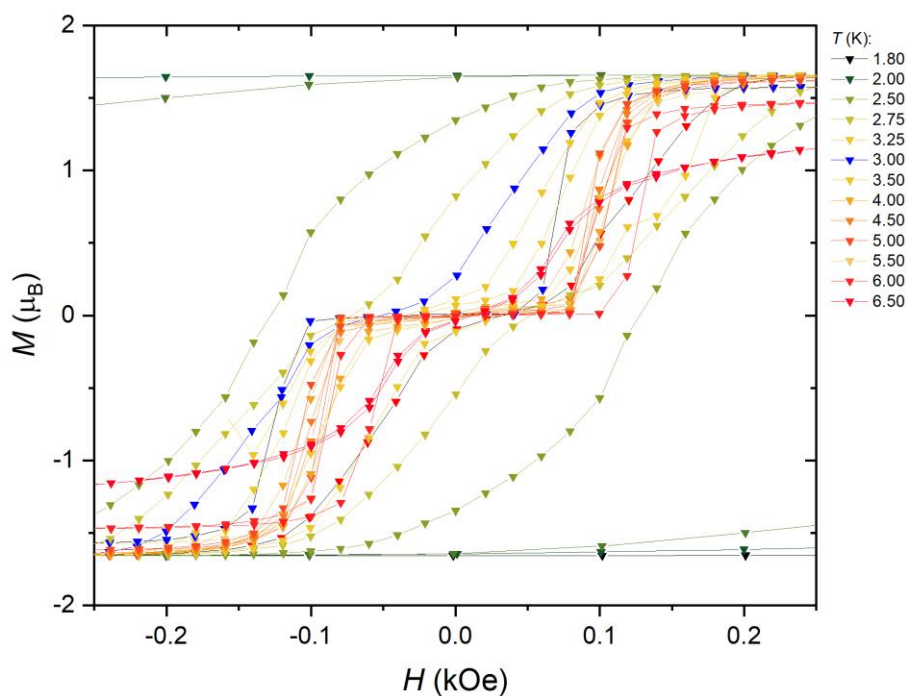


Figure 5.3.13 Enlargement of Fig. 5.3.12. The field dependence of magnetization measured for **Co-3-c** along **Y** at different temperatures.

The magnetization curves together with a crystal structure analysis provide a reasonable explanation for the magnetic behavior of **Co-3**. There are two types of chains in the structure, which are related to each other by a 2-fold symmetry axis. The single ions in

these chains are in the identical surrounding of four nitrogen atoms and two sulfur atoms, which crystal field causes the Ising-like anisotropy, $S = 1/2$. This was proven based on the *ab initio* calculations.[61] The spin chains overlap with the structural chains, the exchange interaction is mediated through the NCS bridges. This interaction is ferromagnetic (see section 5.3.8.) and will be described here with J_1 . Between the structural chains among the *bc* planes, there are present the hydrogen bonds: $\text{N}_{\text{aniline}}\text{-H}\cdots\text{S-Co}$. Through this bond, the exchange can be mediated. This interaction will be described here with J_2 . The planes can also interact with each other, however, there is no hydrogen bonding in the structure between the *bc* planes or π - π stacking, therefore, if there is such interaction, it is probably of dipolar origin. It will be described here as J_3 .

In the neighboring chains, the Co^{II} ions' easy axes are related by the same symmetry as chains, and they are: $\mathbf{m}_1 = (m_x, m_y, m_z)$ and $\mathbf{m}_2 = (-m_x, m_y, -m_z)$. It means, that in the neighboring chains, the easy axis is differently oriented. This results in the presence of the ferromagnetic component, despite the antiferromagnetic interaction between the chains. For **X** and **Z**, the easy axes in the neighboring chains comprise in a way, the ferromagnetic component vanishes, for **Y**, the component remains. The coercive field is large: 2.85 kOe at 1.8 K for **Y**. The component in **X** and **Z** does not vanish, but the reason for that can be not perfect aligning of the sample along the assumed direction. This can be caused by the imperfect positioning of the sample on the holder, but also by some curvature of the straw.

The main metamagnetic transition, (a), is related to the antiferromagnetic interaction between the chains among the planes (J_2). The interaction between the planes (J_3) is visible as the third metamagnetic transition (c) emerging along **Y** at a higher temperature (Figure 5.3.13). The interactions can be estimated within the equations:

$$2H_{cX}\mathbf{m}_1 \cdot \mathbf{X} = -2S^2zJ_2, \quad (5.3.1)$$

$$2H_{cY}\mathbf{m}_1 \cdot \mathbf{Y} = -2S^2zJ_3, \quad (5.3.2)$$

where H_{cX} is the critical field for **X** in 1.8 K equal to 6456 Oe, H_{cY} is the critical field for **Y** in 5.5 K equal to 82 Oe. One spin interacts with z spins with the specific J . From that estimation, J_2/k_B is -1.02 K (for $z = 4$), and for J_3/k_B is -0.02 K (for $z = 2$).

The low value of the energy of interplane interaction, J_3 , in comparison to the interchain interaction, J_2 , suggests that the interplane interaction can be neglected, and the system can be treated within the 2D Ising model.

5.3.4. Specific heat

The specific heat measurements were performed for **Co-3-c** along the **X** direction, without and with the applied external magnetic field. The measurement performed without the external magnetic field in the range from 2 to 40 K is presented in Figure 5.3.14. A very sharp peak is observed at 6.49 K, indicating the presence of magnetic ordering, as suspected from the analysis of the magnetization curves. To the experimental points, the combination of Debye, Einstein, and 2D Ising (Onsager) [91] models are fitted. The fit was performed by M. Rams. The fit is performed assuming the rectangular lattice: one spin interacts with two neighboring spins in a chain with J_1 and with two neighboring spins from two neighboring

chains with $2J_2$. In the real system, one spin interacts with four spins from two neighboring chains. In the fit of the 2D Ising model, it is approximated with two spins and interaction scaled by factor 2. The values for the lattice contribution obtained from the fit are: $\Theta_D = 86.6(4.5)$ K, $\alpha_D = 2.20(28)$, $\Theta_E = 155(14)$ K, $\alpha_E = 4.83(56)$. The values of the exchange interactions: $J_1/k_B = 31.3(4)$ K and $2J_2/k_B = -2.23(7)$ K. The 2D Ising model reproduces the peak, indicating that for the ordering the interaction along the chains and between them among the planes is responsible. The signs of the exchange constants are chosen in a way to obtain agreement with the interpretation of magnetization curves. The reason is that in the Onsager model, these signs do not influence the fit of the specific heat at zero field. Therefore, the interaction along the chains is ferromagnetic, and between the chains – antiferromagnetic.

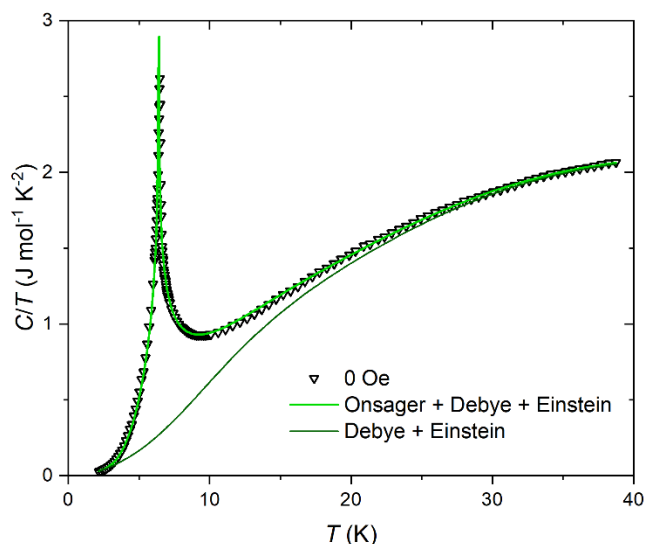


Figure 5.3.14 The temperature dependence of the specific heat measured for **Co-3-c** without the field. The line represents the fit of the combination of Debye, Einstein, and Onsager models.

The magnetic contribution was obtained by subtraction of the lattice contribution (Debye + Einstein) from the total specific heat. The integral over the C_{magn}/T vs. T at 0 Oe, gives the change of the entropy related to the ordering and is equal to $5.39 \text{ J mol}^{-1} \text{ K}^{-1}$. The theoretical value is $5.76 \text{ J mol}^{-1} \text{ K}^{-1}$, for ordering of $\frac{1}{2}$ spins. In Figure 5.3.15, there is presented the magnetic contribution to the specific heat at 0 Oe, analyzed with the 1D and 2D Ising models, for comparison. The curve of the 1D Ising was calculated for J_1 obtained from the fit of the 2D Ising model. The 1D Ising model does not reproduce the peak, as the ordering is not possible for the model 1D system. For the 2D system, the ordering occurs, similarly to the 3D structure. **Co-3** is indeed a 3D structure, which is visible in Figure 5.3.15 (bottom), as a slight shift of the experimental data from the Onsager model.

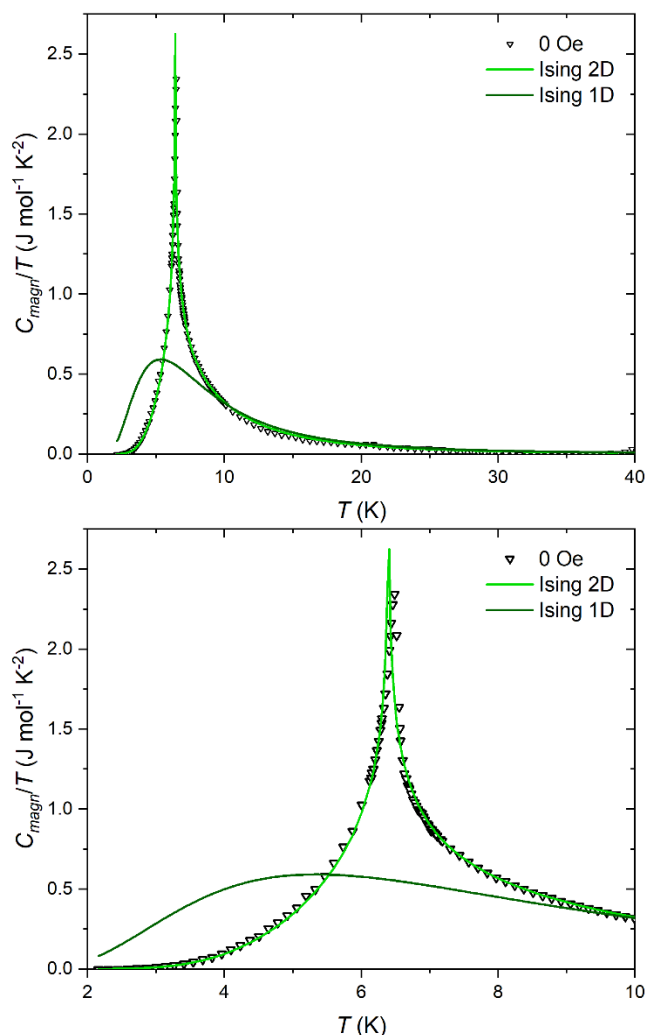


Figure 5.3.15 The temperature dependence of the magnetic contribution to the specific heat measured for **Co-3-c** without the field. Curves calculated within the 1D and 2D Ising models are shown with lines. Top: 0 – 40 K. Bottom: 2 – 10 K.

The shift from 6.41 K (fit) to 6.49 K (experimental), results from the neglecting of the J_3 interaction in the fit. However, the shift is very small, confirming the weak interaction between the planes. Therefore, such interaction can be neglected, and the system can be described within the 2D model.

The magnetic contribution to the specific heat for different fields is presented in Figure 5.3.16, top. The shift of the peaks with the increasing field is clearly visible. For 8 kOe, the peak is already flattened, and determining its position is impossible. The peaks' positions were included in the phase diagram (section 5.3.5).

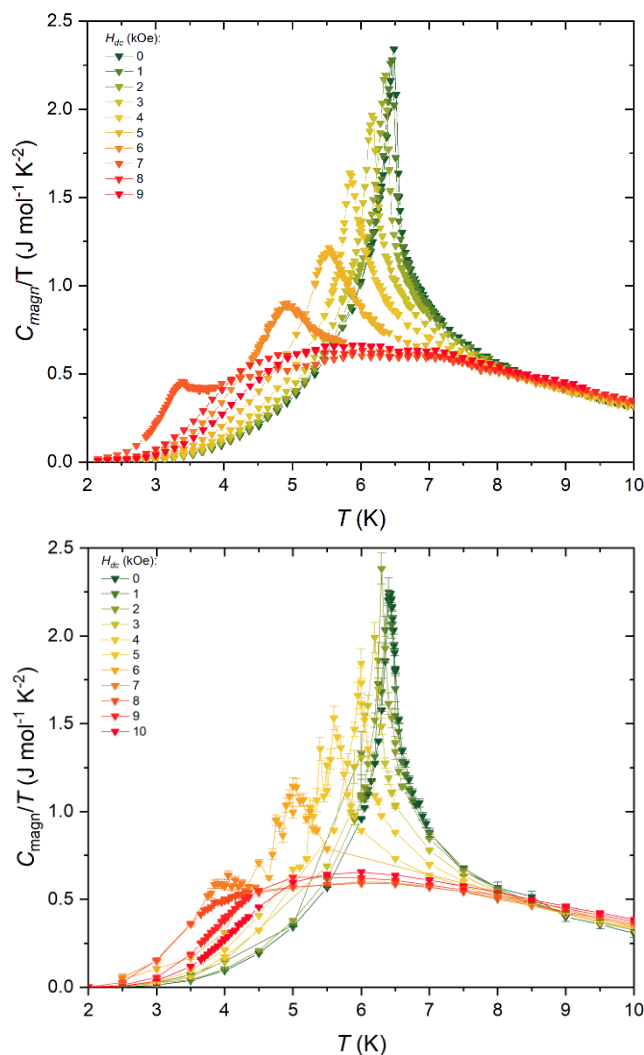


Figure 5.3.16 The temperature dependence of the magnetic contribution to the specific heat for a single crystal sample of **Co-3-c** at different fields along **X**. Top: experimental data. Bottom: data simulated with ALPS package.

The specific heat was also simulated with the ALPS package, for the parameters determined from the fit of the 2D Ising model ($J_1/k_B = 31.3$ K, $2J_2/k_B = -2.23$ K) and for a crystal structure of the *bc* planes of **Co-3**, but assuming interaction of one spin with two spins from the neighboring chains (Figure 5.3.17). The simulation was performed for classical spins, in the range from 2 to 10 K, at zero and non-zero fields. The initial parameters set was spin: 1/2, thermalization: 50000, sweeps: 400000, model: Ising. To run the simulation, the *spinmc* program was used.

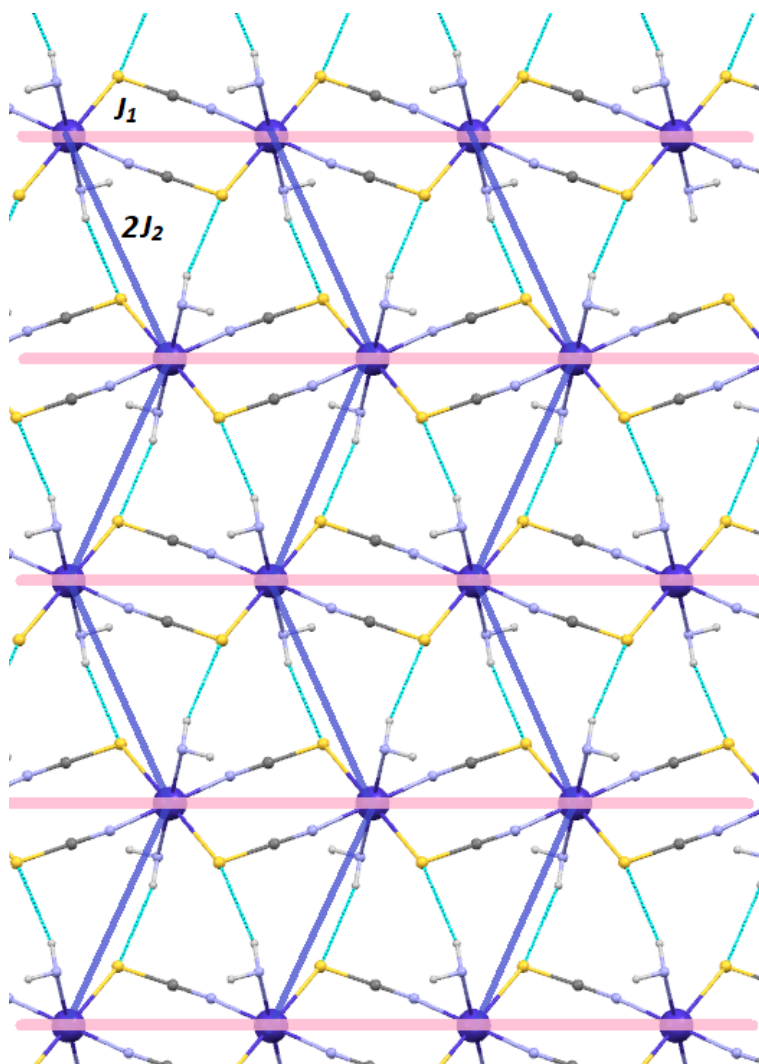


Figure 5.3.17 The view on the bc plane used for simulations of the specific heat for **Co-3**. The spins are located in the Co^{II} ions (dark blue balls). The pink lines represent the interaction along the chains (b direction; J_1), the blue lines represent the interactions between the chains ($2J_2$). For every spin, two of the interchain interactions are omitted.

The size of the system was chosen based on trials. There were checked the following system sizes ($L \times W$, where L is b and W is c direction) in the range from 6 to 6.9 K and without field: 32×32 , 64×32 , 128×32 , 256×32 , 32×64 , 32×128 , 32×256 . The comparison of these trial simulations is presented in Figure 5.3.18 and Figure 5.3.19. The chosen size of the system was 256×32 , as for the higher W , the C_{magn}/T value does not change and $L = 256$ gives a sharp peak at zero field. The larger values of L would cause a prohibitively long time of the simulation.

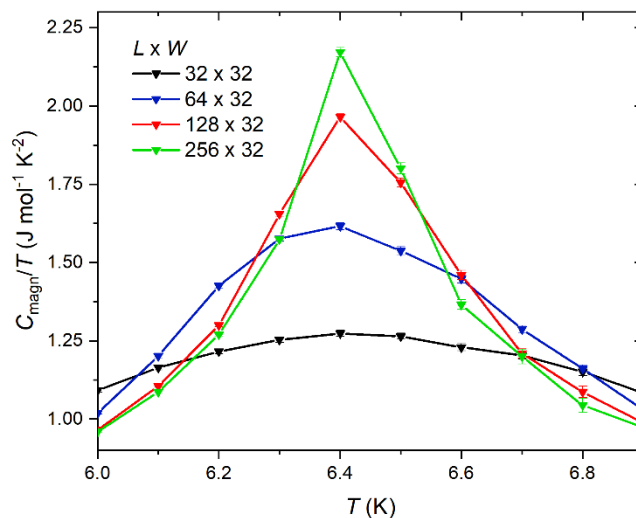


Figure 5.3.18 The result of the trial simulation of the specific heat at zero field for **Co-3** for different sizes of the system.

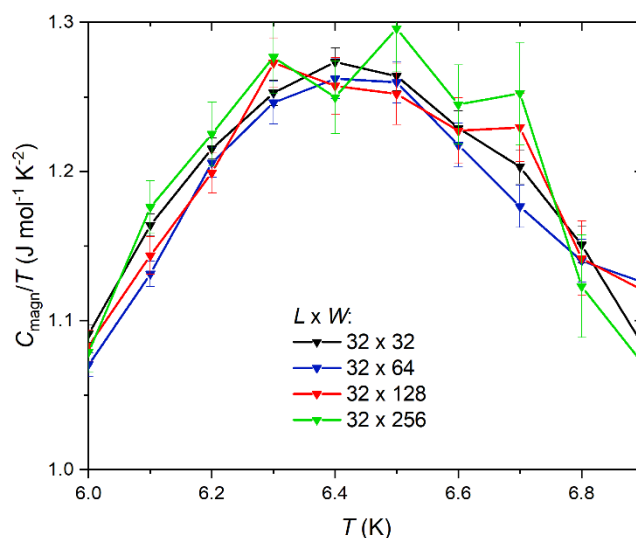


Figure 5.3.19 The result of the trial simulation of the specific heat at zero field for **Co-3** for different sizes of the system.

The simulated specific heat at zero field is presented in Figure 5.3.20, top. The simulation reproduces the experimental results qualitatively. The C_{magn}/T value obtained in the ALPS simulation is slightly lower ($0.1 \text{ J mol}^{-1} \text{ K}^{-2}$ difference, Figure 5.3.20), and is caused by the finite size of the simulated system. The peak is at 6.43 K, in between the experimental data and the fit of the 2D Ising model. The results for the different fields are presented in Figure 5.3.16, bottom. The differences between the simulated and experimental curves are also very small.

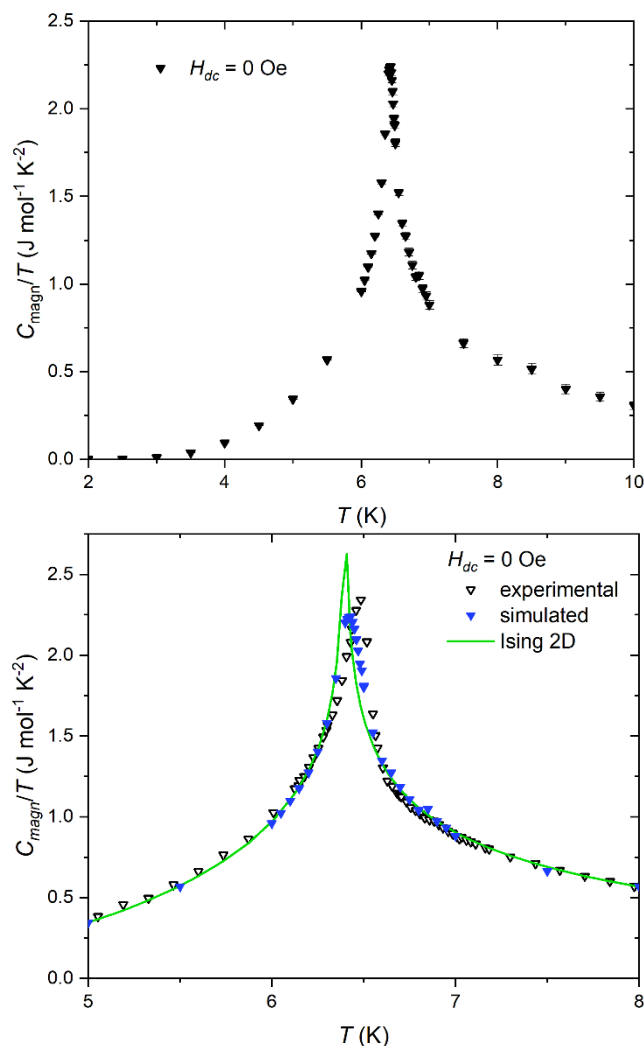


Figure 5.3.20 Top: Simulated specific heat for **Co-3**, without the field. Bottom: Comparison of the specific heat at 0 Oe close to T_C : experimental, simulated (ALPS), and fitted (2D Ising) data.

An example of a similar 2D system is $\text{Fe}(\text{NCS})_2(\text{pyrazine})_2$ compound.[31] The exchange in this compound is mediated through the pyrazine ligand. The Fe^{II} ions with effective spin $S = 1/2$, are connected through the pyrazine ligands into a square plane, the chains cannot be distinguished. The system can be therefore described with one J , the interactions in two dimensions cause the ordering of the system.

5.3.5. Phase diagram

The phase diagram was drawn based on specific heat and magnetization data. It is presented in Figure 5.3.21. The points from magnetization were determined as the inflection points, as marked in Figures 5.3.8, 5.3.9 and 5.3.10. The points from specific heat were determined as the maximum at the C_{magn}/T vs. T dependence. The point from specific heat seems to be related to the metamagnetic transition (a). The other two transitions are not visible in the specific heat. This proves, that for the ordering, there are mainly responsible interactions in 2 dimensions: the intrachain interaction (J_1) and the interaction

between the chains among the planes (J_2). Transition (c) is related to the weak interaction between the planes. The origin of transition (b) can be related to the positioning of the sample. The small hysteresis for X and Z is observed probably because of the slightly tilted orientation of the sample from the assumed direction of the measurement. If so, this small hysteresis is related to the same hysteresis observed for Y , however, in a different direction and its coercive field can be different.

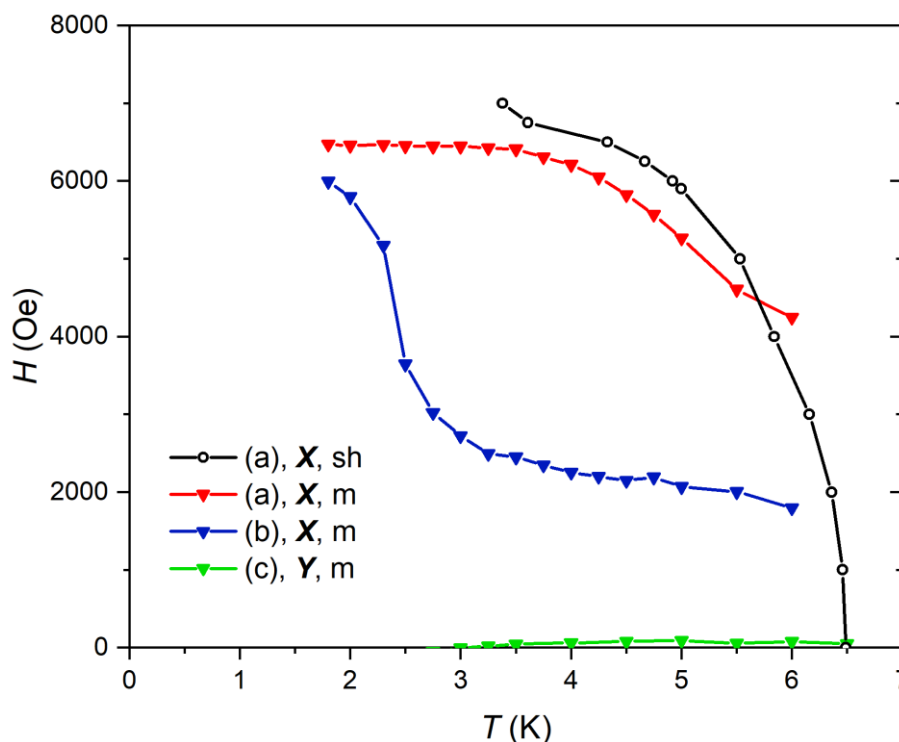


Figure 5.3.21 A phase diagram for **Co-3-c**. m – points from magnetization, sh – points from specific heat.

5.3.6. Easy axis determination

The values of saturation of magnetization at zero field were used to determine the easy axis direction experimentally. From the *ab initio* calculations, it is known, that the easy axis is tilted from the Co- N_{aniline} bond by 23.1° .^[61] The g factors values and the energy gap between the ground and the first excited state are presented in Table 5.3.3. The *ab initio* calculations were performed by dr Michael Böhme from Jena University.

Table 5.3.3 The values of g factors and the energy gap between the ground and the first excited states for the Co^{II} ion in **Co-3**, derived from the *ab initio* calculations.^[61]

g_x	g_y	g_z	E (K)
1.986	2.899	7.540	328

The calculations were performed using the Mathematica software. To recalculate the crystallographic system to the Cartesian system, the following equation was used:

$$\begin{pmatrix} x_c \\ y_c \\ z_c \end{pmatrix} = \begin{pmatrix} a & 0 & a \cos \beta \\ 0 & b & 0 \\ 0 & 0 & c \sin \beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \quad (5.3.3)$$

where x_c , y_c , and z_c represent the coordinates of the vector in the Cartesian system, a , b , c , and β are the unit cell parameters, the matrix is the conversion matrix for the monoclinic system, and x , y , z represents the crystallographic coordinates. There are distinguished easy axes directions depending on the chain. The magnetic easy axis vectors in the Cartesian system are:

$$\mathbf{m}_1 = \begin{pmatrix} m_x \\ m_y \\ m_z \end{pmatrix}; \quad \mathbf{m}_2 = \begin{pmatrix} -m_x \\ m_y \\ -m_z \end{pmatrix}. \quad (5.3.4)$$

On that basis, there were created 3 equations:

$$M_X = \frac{1}{2} (|\mathbf{m}_1 \cdot \mathbf{X}| + |\mathbf{m}_2 \cdot \mathbf{X}|), \quad (5.3.5)$$

$$M_Y = \frac{1}{2} (|\mathbf{m}_1 \cdot \mathbf{Y}| + |\mathbf{m}_2 \cdot \mathbf{Y}|), \quad (5.3.6)$$

$$M_Z = \frac{1}{2} (|\mathbf{m}_1 \cdot \mathbf{Z}| + |\mathbf{m}_2 \cdot \mathbf{Z}|), \quad (5.3.7)$$

where M_X , M_Y , and M_Z are the values of magnetization saturation from the experiment. This system of 3 equations was solved and 4 solutions for $\mathbf{m}_1$ were obtained: (1.74, -1.66, 3.08) μ_B , (1.74, 1.66, 3.08) μ_B , (2.86, -1.66, -2.08) μ_B and (-2.86, -1.66, 2.08) μ_B . The first one was assumed to be correct, as it is the closest solution to the easy axis determined from *ab initio* calculations: (1.63, -1.70, 2.95) μ_B . The angle between the easy axis determined experimentally and theoretically is 1.8°. The angle between the easy axis determined experimentally and the direction of the Co-N_{ligand} bond is 21.6°. The angle between the easy axis determined theoretically and the direction of the Co-N_{ligand} bond is 23.1°. This confirms the agreement of the theory and experiment.

5.3.7. Magnetic susceptibility

Magnetic susceptibility for three directions of **Co-3-c** confirms the above-presented interpretation of the interactions in the system. The zfc and fc curves are presented in Figure 5.3.22, the ac magnetic susceptibility at 0 Oe is in Figure 5.3.23. For **Y**, ferromagnetic behavior is observed. At 400 Oe, the fc curve is saturated (Figure 5.3.22, middle). At 0 Oe, a sharp peak around 6.5 K is observed (Figure 5.3.23, middle). For **X** and **Z**, the peak in any of the fields is not sharp, which is the result of the ferromagnetic component. The susceptibility value is also significantly larger for **Y**.

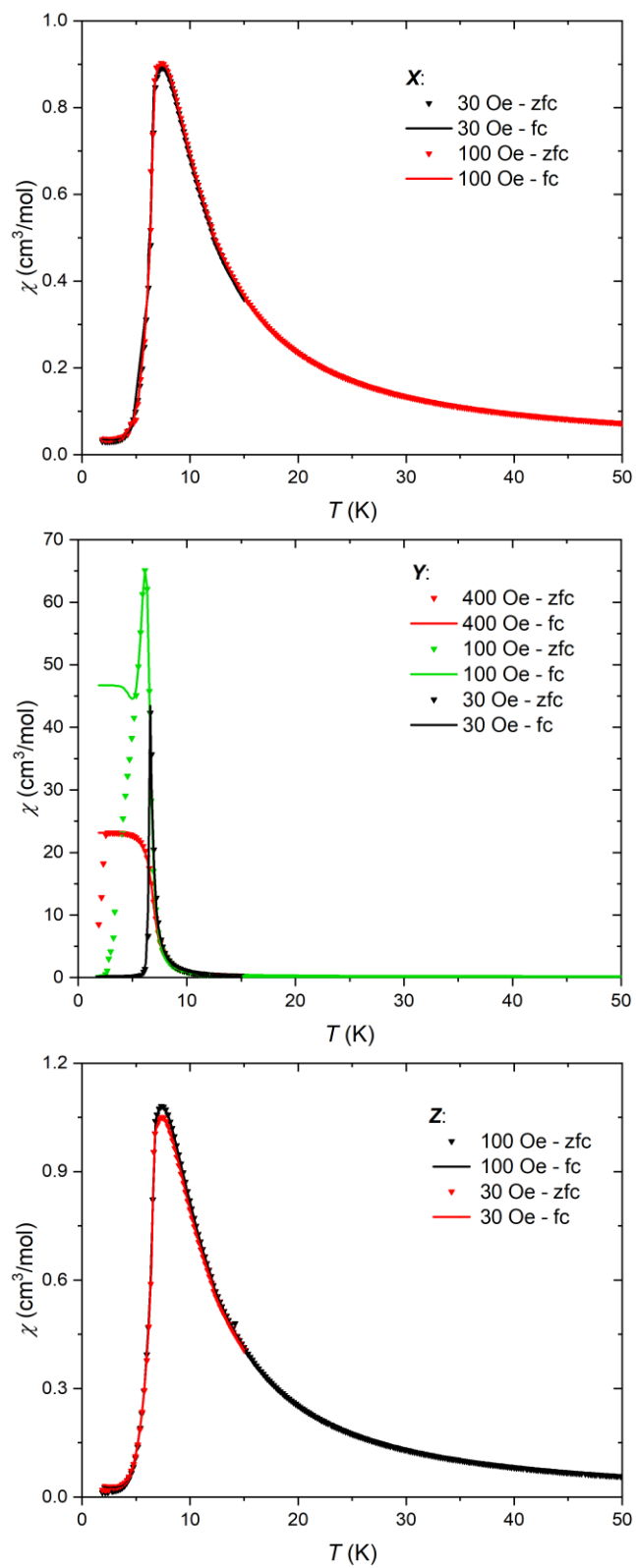


Figure 5.3.22 Zero-field and field cooled susceptibilities measured for **Co-3-c** along **X**, **Y**, and **Z**.

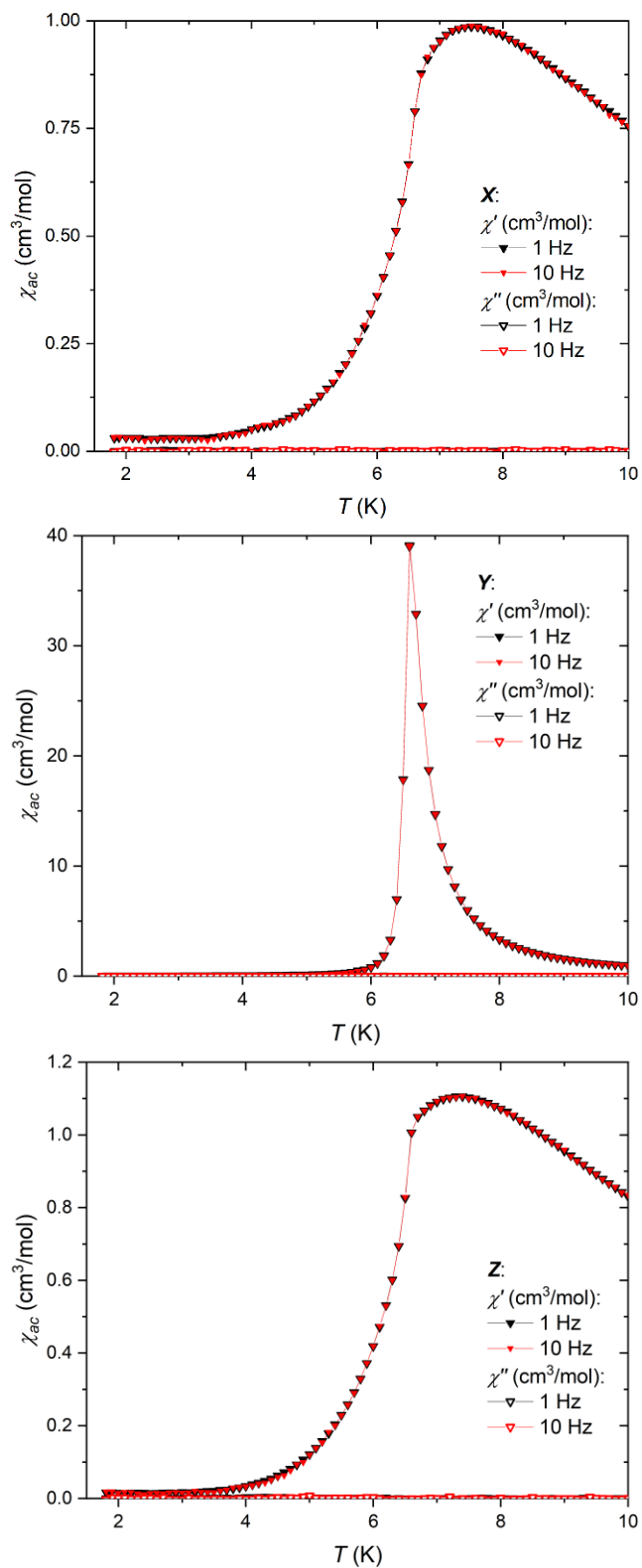


Figure 5.3.23 The ac magnetic susceptibility measured for **Co-3-c** at 0 Oe, along **X**, **Y**, and **Z**. Data for 1 Hz and 10 Hz overlap.

For the 2D Ising model, there is no analytical solution for the magnetic susceptibility. Also, simulating it with the ALPS package is not fully possible, because only the susceptibility parallel to the exchange z axis can be simulated, while the perpendicular component is not available. Therefore, such analysis is not included. However, to the high-temperature (10 – 50 K) part of the magnetic susceptibility measured for the powder sample **Co-3-p**, the 1D Ising model was fitted according to equations 1.5.7 – 1.5.10 (Figure 5.3.24). This is to show the discrepancies which arise in the low temperature. The fit gives the following values: $J_{\text{Ising}}/k_B = 28.5(2)$ K, $zJ'/k_B = 0.67(9)$ K, $g_z = 7.10(1)$, $g_{\perp} = 2.5$ (fixed). The fit deviates from the experimental points below 10 K, which confirms the inaccuracy of the 1D Ising model in this case.

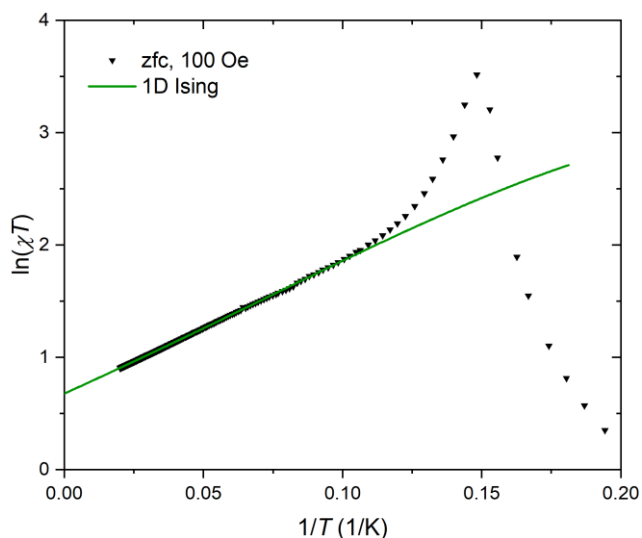


Figure 5.3.24 The zfc magnetic susceptibility for **Co-3-p**, analyzed with the 1D Ising model.

5.3.8. Magnetic relaxation

The magnetic relaxation of single chains was not observed for **Co-3-p** previously.[61] For a powder sample some relaxations were measured at a very low field, however, χ'' was small, the experimental points deviated significantly from the fits of the Cole-Cole model and the estimated energy barrier was too high (~ 100 K) comparing to similar compounds. This could not be assigned to the single chain relaxation or any other relaxation. The ac magnetic susceptibility at higher fields was not measured, assuming, that at such a large field as 6 kOe, the single chain relaxation would not exist.

For a single crystal sample, **Co-3-c**, the ac magnetic susceptibility measurements were performed at the fields around 6 kOe, for **X** and **Z**. For **Y**, the relaxations are not observed – at 0 Oe, there is no imaginary component visible (Figure 5.3.23, middle). The frequency dependence of ac magnetic susceptibility for **X** and **Z** were measured at 6500 Oe (Figure 5.3.25, **X**), 6750 Oe (Figure 5.3.26, **X**), and 5900 Oe (Figure 5.3.27, **Z**), 6250 Oe (Figure 5.3.28, **Z**), respectively. The results were further analyzed with the Cole-Cole model. The determined times are presented in Figure 5.3.29.

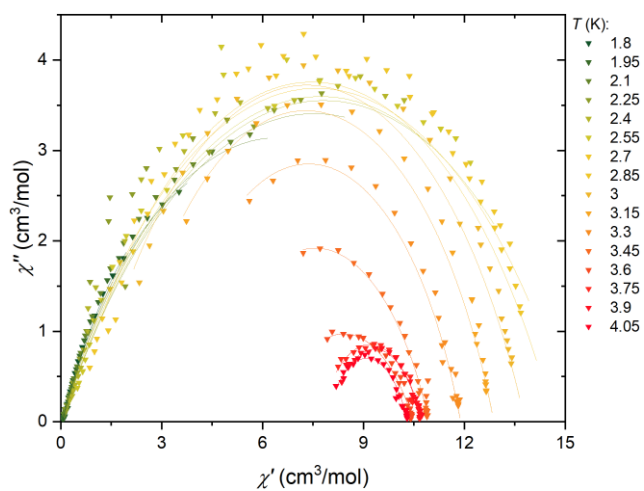


Figure 5.3.25 The ac magnetic susceptibility measured for **Co-3-c** at 6500 Oe, along direction **X**. The lines are the fits of the single-mode Cole-Cole model.

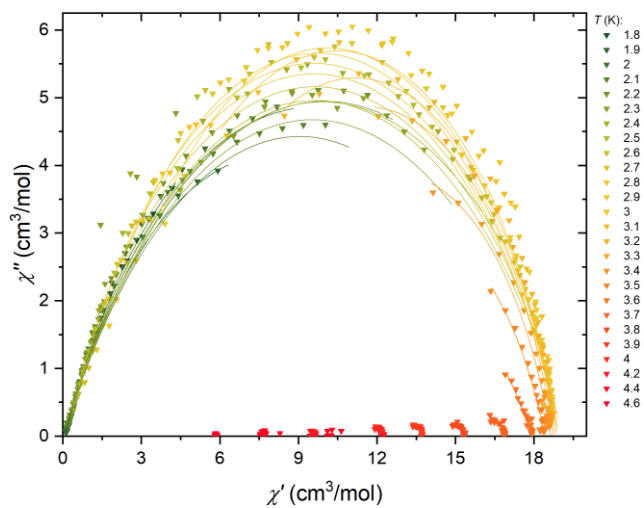


Figure 5.3.26 The ac magnetic susceptibility measured for **Co-3-c** at 6750 Oe, along direction **X**. The lines are the fits of the single-mode Cole-Cole model.

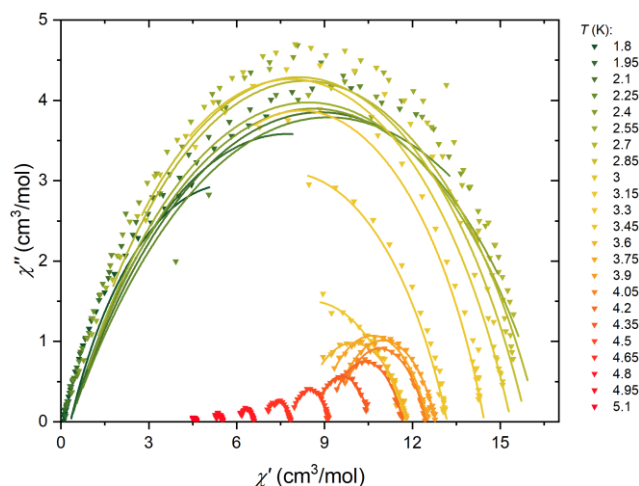


Figure 5.3.27 The ac magnetic susceptibility measured for **Co-3-c** at 5900 Oe, along direction **Z**. The lines are the fits of the single-mode Cole-Cole model.

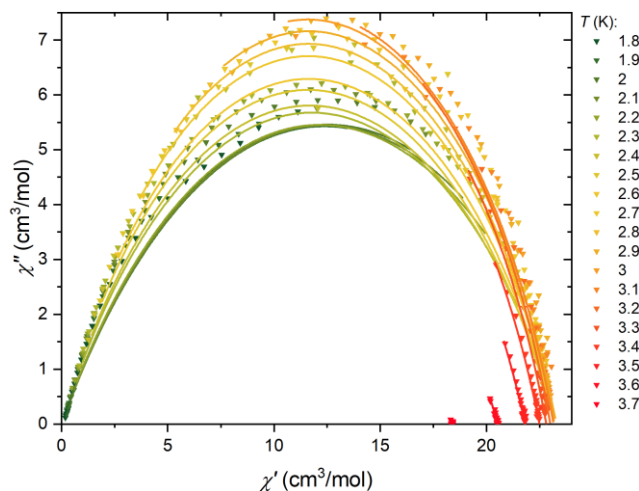


Figure 5.3.28 The ac magnetic susceptibility measured for **Co-3-c** at 6250 Oe, along direction **Z**. The lines are the fits of the single-mode Cole-Cole model.

The temperature dependence of the relaxation times presented as the Arrhenius plot shows two relaxation processes. The first one, at the low temperature, is the single chain relaxation, called here process **A-Co-3**. In the high temperature, there is visible a temperature-independent process **B-Co-3**, the same as **B-Co-2**. For process **A-Co-3**, the dependence is not linear, an inflection is visible, which can be interpreted as a crossover. The fits of the Arrhenius law give the values around 20 – 30 K in the supposedly finite regime and 50 – 55 K in the supposedly infinite regime. This estimation could support the hypothesis about the crossover, however, the points in the infinite size regime for different fields do not lay in the same course. The field dependency was not observed for **Co-2-c**. For **Co-3-c**, it can indicate that at such high fields, the relaxing chains have different length at different fields.

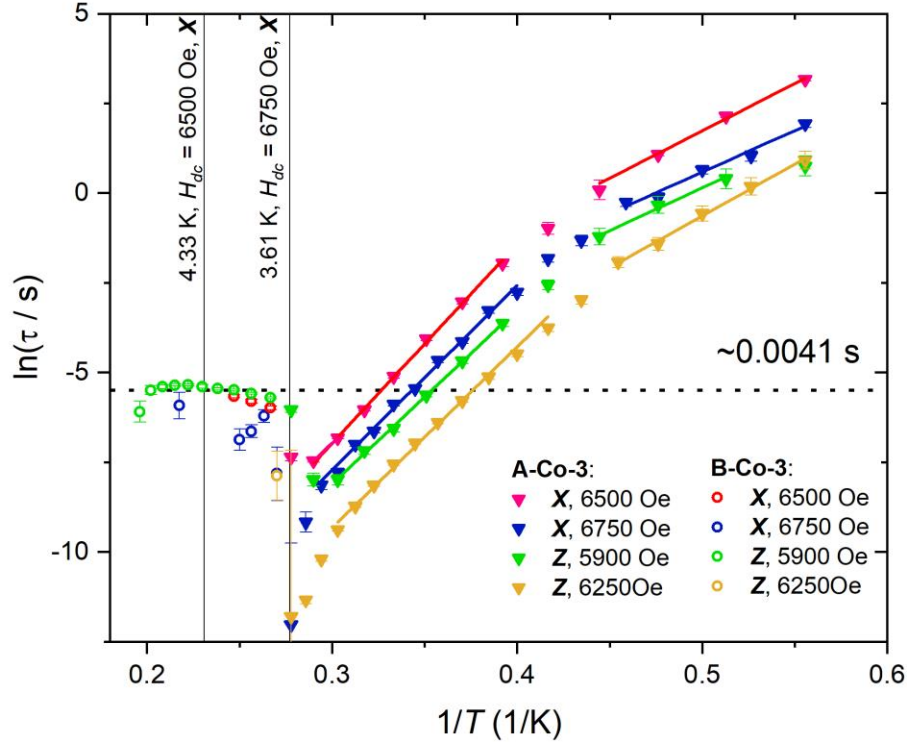


Figure 5.3.29 The temperature dependence of the relaxation times presented in the Arrhenius plot for **Co-3-c** with the fits of the Arrhenius law.

The other explanation can be the impact of the single spin relaxation processes. The single ion properties are not different, however, in the single spin contribution, the field-dependent processes are included. For the **Co-3**, the single spin relaxation process is not the Orbach process, for the same reason as for **Co-1** and **Co-2**. The possible are direct and qtm, as the two processes include the field as a variable. The temperature dependence is not linear, the direct process would not cover such curvature, therefore the Raman process is not excluded. Assuming the inflection is a crossover, there were performed some trials to fit the modified approach as in subchapter 5.1, but with the single spin impact at non-zero field. The field put into the equation was a field value, perpendicular to the easy axis, as it was proven for **Co-1**, that the parallel field is zero. However, this approach did not give satisfactory results. It was impossible to fit the four curves simultaneously, with the same parameters. The conclusion is that the inflection in the experimental points cannot be treated as a crossover. Therefore, the only possible reason for such behavior is that the observed relaxation is in the finite size regime as for **Co-2**.

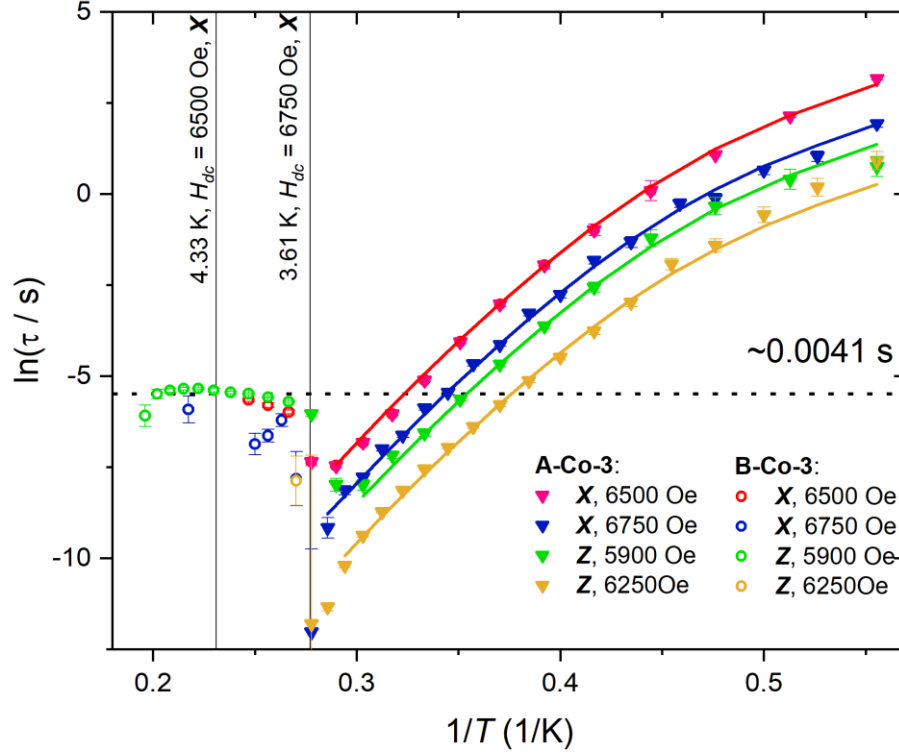


Figure 5.3.30 The temperature dependence of the relaxation times presented in the Arrhenius plot for **Co-3-c** with the fits of equation 5.3.6.

In the crossover approach, the perpendicular field was treated as non-zero, despite, that from simulations for **Co-1**, it turned out, that this field is also close to 0. Using the non-zero value of the field was just a trial, to check if the field does have an impact on relaxation in such a system. Therefore, for the hypothesis with the finite size regime relaxation, the field is zero. The inflection point is assumed as the result of the Raman process with a high n value. Therefore, for all four curves, the following equation was fitted simultaneously:

$$\tau_{finite} = \frac{p}{2} \exp\left(\frac{\Delta_\xi}{k_B T}\right) \frac{1}{C T^n + B_1}, \quad (5.3.8)$$

where p is the parameter related to the chain length. This parameter is different for every measurement and was estimated in relation to the relaxation time measured for **Co-3-c** at 6500 Oe along **X**. The relaxation times were simply divided by each other, assuming the change is constant over the accessible range of temperatures. Their values are presented in Table 5.3.4. Indeed, the p parameter should be N , the number of units in a chain. However, this parameter is dependent on the C and B_1 parameters from the single spin contribution, for that reason, it is impossible to fit the N parameter and the real values of C and B_1 parameters. The fitted are therefore values: $C_{fitted} = C/N$, $B_{1-fitted} = B_1/N$. The p parameter is fixed in the fit, the same as Δ_ξ (on the value determined from the fit of the Onsager model to the specific heat, $\Delta_\xi/k_B = J_1/2k_B = 15.65$ K). The fit gives the values: $C_{fitted} = 0.0074(20) \text{ s}^{-1}\text{K}^{-n}$, $n = 13.07(24)$, $B_{1-fitted} = 130.3(9.7) \text{ s}^{-1}$. The value of n is very similar to the value obtained for **Co-1**. The fit is presented in Figure 5.3.30.

Table 5.3.4 The values of p parameters for the relaxation at different fields and different directions for **Co-3-c**.

Direction	Field (Oe)	p
X	6500	1
X	6750	1/3.03
Z	5900	1/5.21
Z	6250	1/15.69

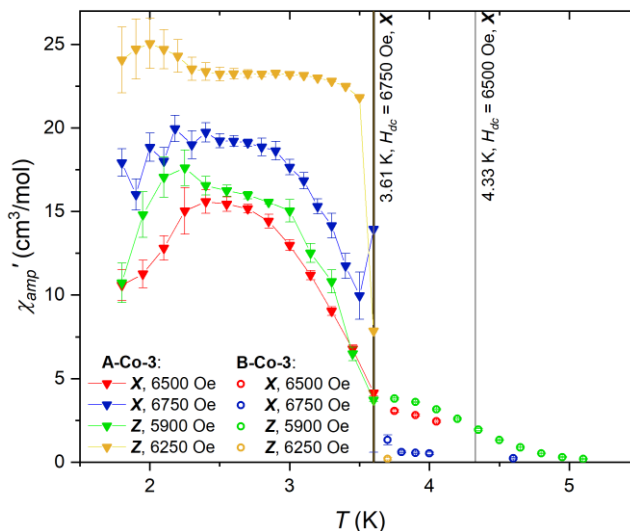


Figure 5.3.31 The temperature dependence of the amplitude of the relaxation process for **Co-3-c**.

Process **A-Co-3** is observed below the critical temperature, whereas process **B-Co-3** is observed close to that temperature and above it. The relaxation time of **B-Co-3** is around 0.0041 s. Its characteristic is the same as for process **B-Co-2** for **Co-2-c**, however, the process is visible a little bit worse than for **Co-2-c**. The reason for that can be the large fields or the quality of the samples, it is, the small amounts of short chain fragments in the sample. The **Co-1-c** and **Co-2-c** samples were cut out of the larger crystals, the single crystal of **Co-3** was used as it was from the synthesis, it was not cut, therefore, a sensible hypothesis is, that in this sample, there are fewer defects than in the other single crystals. Process **B-Co-3** seems to be better visible in the fields closer to the critical field. The amplitude confirms that (Figure 5.3.31). This may be caused by the different magnetic structures at different fields and therefore more or less short fragments of chains.

The α parameters are not significantly different for processes **A-Co-3** and **B-Co-3** (Figure 5.3.32). They are slightly larger at lower temperatures, and lower at higher. This parameter describes the distribution of the relaxation times. In this case, there is impossible to draw a reasonable conclusion, as the differences are too small.

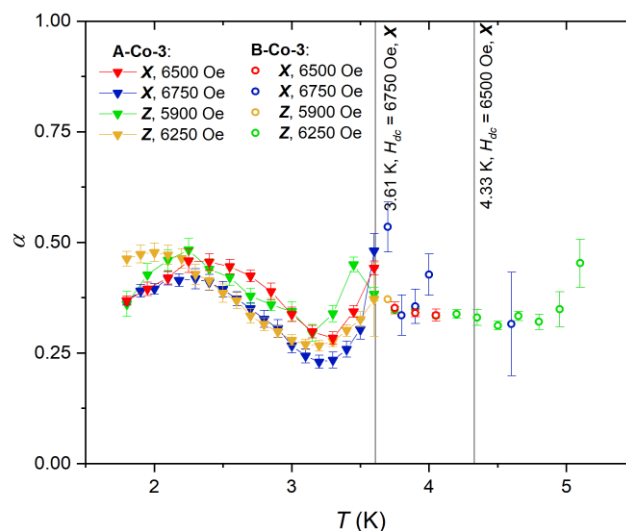


Figure 5.3.32 The temperature dependence of the α parameters of the relaxation process for **Co-3-c**.

To check, if the relaxation time will also change for a powder sample with smaller crystallites, similar supporting investigations as for **Co-2-c** were performed. Due to the low amount of the other single crystal samples, only one ground sample was created, **Co-3-g**. The crystals were ground mildly. As a sample with smaller crystallites, it was used the previously investigated powder sample, **Co-3-p**. The sizes of the crystallites in the samples were checked with the optical microscope. The photos are shown in Figure 5.3.33 and Figure 5.3.34. The sizes were determined by averaging the individual crystallite sizes over the volume. They are 98(2) μm and 1.7(4) μm , for **Co-3-g** and **Co-3-p**, respectively.

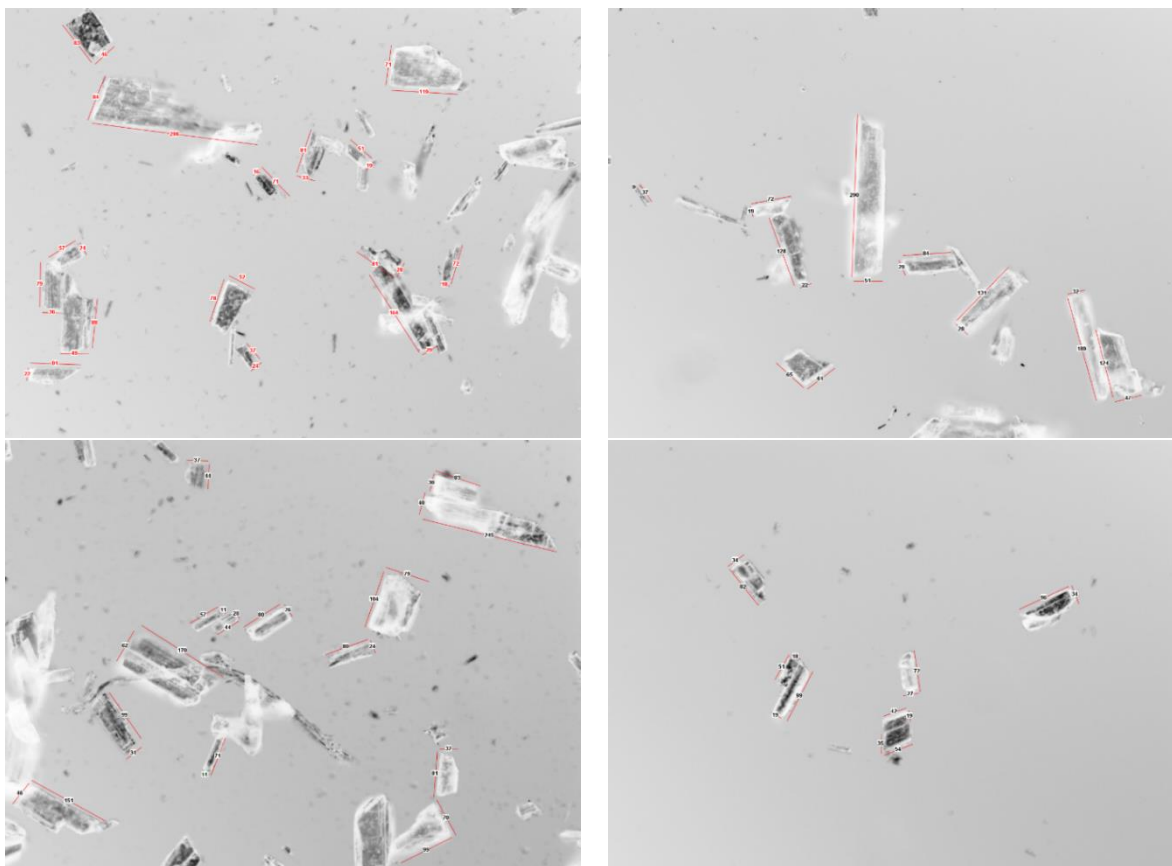


Figure 5.3.33 The photo of crystallites in the **Co-3-g** sample (1024 × 766 μm). The red lines are the measured distances, the red numbers are their lengths (μm).

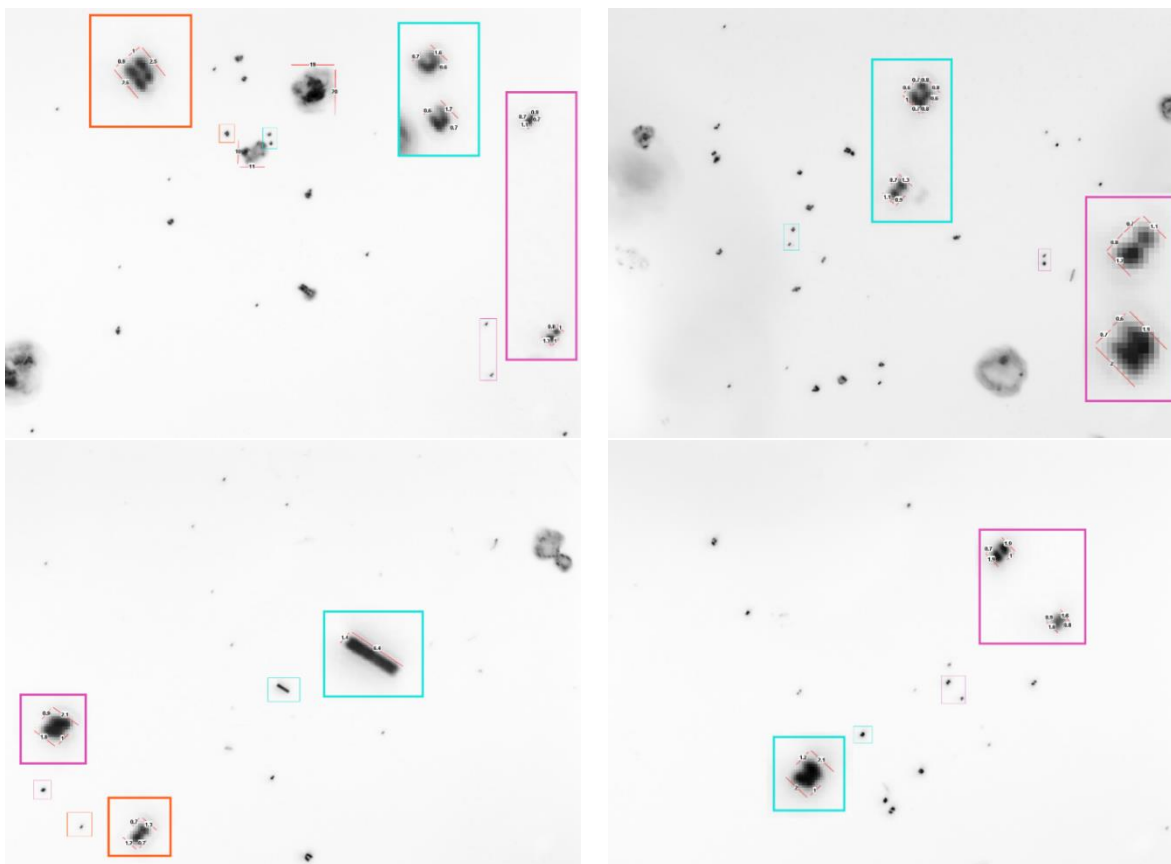


Figure 5.3.34 The photos of crystallites in the **Co-3-p** sample (356 × 192 μm). The red lines are the measured distances, the red numbers are their lengths (μm). The frames represent the enlarged areas.

The **Co-3-g** sample was checked with EA and PXRD to exclude the presence of impurities. The results of EA are presented in Table 5.3.5, the PXRD pattern is presented in Figure 5.3.35. The pattern is the same as the one for the previously investigated powder sample and the theoretical one calculated based on the crystal structure.[61] Additionally, the magnetization curves were measured for both of the samples, to check the position of the metamagnetic transition. For **Co-3-g** (Figure 5.3.36), the transitions are significantly sharper than for a powder (Figure 5.3.37).

Table 5.3.5 The results of the elemental analysis for powder obtained from the crystals of **Co-3-g**, compared with the theoretical values.

$\text{CoC}_{14}\text{H}_{14}\text{N}_4\text{O}_2\text{S}_2$	C	N	H	S
Elemental Analysis	45.95	15.30	3.898	17.773
Theoretical	46.53	15.51	3.91	17.75

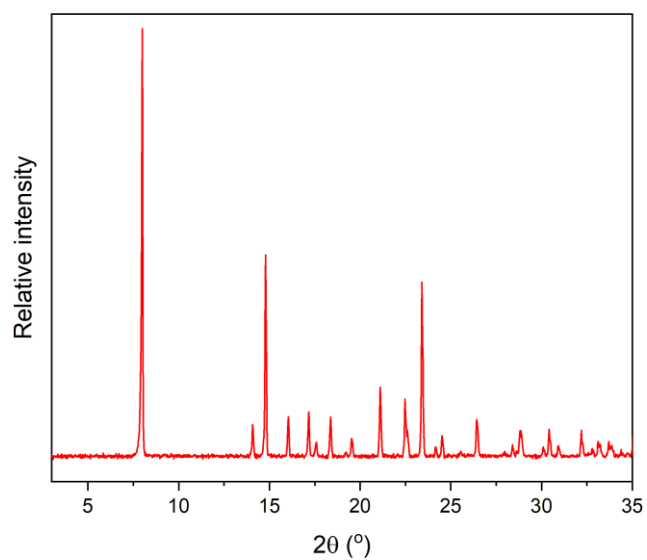


Figure 5.3.35 The powder X-Ray diffraction pattern obtained for **Co-3-g**.

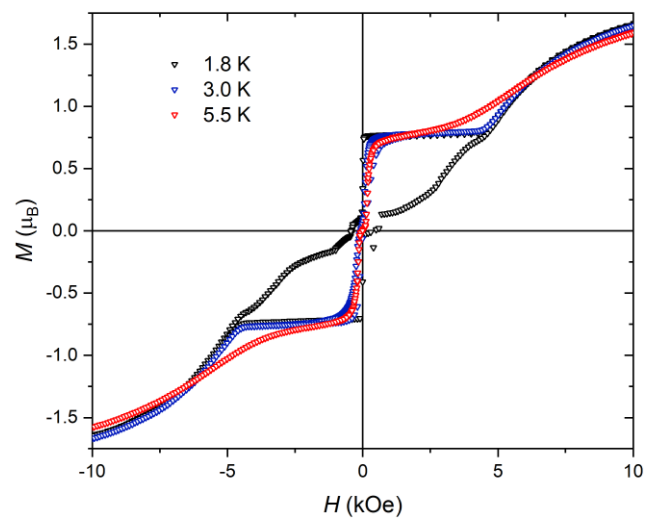


Figure 5.3.36 The magnetization curves measured for **Co-3-g** at different temperatures.

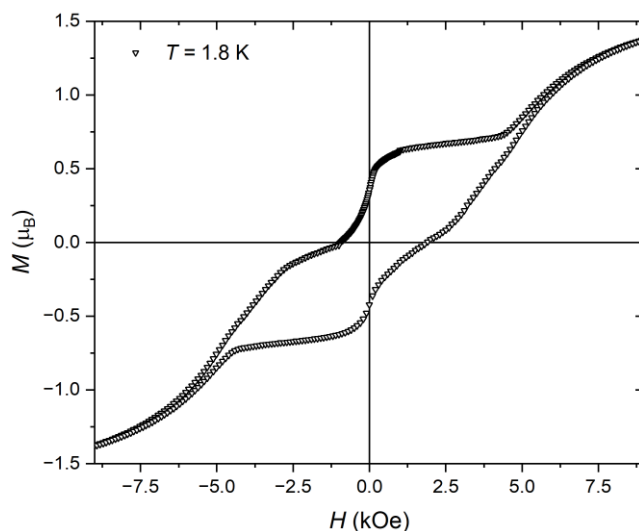


Figure 5.3.37 The magnetization curve measured for **Co-3-p** at 1.8 K.

The frequency dependence of ac magnetic susceptibility at 5 kOe is presented in Figure 5.3.38 for **Co-3-g** and Figure 5.3.39 for **Co-3-p**. The data were analyzed with the Cole-Cole model. The relaxation times are presented in Figure 5.3.40, together with the times obtained for a single crystal.

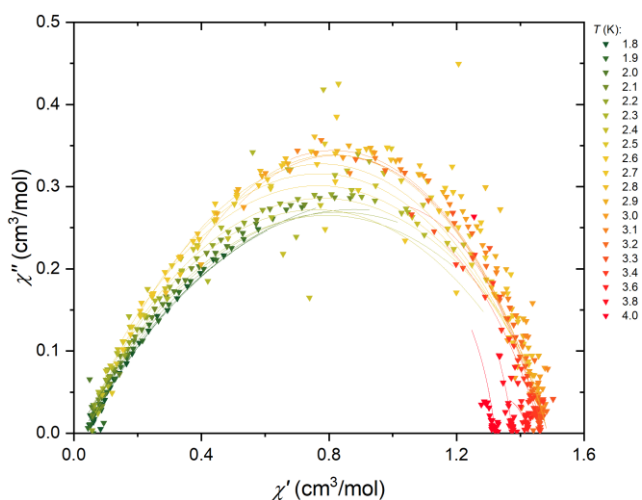


Figure 5.3.38 The ac magnetic susceptibility measured for **Co-3-g** at 5000 Oe. The lines are the fits of the single-mode Cole-Cole model.

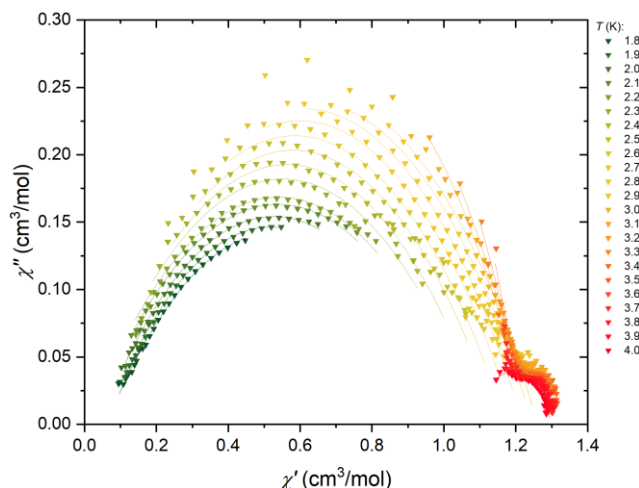


Figure 5.3.39 The ac magnetic susceptibility measured for a previously investigated powder, **Co-3-p**, at 5000 Oe. The lines are the fits of the single or double-mode Cole-Cole model.

The relaxation times for **Co-3-g** are just in between the relaxation times for a single crystal (**X**, 6500 Oe, and **Y**, 6250 Oe). The points at the lowest temperature have larger uncertainty, probably due to the distortion of the ac magnetic susceptibility data. This can be caused by the large noise, as the sample was very small. For a powder sample, the relaxation times are significantly lower, 245 lower than the time for the single crystal, **X**, 6500 Oe. The time is equally lowered in the whole accessible temperature range. This confirms that the observed relaxation is in the finite size regime.

There is also observed the third process, **C-Co-3** for **Co-3-p** (Figure 5.3.40). It seems to obey the Arrhenius law, however, the amount of data is not enough to draw a reasonable conclusion.

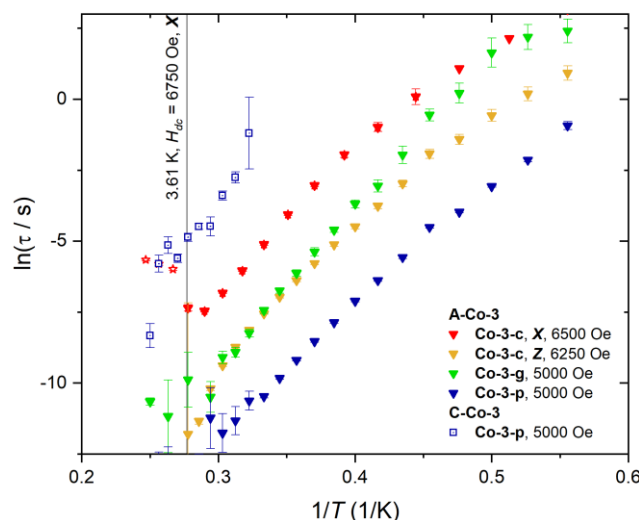


Figure 5.3.40 The temperature dependence of the relaxation times presented in the Arrhenius plot for **Co-3-c**, **Co-3-g**, and **Co-3-p**.

5.3.9. Summary

$\text{Co}(\text{NCS})_2(\text{aniline})_2$ is a compound in which every Co^{II} ion is coordinated by four NCS bridges and two aniline ligands. This coordination is *trans-trans-trans*, which makes the structural chains linear. The intrachain interaction is mediated through the NCS bridges and is ferromagnetic. Between the small aniline ligand and the NCS bridge of the neighboring chains, hydrogen bonds are present. These hydrogen bonds are a pathway of the interchain interaction which is antiferromagnetic and creates planes along crystallographic *bc* direction. The coexistence of the ferromagnetic intrachain and antiferromagnetic interchain interactions causes the antiferromagnetic ordering at 6.49 K.

The investigation of the single crystal of $\text{Co}(\text{NCS})_2(\text{aniline})_2$ was performed to get more information about the interactions in the system and to check if the chains in the system relax. The easy axis direction was also experimentally confirmed for this compound. There are two types of chains in the system which are related to each other by the 2-fold rotation symmetry. This, together with the weak antiferromagnetic interchain interaction results in the canted orientation of the spins in the neighboring chains. In some directions at the proper temperature and field, the magnetic moment cancels, and then the antiferromagnetic properties are observed for the system. For other directions, the magnetic moment does not cancel, and then, the ferromagnetic properties are observed. The ratio of inter to intrachain interaction, $|zJ_2/J_1|$, reaches 0.14 value, which is significantly higher than for **Co-1** and **Co-2**. For that reason, the system is approximated as a two-dimensional system, but some of the single chain properties are still observed.

For a single crystal, there are also observed two relaxation processes: process **A-Co-3**, which is a single chain relaxation at the fields corresponding to the metamagnetic transition, and process **B-Co-3**, assigned here to the relaxation of short fragments of chains as single molecules by qtm or a coherent rotation of 1D domains in a ferromagnetic chain. For a powder sample, process **A-Co-3** is also observed, but its relaxation time is shorter, which behavior is interpreted the same as for process **A-Co-2**, it is, the relaxation in the finite chains regime. The relaxation time of this process is field dependent, and this is assigned to the different chain lengths in a different state of the metamagnetic transition.

6. Realization of the thesis purposes

Below, there is presented a summary of the realization of the thesis purposes.

Compounds designations:

Mn-1 - $[\text{Mn}(\text{NCS})_2(3\text{-bromopyridine})_2]_n$

Ni-1 - $[\text{Ni}(\text{NCS})_2(3\text{-ethylpyridine})_2]_n$ (linear chains)

Ni-2 - $[\text{Ni}(\text{NCS})_2(3\text{-ethylpyridine})_2]_n$ (linear and corrugated chains)

Co-1 - $[\text{Co}(\text{NCS})_2(4\text{-(3-phenylpropyl)pyridine})_2]_n$

CoCd-1 - $[\text{Co}_x\text{Cd}_{1-x}(\text{NCS})_2(4\text{-(3-phenylpropyl)pyridine})_2]_n$, $x = 0.013$

Co-2 - $[\text{Co}(\text{NCS})_2(4\text{-methoxypyridine})_2]_n$

Co-3 - $[\text{Co}(\text{NCS})_2(\text{aniline})_2]_n$

Development of the synthesis' method of large single crystals of $\text{Co}^{\text{II}}(\text{NCS})_2(\text{ligand})_2$ for magnetic measurements.

The syntheses of all the compounds were performed from the solution. In table 6.1, there are compared the salt : ligand molar ratio and solvents used for the syntheses of the investigated samples. For Ni and Mn compounds, the salt : ligand ratio is 1:2, for Co compounds, the ratio depends on the form – single crystal or powder. The most used solvent is ethanol. There is no simple correlation between the salt : ligand molar ratio/solvent and the composition of the compound. During the synthesis of a new compound from the investigated family, there is performed many trials with different ratios and solvents. Deciding are also the conditions like temperature. As a result, a lot of other, in most cases discrete compounds, are obtained. Therefore, there cannot be derived a unified recipe for the syntheses of the chain compounds from $\text{M}^{\text{II}}(\text{NCS})_2(\text{ligand})_2$ family.

There is, however, a significant difference between the syntheses of powders and large single crystals. In powder synthesis, to obtain a homogenous product, the mixture is usually stirred for the whole time of the synthesis. In the case of small crystals for SCXRD, the mixture is not stirred to enable the crystallization of crystals. In the case of large single crystals, a clear solution is left without moving for a long time to enable the solvent to slowly evaporate. Time is the most important factor. The minimal time is a few weeks, and sometimes also recrystallization is needed. In general, the obtained crystals are fragile, and many crystals of **Co-2** and **Co-3** were broken during extraction from the vial. The other thing is the monocrystalline character – not all the synthesized crystals were single crystals. For all that reasons, the synthesis of a single crystal not only demands a proper ratio or solvent matching but also many trials and practice with them.

Table 6.1 Comparison of the syntheses of $M^{II}(\text{NCS})_2(\text{ligand})_2$: substrates ratio and solvents.

CN – the group of prof. Christian Näther, MF – the author of the thesis.

Sample	Provider of the sample	Salt : ligand molar ratio	Solvent
Mn-1-p	CN	1:2	<i>n</i> -butanol
Ni-1-p	CN	1:2	Water, ethyl acetate
Ni-2-p	CN	1:2	Water, ethyl acetate
Co-1-c	CN	1:2	Ethanol
Co-1-p [59]	CN	1:2	Ethanol
Co-2-c	MF	1:1	Ethanol
Co-2-p [60]	CN	2:3	Ethanol
Co-3-c	MF	2:1	Ethanol
Co-3-p [61]	CN	1:2	<i>n</i> -butanol

The single crystal samples have many advantages over the powder samples. For a powder, the measured properties are averaged, as the crystallites are differently oriented in relation to the external field. For a single crystal, the field can be applied in a specific direction. This enables for example determination of the easy axis direction. In this thesis, such determination confirmed the *ab initio* calculations results for the Co-based compounds, on which the interpretation of the magnetic properties is partially based.

Determination of the influence of the crystal structure of the compounds and the electronic structure of the transition metal ions on the magnetic behavior of $M^{II}(\text{NCS})_2(\text{ligand})_2$ spin chains.

The crystal structure aspects of the investigated chains are compared in Table 6.2. All the compounds crystallize in the triclinic or monoclinic system. For all of them, the magnetic ions are connected into chains by NCS bridges. There are in most of them hydrogen bonds between the neighboring chains. The connections through the NCS bridges and the hydrogen bonds are crucial for the magnetic properties, as they can be the pathways of the magnetic interaction. This mediation is dependent mostly on the direction of the bonds and the number of interacting spins. For the interaction along the chain, an important thing is the coordination of the metal centers. In any of the investigated compounds, they are surrounded by two N atoms from the NCS bridges, two S atoms from other NCS bridges and two N atoms from the ligands. The most common is their *trans-trans-trans* coordination, which makes the chain linear. The *cis-cis-trans* coordination makes the chain corrugated. For the corrugated chain, the exchange intrachain interaction should be smaller. The number of chain types in a structure and the relation between them can also influence the magnetic properties. For $\text{Co}(\text{NCS})_2(\text{aniline})_2$ the antiferromagnetic interactions between the chains are present, but the two types of chains are related with 2-fold symmetry, therefore, for some directions, ferromagnetic component is observed.

Table 6.2 Comparison of the crystal structure aspects of $M^{II}(\text{NCS})_2(\text{ligand})_2$.

Compound	Hydrogen bonds	Coordination of the M^{II} ion	Comments
Mn-1	No	<i>trans-trans-trans</i>	1 Mn^{II} position, 1 type of linear chain
Ni-1	Yes	<i>trans-trans-trans</i>	2 Ni^{II} positions, 1 type of linear chain
Ni-2	Yes	<i>trans-trans-trans</i> and <i>cis-cis-trans</i>	2 Ni^{II} positions in 1 type of linear chain, 1 Ni^{II} position in 1 type of corrugated chain
Co-1	No	<i>trans-trans-trans</i>	2 Co^{II} positions, 2 types of linear chains related with 2-fold symmetry
Co-2	Yes	<i>trans-trans-trans</i>	2 Co^{II} positions, 1 type of linear chain
Co-3	Yes	<i>trans-trans-trans</i>	1 Co^{II} position, 2 types of linear chains related with 2-fold symmetry

The summary of magnetic investigations for the investigated samples is presented in Table 6.3. The interchain interaction is significantly weaker than the intrachain interaction, and for that reason, the chain properties are observed for these systems. The Ni-based and Co-based chains show the ferromagnetic intrachain interaction, whereas for Mn-based chain, this interaction is antiferromagnetic. For the Ni-based and Mn-based chains, the intrachain interaction is significantly weaker than for Co-based chains. For **Ni-2**, the intrachain interaction energy is impossible to determine due to the mixture of linear and corrugated chains in the isomer – only the averaged value can be determined. The coexistence of the intra and interchain interactions causes the magnetic ordering of these systems. The interchain interaction is in most cases mediated through the hydrogen bonds. However, for **Co-1**, the hydrogen bonds are not present, and dipolar interactions are responsible for the interchain interaction. For **Mn-1**, the hydrogen bonds between the chains are not present, and the magnetic ordering is not observed down to 1.8 K. The intrachain interaction value was possible to determine only for the Co chains. For **Co-3**, the ratio between the inter and intrachain interaction is the highest and the interchain interaction is mediated within the crystallographic *bc* planes. Therefore, the 2D Ising model is used in **Co-3** analysis.

The relaxation of single chains is observed only for $\text{Co}(\text{NCS})_2(\text{ligand})_2$ chains, due to the easy-axis anisotropy of the single Co^{II} spins. For $\text{Ni}(\text{NCS})_2(\text{ligand})_2$ and $\text{Mn}(\text{NCS})_2(\text{ligand})_2$ chains it is not observed.

Table 6.3 Comparison of the magnetic properties of $M^{II}(\text{NCS})_2(\text{ligand})_2$.

Sample	Effective spin	Intrachain interaction	Interchain interaction	Magnetic ordering, T_c	Single chain relaxation
Mn-1-p	5/2	Heisenberg, AF, -5.76 K	?	Not observed down to 1.8 K	No
Ni-1-p	1	Heisenberg, FM, 10.42 K	?	1.34 K	No
Ni-2-p	1	Heisenberg, FM, impossible to determine.	?	1.30 K	No
Co-1-c	1/2	Ising, FM, 31.7 K	FM, 0.1 K	3.39 K	Yes
Co-2-c	1/2	Ising, FM, 34.0 K	AF, -0.38 K	3.94 K	Yes
Co-3-c	1/2	Ising, FM, 31.3 K	AF, -4.42 K	6.49 K	Yes

Investigations of the relaxation mechanisms in $\text{Co}^{II}(\text{NCS})_2(\text{ligand})_2$ chains.

The relaxation mechanisms were investigated for single crystals of Co-based compounds on the basis of the ac magnetic susceptibility measurements and were compared with the investigations of the powder samples.

All three compounds belong to the same family and the relaxations observed for them are in general similar. For all the compounds, the single chain relaxation is observed, however, the presence of this relaxation can depend on the sample form. The sample form is also important when it comes to the observation of other relaxation processes: for single crystals of all three compounds at least two different relaxations are observed, regardless of the ground state. Therefore, the presence of multiple relaxation processes may be the feature of the whole $\text{Co}(\text{NCS})_2(\text{ligand})_2$ family. The second relaxation can be associated with the relaxation of short fragments of chains, a coherent rotation of 1D domains in a ferromagnetic chain or the spin waves excitations.

The investigations of single crystals gave therefore a lot of new information about the single chain relaxation in this system. The investigations for **Co-1-c** revealed that the relaxation of single spins in this system, comprising on the relaxation of the single chains, does not occur through the Orbach process. Usually, for analysis of the single chain relaxation time, it is used the conventional approach which includes only the Orbach process as the mechanism of the single spin relaxation. The result obtained for **Co-1-c** shows that this can be incorrect for some systems, due to the well-separated ground and excited states, which in turn causes the other single spin relaxation processes have a larger probability: in the case of **Co-1-c**, it is Raman, direct and qtm. Even if, the $\ln(\tau)$ vs. $1/T$ dependence for a single chain relaxation is linear (or the two linear regimes can be distinguished), it does not necessarily mean that the Arrhenius law can be fitted, and the energy barriers estimated this way are correct. It is necessary to compare the obtained Δ_A barrier with the energy levels scheme of the single ion. Such estimation is useful sometimes,

e.g., if one wants to assess if the process is the single chain relaxation. In the proposed approach, the Orbach process is replaced with other processes, which gives a reasonable value of the energy of a domain wall, Δ_{ξ} .

The investigations of **Co-2-c** revealed another very important aspect of the single chain relaxation in the investigated systems. By supporting the single crystal measurements with the powder measurements, it was proved, that the relaxation in this system will always occur in the finite chain regime, as in the ordered system the correlation length can spread to infinity. However, it is enough for the correlation length to be at every temperature below T_c longer than the lengths of the chains. For **Co-1-c**, the correlation length is shorter, despite the ordering, as the crossover is observed.

The investigations for **Co-3-c** were performed as a continuation of the single crystal research and it was chosen as it is the compound with the non-pyridine-based ligand. The investigations of this crystal support the interpretation provided for the **Co-1-c** and **Co-2-c**. The observed single chain relaxation is also in the finite chain regime. The visible inflection on the $\ln(\tau)$ vs. $1/T$ dependence for this relaxation can resemble the crossover, but such a possibility was excluded, as in the infinite regime, the relaxation time should be the same, whereas here, the change of the relaxation time is equal in the whole temperature range for measurements at different fields and different forms of samples. The proposed analysis assumes the relaxation in the finite size regime and the relaxation of single spins through the Raman and qtm processes. The change in the chain lengths in different fields can be caused by the different magnetic structures. For **Co-2-c**, such a field dependence of the relaxation time of the single chain relaxation is not observed, probably because of the significantly lower fields, at which the relaxations are investigated.

Therefore, the observation of differences in the relaxation processes for powders and single crystals are caused by the different lengths of the chains. The possibility of measurements of the single crystals enabled to collect more data than for a powder and data with better quality. Such thorough investigations of the mechanisms of the relaxations in chain compounds would not be possible for powders.

There are of course open questions left in the presented research, for example, verification of the origin of the second relaxation processes observed for the single crystal samples of Co-based compounds or inclusion of the zero-field splitting effect in the analysis of the Ni-based compounds. Answering them can take a significant amount of time and a lot of further research, however, the results obtained by now are already a huge step forward in the understanding of the magnetic behavior of the $M^{II}(\text{NCS})_2(\text{ligand})_2$ systems.

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