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**Effect of dimensionality on magnetism
of van der Waals materials**

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Abstract: Van der Waals (vdW) magnets represent an exciting platform for 2D spintronic applications. Among them, the ferromagnet VI_3 stands out due to its unquenched orbital moment [1], contrasting the well-studied ferromagnet CrI_3 [2]. However, recent experiments reported an unexpected quenching of this moment at 40 K [3]. In this thesis, we complement the XMCD study of D. Hovančík et al. [1] with our analysis of XAS and XMCD spectra of a different VI_3 crystal around 40 K, including both L-edge data from PSI and K-edge data from ESRF. Our L-edge analysis contradicts the quenching by showing an increase in the size of the orbital moment at 40 K. The K-edge XMCD gave a non-zero signal, confirming an unquenched orbital moment, but pointed out the possible sample dependence. The K-edge spectra are further compared to those of VBr_3 , an intralayer antiferromagnet with out-of-plane anisotropy, showing a clear ligand field shift with a possibility of a valence shift. No additional hybridization of $3d$ and $4p$ states was observed. In the end, we briefly discuss VCl_3 , the least studied member of magnetic Vanadium trihalides. VCl_3 is a potential host of altermagnetism [4] with possible polaronic states [5], which makes it no less interesting. In this thesis, we present the temperature evolution of its infrared spectra measured on samples of varying thicknesses, prepared via dry exfoliation. The goal was to assign phonon modes and find possible signs of magnons - quasiparticles describing spin waves.

Keywords: Van der Waals, magnetism, trihalides, infrared spectroscopy, XMCD

Název práce: Vliv dimenzionality na magnetismus van der Waalsovských materiálů

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Abstrakt: Van der Waalsovské (vdW) magnety představují atraktivní skupinu materiálů pro 2D spintronicke aplikace. Feromagnetický materiál VI_3 mezi nimi vyniká díky nezamrzlému orbitálnímu momentu [1], což ho odlišuje od známého feromagnetu CrI_3 [2]. Nedávne experimenty však překvapivě zaznamenaly zamrznutí tohoto momentu při 40 K [3]. V této práci doplníme XMCD studii D. Hovančíka a ostatních [1] o další XAS a XMCD spektra, včetně měření při zmiňovaných 40 K. Spektra obsahují jak L hrany, měřené v PSI, tak i K hranu z ESRF. Naše analýza L hran vyvrací zamrznutí orbitálního momentu při 40 K, naopak ukazuje jeho nárůst. U K hrany též vidíme nenulový XMCD signál, což náš závěr utvrzuje. Zároveň ale poukazuje na možnou závislost na vzorku. Spektra VI_3 z K hrany jsme následně porovnali s těmi od VBr_3 , což je antiferomagnet v rámci roviny s anizotropií mimo rovinu. Výsledkem byl znatelný posun absorpční hrany díky silnějšímu ligandovému poli a možné změně valence. Nebyla pozorována přidaná hybridizace $3d$ a $4p$ stavů. Na konci práce jsme se věnovali antiferomagnetu VCl_3 , nejméně studovanému členu z trojice magnetických vanadových trihalogenidů. Jelikož se jedná o potenciálního altermagnetického kandidáta [4] s možným výskytem polaronů [5], není o nic méně zajímavý. V práci prezentujeme teplotní vývoj jeho infračervených spekter, naměřených na různě tenkých vzorcích, které byly připraveny metodou suché exfoliace. Cílem bylo přiřadit fononové módy a nalézt známky magnonů – kvazičástic popisujících spinové vlny.

Klíčová slova: Van der Waals, magnetismus, trihalogenidy, infračervená spektroskopie, XMCD

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Introduction

Van der Waals (vdW) magnets offer a promising future for the world of 2D magnets, with a possible application in spintronics and other modern devices. They possess a unique property - using conventional adhesive tapes, one can obtain a molecular monolayer. Such was the successful preparation of monolayer graphene, an accomplishment worthy of the Nobel Prize in 2010.

The next breakthrough happened with an experiment proving a magnetic ordering in a monolayer of vdW ferromagnet CrI_3 [6]. Such ordering is impossible in an isotropic 2D Heisenberg model. It is thus sustained by a magnetocrystalline anisotropy [7, 8]. The anisotropy usually originates from the spin-orbit coupling - a coupling between the spin $\mathbf{S}$ and orbital $\mathbf{L}$ momenta. However, due to the ligand field, transition metals often experience a quenching of the orbital momentum. This was also the case in CrI_3 , which has a different source of anisotropy [2].

Its sibling VI_3 is a completely different story. The combination of its unfilled $3d^2$ orbital and the ligand field allows for an unquenched orbital moment. A high value of $0.6 \mu_B$ was later confirmed by XMCD experiments [1]. A different study then observed a quenching at 40 K, only [3]. This result was surprising and rather suspicious.

In this thesis, we will accompany the XMCD study done by D. Hovančík et al. [1] with our analysis of XAS and XMCD spectra of a different VI_3 crystal at temperatures around 40 K. The analysis contains not only the spectra of L-edges, measured at PSI, but also those of the K-edge, collected at the hard-X-ray beamline at ESRF. Moreover, we will compare the K-spectra to those of VBr_3 , measured during the same session.

Contrary to its heavier relative, VBr_3 is an antiferromagnet with a complex structure of alternating antiferromagnetic and ferromagnetic layers, an attractive magnetic structure for applications [9]. The VX_3 triad is then completed by VCl_3 , the least studied of the three. It also behaves as an antiferromagnet, according to bulk magnetization measurements. Some of the measurements were of our own and are yet to be released. Nonetheless, a little snippet is contained in this thesis. VCl_3 may also experience its hype, given recent reports of the existence of polarons [5] and of a structure, which could host altermagnetism [4].

Here we focus on different quasiparticles, phonons and magnons, and thus will share the temperature evolution of their infrared spectra. At the end, the spectra will be compared to a room-temperature calculation for a better assignment of observed peaks to existing phonon modes.

1. Theoretical background

1.1 Introduction to magnetism

1.1.1 Magnetic field

To describe the magnetic field, two vector fields are used - the magnetic induction (also called the magnetic flux density) $\mathbf{B}$ and the magnetic field strength $\mathbf{H}$. In a vacuum, they are connected by a simple relation:

$$\mathbf{B} = \mu_0 \mathbf{H}, \quad (1.1)$$

using the universal constant μ_0 called the permeability of vacuum. [10], [11]

In a material environment, an extra vector field needs to be introduced. This so-called magnetization $\mathbf{M}$ reflects the intrinsic magnetic behaviour of the matter and its reaction to the applied external magnetic field $\mathbf{H}$. The equation 1.1 is then accordingly modified [11]:

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}). \quad (1.2)$$

As a consequence, $\mathbf{H}$ and $\mathbf{B}$ need not be of the same magnitude nor parallel (as is the vacuum case).

In so-called linear materials, there is a relation between $\mathbf{H}$ and $\mathbf{M}$ [11]:

$$\mathbf{M} = \chi \mathbf{H}. \quad (1.3)$$

Susceptibility χ quantifies the material's response to the applied field. Its sign determines the direction of the magnetization with respect to $\mathbf{H}$. Even though the susceptibility alone is a macroscopic quantity, it can give insight into microscopic properties. [11]

1.1.2 Magnetic moment

An elementary object of magnetism is the magnetic moment of ions $\boldsymbol{\mu}$. In a classical description, it can be portrayed as a current loop inducing a magnetic field. However, according to the Bohr-van Leeuwen theorem, no net magnetization is sustainable in a solid when using classical physics. One must then use the quantum theory.

An electron possesses two distinct quantized angular momenta - spin $\mathbf{s}$ and orbital $\mathbf{l}$. In an atom, the respective angular momenta add together to form the total angular momenta of an atom $\mathbf{S}$ and $\mathbf{L}$, which give rise to the magnetic moment of the atom. Let us represent the spin or orbital momentum by a variable $\mathbf{X}$. The magnetic moment corresponding to the related angular momentum is

$$\boldsymbol{\mu}_X = -\mu_B g_X \mathbf{X}. \quad (1.4)$$

g is a so-called g factor. For electrons, it's approximately $g_S \approx 2$ in the case of spin angular momentum and $g_L \approx 1$ for the orbital one. μ_B is called a Bohr

magneton, the magnetic moment of an electron of rest mass m_e and charge e orbiting a proton:

$$\mu_B = \frac{e\hbar}{2m_e}. \quad (1.5)$$

$\hbar$ is a reduced Planck constant. [10], [12]

The angular momenta $\mathbf{S}$ and $\mathbf{L}$ couple with each other via the spin-orbit (SO) interaction. If the interaction is significant, a total angular momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S}, \quad (1.6)$$

is conserved instead of the pair separately. [11]

We can define two inequivalent magnetic moments illustrated in Figure 1.1:

$$\boldsymbol{\mu}_J = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S = -\mu_B(g_L\mathbf{L} + g_S\mathbf{S}) = -\mu_B(\mathbf{L} + 2\mathbf{S}), \quad (1.7)$$

$$\boldsymbol{\mu}_{eff} = -\mu_B g_J \mathbf{J}. \quad (1.8)$$

μ_{eff} is called the effective moment,

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \quad (1.9)$$

is the Landé g-value, which is defined using quantum numbers connected to their respective angular momenta. [11]

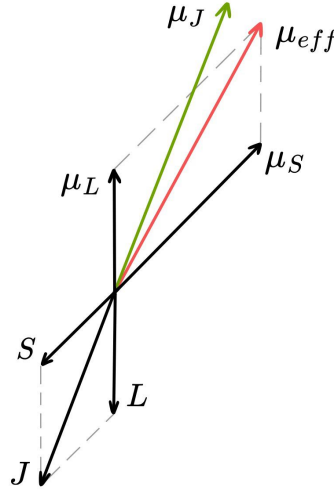


Figure 1.1: Vector representation of angular momenta and magnetic moments. The magnitudes are illustrative.

1.1.3 Ground state of a magnetic ion

We define quantum numbers S , L and J to quantize the magnitude of angular momenta and m_S , m_L and m_J to quantize their projection on a particular axis (usually the z-axis) [11]

$$|\mathbf{J}| = \hbar\sqrt{J(J+1)}, \quad (1.10)$$

$$J_z = \hbar m_J. \quad (1.11)$$

Equations 1.10 and 1.11 are of the same format for $\mathbf{S}$ and $\mathbf{L}$. Given J , the options of m_J run from $-J$ to J by an increment of 1.

The electrons within atomic shells occupy states with minimal overall energy. The quantum numbers of the ground state (a state with minimal energy) can be predicted using three Hund's rules.

The first rule requires the electrons to arrange in order to maximize the $\mathbf{S}$. When the rule is obeyed, they need to maximize $\mathbf{L}$. Both rules reflect the Coulomb repulsion between electrons. [11]

The third rule aims to minimize the SO energy. J is calculated based on the degree of shell filling: $J = |L - S|$ if the shell is less than half full and $J = |L + S|$ in the opposite case. [11]

Atoms with all shells filled have zero $\mathbf{L}$ and $\mathbf{S}$. Only partially filled shells thus contribute to the magnetic moment and drive the magnetic properties. For that reason, we will refer to chemical elements using their unfilled valence shells as nL , where $L = s, p, d, f$. [12]

The Hund's rules are better obeyed in rare earths with isolated $4f$ shells. However, in non-localized shells of transition metals, a $3d$ shell of Vanadium in our case, we need to take into account the ion's local environment. [11]

1.1.4 Energy levels and degeneracy

The states in which electrons exist are defined by combinations of quantum numbers (connected to specific physical properties). However, we need to mention the main quantum number n for a complete description. n mainly scales the energy of the state. Without interactions, the energy levels are degenerate, meaning they depend only on n and l , while states with different l_z and other quantum numbers remain energetically identical.

In reality, we have to count with interactions. First, the SO coupling raises the degeneracy by the total j of the state, meaning that states with different j are not on the same energy level. Moreover, the applied magnetic field splits the levels further by the projection of the total orbital moment into the field j_z . This is called the Zeeman effect. Both effects of SO interaction and a magnetic field are illustrated in Figure 1.2.

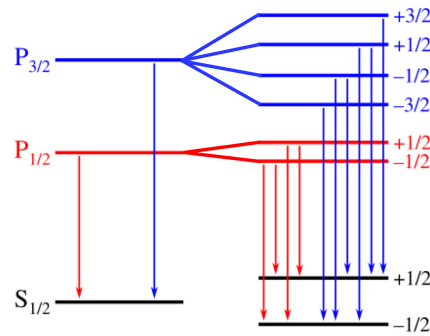


Figure 1.2: Splitting of P energy levels due to SO coupling (left) and applied magnetic field (right) [13].

1.1.5 Crystal field

The Crystal Field Theory (CFT) describes how surrounding ligands influence the energy levels of an ion's valence orbitals, in our case, the d -orbitals. In an isolated ion, all d orbitals are degenerate. In a real structure, the transition metal ion is surrounded by ligands and experiences nonspherical electrostatic potential. Moreover, its d orbitals are also not spherically symmetric. This means that some states have a larger overlap with those of the surrounding atoms and thus undergo a stronger repulsion, which leads to an increase in their energy.

On the other hand, states with smaller overlaps are relatively unaffected and become energetically favourable. The crystal field arising from the ligands thus lifts the degeneracy of the d states. The splitting is dependent on both the symmetry of the ion's valence orbitals and its local environment. Figure 1.3 shows an example of the energy shifts in the case of an octahedral geometry, which is the case for our VX_3 compounds. [14, 11, 15, 16]

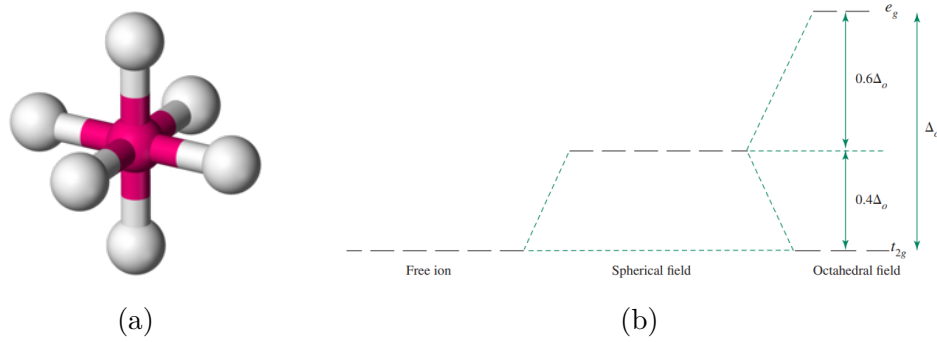


Figure 1.3: (a) The octahedral geometry [17] (In VX_3 , V atom is pink, white are halogen atoms) and (b) its energy splitting diagram [16].

The e_g marks the $d_{x^2-y^2}$ and d_{z^2} orbitals, which are raised in energy. t_{2g} symmetry corresponds to d_{xy} , d_{xz} and d_{yz} states. The Δ_o identifies the energy difference. [16]

To further lift the degeneracy, the octahedral molecular system can lower its symmetry by elongation or compression, called the Jahn-Teller effect. [18, 11]

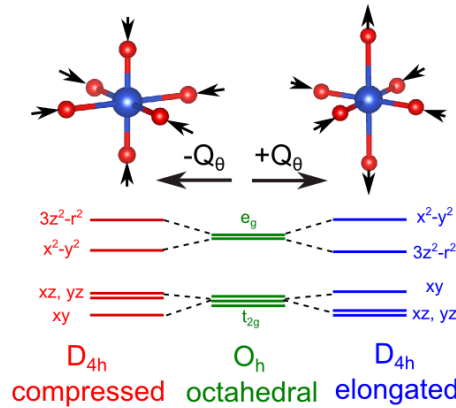


Figure 1.4: The Jahn-Teller effect on $3d$ orbitals in an O_h ligand field [19].

The splitting in other symmetries is summarized in Fig. 1.5.

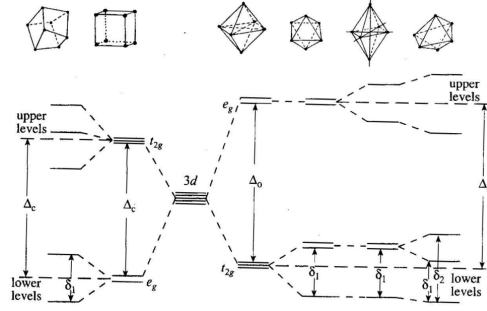


Figure 1.5: The crystal field splitting in various geometries [20].

The order in which electrons fill the orbitals depends on the strength of the crystal field. The electrons try to minimize the pairing energy, the energy of two electrons being in the same orbital. If the field is weak (the crystal field energy is lower than the pairing energy), electrons first fill all orbitals and then start to share them. This scenario results in the so-called high-spin state. On the contrary, the strong-field case results in a low-spin state. Both spin states of $3d$ orbitals are depicted in Figure 1.6 for various numbers of electrons.

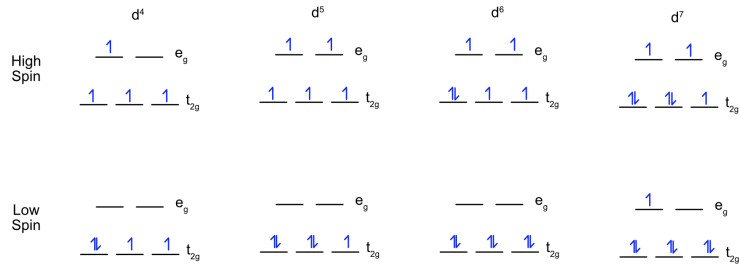


Figure 1.6: High- and low-spin states of $3d$ orbitals.

In $3d$ orbitals, the crystal field interaction (in the order of eV) is much more prevalent than SO coupling (in the orders of 0.01 - 0.1 eV). This leads to a violation of Hund's third rule. Instead, the systems then choose the ground state of $L = 0$. This effect is called orbital quenching. [16, 21, 11]

2. State of the art

2.1 Van der Waals systems

The rapid advancement of modern technologies and computational devices demands a dramatic downscaling of their components while simultaneously striving to maintain—or even enhance—their efficiency and performance. In this context, van der Waals (vdW) materials have emerged as a game-changing tool thanks to their natural ability to be cleaved down to a monolayer limit. [22, 23].

The field of 2D magnets gained momentum following the successful preparation of a monolayer graphene, which earned the Nobel Prize in Physics in 2010. Graphene, a single layer of carbon atoms arranged in a honeycomb lattice (Fig. 2.1), demonstrated the attractive potential of two-dimensional materials.

The vdW materials are characteristic of their stacked structure of molecular layers, which are bound together by a weak van der Waals (vdW) bond, hence the name. Its bonding energy is around 10^{-2} eV. The force arises from electrostatic dipole-dipole interactions, such as the attraction of the oppositely charged ends caused by nonuniform charge distribution. [24]

Opposite to that, we have a much stronger intralayer bond, usually a covalent bond with bonding energies of 1 to 10 eV. When cleaving the material, the interlayer (between layers) bonds break first, leaving us with separated layers with the possibility of achieving a single-layer sample. [25]

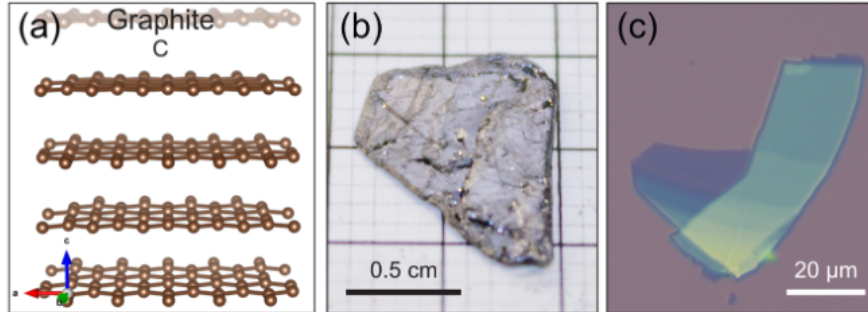


Figure 2.1: Graphite: (a) 3D model of the structure, (b) picture of a rock, (c) optical microscopy image of a few-layered sample [26].

2.1.1 Magnetic vdWs

Magnetic ordering in 2D and 1D materials originates from the magnetocrystalline anisotropy. As stated by the Mermin-Wagner-Brezinskii theorem, the isotropic Heisenberg 2D model contradicts any existence of a long-range ordering since there is no energy cost at orienting the spins freely. The anisotropy, arising from the SO interaction, introduces the energy cost and makes certain spin orientations preferable. Moreover, it suppresses fluctuations, which maintains the order. [7, 8, 11].

The stable long-range ferromagnetic (FM) ordering in 2D materials on mono- or bi-layers was recently discovered in CrI_3 [6] and $\text{Cr}_2\text{Ge}_2\text{Te}_6$ [27] respectively. Both materials exhibited a strong dependence of the magnetic ordering on the

number of layers. The Curie temperature T_C of $\text{Cr}_2\text{Ge}_2\text{Te}_6$ decreased from 65 K in bulk to 30 K at bilayer [27] and the T_C of CrI_3 shifted from 61 K to 41 K in monolayer [6, 28]. The dimensionality also manifested itself in the magnetic order. Opposite to bulk, the CrI_3 bilayer orders antiferromagnetically (AFM) [6]. The ordering can be, however, switched by a pressure tuning of layer stacking [29].

The ordering temperatures of most reported vdW magnets are deeply below room temperature, as seen on both $\text{Cr}_2\text{Ge}_2\text{Te}_6$ and CrI_3 . However, recent papers proved a room-temperature ordering in Fe_3GaTe_2 [30] and its doped variants [31, 32, 22].

The discovery of stable ferromagnetism in a CrI_3 monolayer sparked an interest in the whole vdW family of transition metal trihalides TX_3 (T = transition metal, X = Cl, Br, I). Within the layers, the T^{3+} cations form a honeycomb network in an edge-sharing octahedral coordination of six X ions [14, 1]. In bulk, they exist in a high-temperature rhombohedral lattice, which shifts to a monoclinic variant in low temperatures [33, 14, 34, 9].

The CrX_3 group further contains a ferromagnet CrBr_3 [35] and CrCl_3 with complex magnetic phase diagram [36, 37]. The three $3d$ electrons in an octahedral field fill the t_{2g} levels, resulting in a quenched orbital moment. Truly, the saturated moment was close to $3 \mu_B/\text{Cr}$ for all three compounds, in tune with the spin-only state $S = 3/2$, $L = 0$ [38, 2]. The XMCD of CrI_3 unveiled a small orbital moment, but only of $0.1 \mu_B$ [39]. The magnetocrystalline anisotropy maintaining the long-range order was thus attributed to the SO coupling of the I p orbital through the superexchange mechanism [2].

Nonetheless, this is not the case for Vanadium trihalides. VI_3 , the most famous of the group, has also sustained a FM behaviour down to a monolayer limit [40]. In contrary to CrX_3 halides, the two electrons in the t_{2g} levels enable an unquenched orbital moment, experimentally observed by XMCD [1] and further predicted from bulk measurements in both VBr_3 and VCl_3 .

VI_3 and other members of the vanadium trihalide family are the topic of this thesis and will be explored more thoroughly.

2.2 VI_3

A Mott insulator VI_3 has drawn interest for its distinctive magnetic properties and layered structure, making it a promising candidate for spintronic applications [41].

It is reported to undergo two structural transitions. First occurs at 78 - 79 K [40, 14, 34]. This transition is from a high-temperature rhombohedral lattice with a space group R-3 [14] to likely a monoclinic C2/m one [14]. It can be moved to lower temperatures with a magnetic field [34]. A second structural transition is at 32 K to a triclinic lattice [34]. Figure 2.2 displays 3D models of the crystal structure and highlights the transitions the material undergoes. Figure 2.3 then shows a VI_3 single layer with possible geometry distortions.

The compound is paramagnetic down to $T_C = 49 \text{ K} - 50 \text{ K}$ [42, 40, 34, 14]. Below that, the material is ferromagnetic. Around $T_{FM} = 26 \text{ K}$ [42], the magnetic structure undergoes a transition to a different ferromagnetic phase, characterized by a 30° rotation of the magnetic easy axis relative to the first [43]. However,

Gati et al. suggest the magnetic order-to-order transition at $T_{FM2} = 36$ K [44]. Nonetheless, the transition can be suppressed with high pressure (> 0.9 GPa) [42]. The T_C is also sensitive to pressure, as it doubles up to almost 100 K in 8 GPa [42].

According to calculations, magnetic ordering persists even down to monolayers [41]. This order arises due to the strong magnetocrystalline anisotropy, confirmed in magnetization measurements [1, 14]. Furthermore, these measurements revealed a saturated moment of approximately $1\text{--}1.2 \mu_B/\text{f.u.}$, which is lower than the expected $2 \mu_B/\text{f.u.}$ for a V^{3+} spin-only state ($S = 1$, $L = 0$) [14, 1]. Neutron scattering data suggested a moment of $1.24(5) \mu_B/\text{f.u.}$ at 6 K [45]. These observations indicate an unquenched orbital moment, whose existence was later confirmed by low-temperature XMCD, revealing a value of $0.6 \mu_B$ [1].

Surprisingly, De Vita et al. [3] found the orbital moment drops to zero at 40 K. This behaviour was unexpected, so we devote it a part of our experimental XMCD section (3.2).

On top of that, an NMR study found two inequivalent magnetically ordered V sites below the $T_{FM2} = 36$ K with an occupancy ratio of 2:1, whereas between the T_{FM2} and T_C , only one site existed [44]. Using XMCD, the existence of two inequivalent sites was later associated with the two opposite trigonal distortions of the octahedral symmetry, shown in Fig. 2.3 [1]. Both sites gave different orbital momenta - the orbital moment was quenched in the first and huge in the second. In their method, a well-fitting occupancy turned out to be 1:1, with the average orbital moment corresponding to the experimental $0.6 \mu_B$ [1].

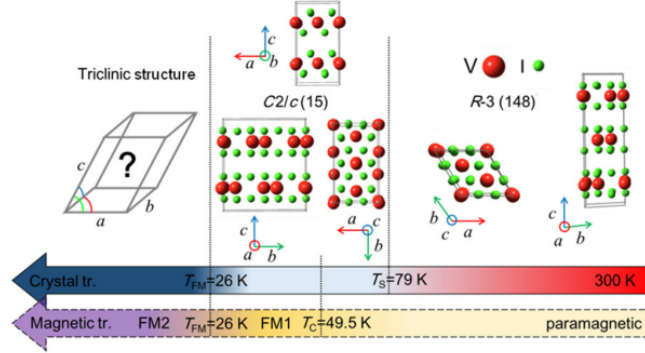


Figure 2.2: VI_3 crystal structure evolution with temperature [43].

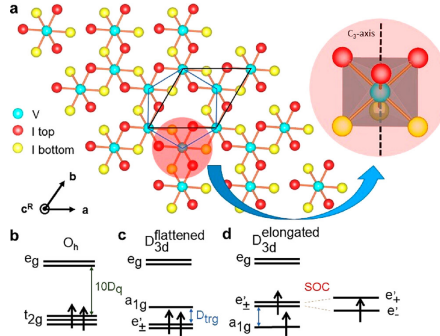


Figure 2.3: (a) Crystal structure of VI_3 monolayer and (b) the crystal field splitting for octahedral O_h and flattened/elongated D_{3h} geometries [1].

2.3 VBr₃

Opposite to VI₃, the lighter halide VBr₃ orders antiferromagnetically below $T_N = 26.5$ K [46, 47, 48, 9]. Additionally, an anomalous increase in susceptibility was observed below 15 K [47], which is unlikely to be associated with any symmetry change but is still reflected in deviations of the neutron reflection intensities [9]. The origin of this behaviour is yet to be unveiled.

The saturated magnetic moment at 50 T is $\mu_{sat} \approx 1.2 \mu_B/V$, similar to the saturated moment in VI₃. A first-order metamagnetic spin-flip transition to a polarized paramagnet region occurred at $\mu_0 H_c = 16.9$ T in the out-of-plane field, whereas in the in-plane field, the spin gradually canted along the field [46]. This behaviour points to an intralayer antiferromagnetism with out-of-plane anisotropy [46, 47], confirmed by the neutrons [9].

A structural transition occurs at 90 K from high-temperature rhombohedral R-3 phase [46, 9, 47, 48]. The expected low-temperature phase was monoclinic C2/m; however, neutron data in low temperatures still agreed with the R-3 space group with likely a monoclinic or a triclinic distortion [9, 49, 48, 47].

The crystal structure is depicted in Figure 2.4.

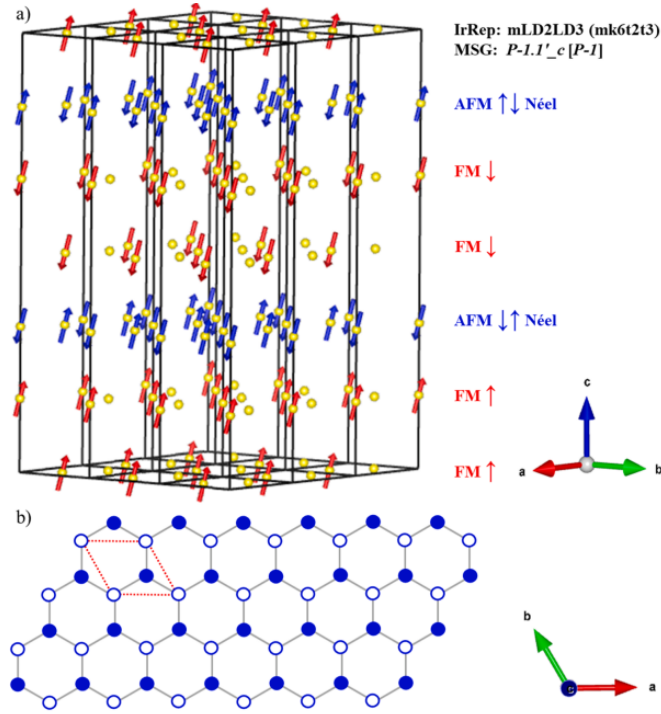


Figure 2.4: (a) A bulk magnetic structure of VBr₃ and (b) a detail of the AFM Néel-type single layer, red dashed lines mark the unit cell with full/empty circles for up/down spin momenta. [9].

2.4 VCl₃

VCl₃ is the least studied member of our VX₃ triad. Monolayers have been theoretically implemented as components in a spin-filter device in a VCl₃-CoBr₃-VCl₃ heterostructure with promising results [50]. According to calculations, a

monolayer should order ferromagnetically at 80 K [51] or even at 425 K [52]. In bulk, a structural transition occurs at 100 - 103 K and an antiferromagnetic one at 22 K [48, 5]. The high-temperature phase was described using the rhombohedral R-3 space group and, interestingly, using two valences V^{3+} and V^{2+} [5]. The honeycomb layered structure of VI_3 and VBr_3 is retained [5]. Additionally, recent studies have identified the presence of a polaron in VCl_3 , highlighting the role of electron-lattice interactions in its electronic properties [5].

2.4.1 Supporting measurements

Regarding VCl_3 , we have a series of unpublished experiments, which we will now briefly introduce.

In a room temperature single-crystal X-ray diffraction, we managed to refine the lattice parameters, which are compared to those of VI_3 and VBr_3 in Fig. 2.5. Moreover, structural measurements indicate the presence of multiple oxidation states of V in the crystal. This was further confirmed using X-ray photoelectron spectroscopy (XPS), which revealed that the material contains not only V^{2+} but also V^{3+} ions. In a study done by Mastrippolito et al. [5], V^{2+} and V^{3+} accounted for approximately 15 % and 81 % of the measured V-2*p* doublet spectra. Additionally, they reported a sparse occurrence of $V^{4+/5+}$ with approximately 4 % of the measured V-2*p* doublet.

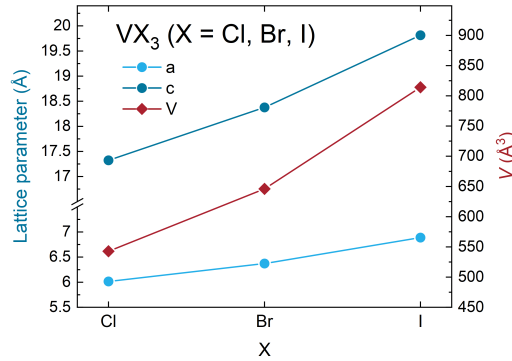


Figure 2.5: Lattice parameters of Vanadium trihalides [40, 47].

We also measured the magnetization in high pulse fields in the Dresden High Magnetic Field Laboratory in Helmholtz-Zentrum Dresden-Rossendorf. The data were then calibrated using a SQUID in the Magnetic laboratory of the Physical Institute of the Czech Academy of Sciences.

In Figure 2.6, we see a significant anisotropy both in the shapes of the magnetization curves and the saturated values. When a magnetic field was applied perpendicular to the crystal basal plane ($\mu_0 H \parallel c$), the induced saturated moment was $\approx 1.1 \mu_B / \text{f.u.}$, whereas a magnetic field along the basal plane ($\mu_0 H \perp c$) gave $\approx 1.5 \mu_B / \text{f.u.}$

We must note that for our Vanadium trihalide systems, the SQUID calibration is quite complicated. The systems degrade quickly on air, which may lead to signs of degradation within the time necessary to put the crystal in the device.

Moreover, they weigh around 1 mg, giving a small signal. These factors may lead to an error of up to 25% in the absolute values of the magnetization curves.

We see this anisotropy even in the temperature dependence in Fig. 2.6b, especially in low temperatures. Similar magnetization curves were obtained in VBr_3 , which leads us to believe VCl_3 orders as in-plane antiferromagnet with out-of-plane anisotropy as well.

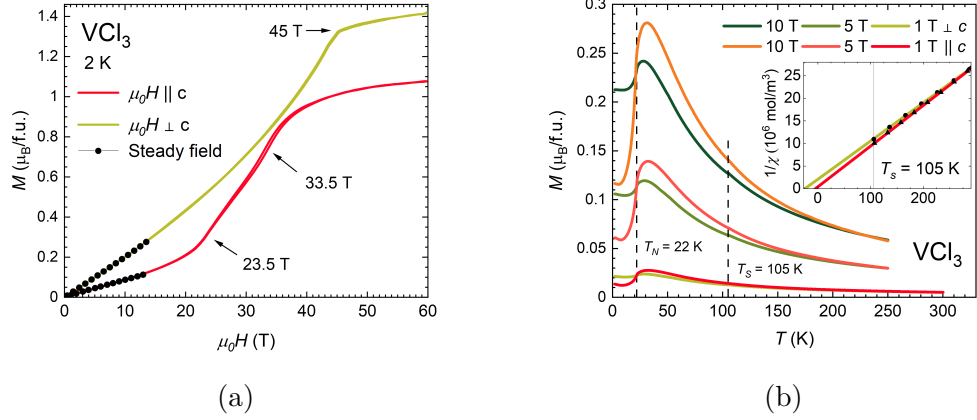


Figure 2.6: (a) Magnetization of VCl_3 as a function of the external magnetic field, and (b) as a function of temperature. The inset shows the inverse magnetic susceptibility. Due to complicated calibration (explained above), the curves may be affected by an error of up to 25% of the absolute values.

3. X-ray absorption

X-ray absorption spectroscopy (XAS) is, in principle, a primitive method - one irradiates a sample with X-rays and observes the intensity of the transmitted light at certain wavelengths. The attenuation is given by

$$I = I_0 e^{-\alpha(\epsilon)d}, \quad (3.1)$$

where I_0 is the intensity of incoming light and I the transmitted intensity through a sample of thickness d , decreased according to the absorption coefficient α , dependent on the beam energy ϵ . The coefficient is further related to the absorption cross section σ_a through

$$\alpha = \frac{\rho_m N_A}{M} \sigma_a(\epsilon), \quad (3.2)$$

where ρ_m is the mass density and N_A and M are Avogadro's number and molar mass, respectively. The equation (3.2) covers only the photoelectric absorption. Thus, one may need corrections to encompass the Compton and Thompson scattering and the positron-electron pair production arising at very high energies. [53]

The principle of the photoelectric effect is illustrated in Figure 3.1. Electrons in an atom are bound with discrete energies, which are element-specific. If the energy of the incoming photon is higher than the energy needed to expel an electron, it can do so while annihilating the photon.

The energy is dependent on the initial and final states. A diagram of different levels (states) is depicted in Figure 3.2, accompanied by their name (K, L, M) and the multiplet term, constructed as $(nl_j)^{2j+1}$. It is noteworthy that the levels are also split by SO coupling, as is the case of L₂ and L₃ edges, split by the SO coupling of the initial p -levels [53]. The effect of SO coupling and the crystal field on the XAS spectrum of a single ion is visible in Fig. 3.4.

The levels are commonly called the absorption edges, as they cause a sudden jump in the absorption cross section σ_a , seen in Figure 3.3. When the photon energy rises above the threshold given by the binding energy of the core level, a new option for absorption appears. This increases the probability of the interaction and, thus, the cross-section. Above the edge K-edge, one can see oscillations coming from the backscattering of the photoelectron wave within the lattice and further interference. In the case of the L-edges, multiplet effects can be seen. [53]

Nevertheless, in this thesis, we will focus on a NEXAFS (Near Edge X-ray Absorption Fine Structure) region, which consists of the edges themselves and their near vicinity.

In reality, it is difficult to shine through samples, especially with soft X-rays, which penetrate just a bit below the surface (the attenuation length of V_L is plotted in Fig. 3.5). Fluorescence from the subsequent de-excitation may be measured instead. A more popular option is to measure the total electron yield (TEY) - the characteristic fluorescent electrons emitted in the decay of the induced core holes. [54, 55, 56, 57]

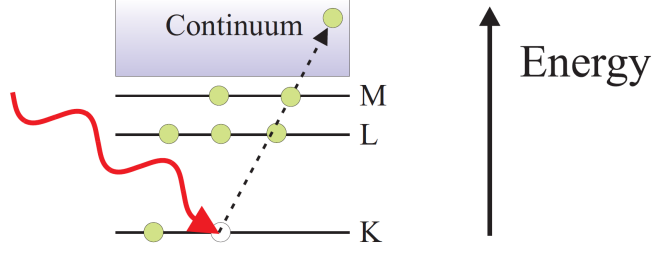


Figure 3.1: Photoelectric absorption [53].

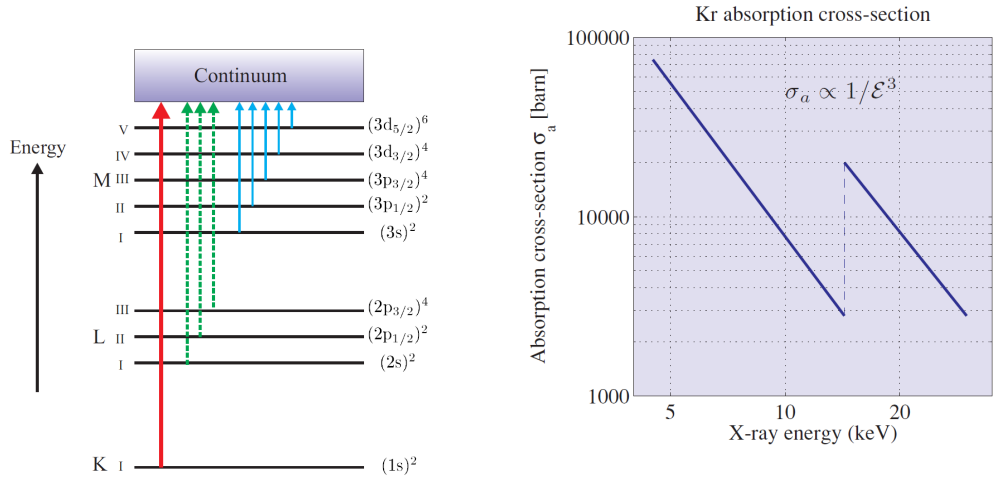


Figure 3.2: Absorption edges [53].

Figure 3.3: Absorption cross section of Kr [53].

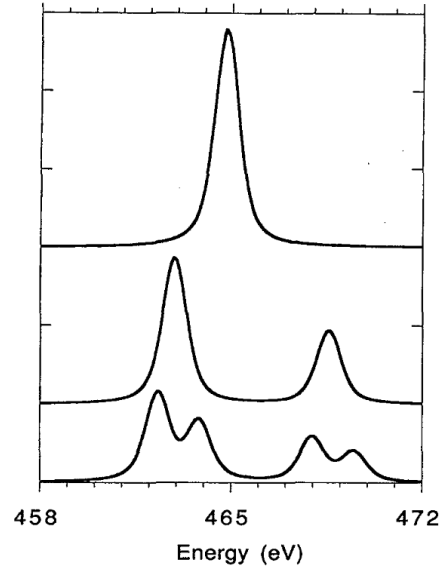


Figure 3.4: Single-ion L-edge XAS peak for the transition $3d^0 \rightarrow 2p^5 3d^1$ (top) and its splitting due to SO coupling (middle) and the crystal field (bottom) [58].

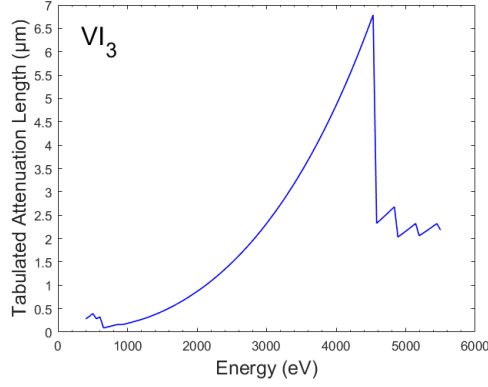


Figure 3.5: Tabulated attenuation length of VI_3 [59].

3.1 X-ray absorption in magnetic materials

3.1.1 XMCD

The abbreviation XMCD stands for X-ray Magnetic Circular Dichroism.

Dichroism is a property of materials that causes them to absorb light differently depending on its polarization. Circular dichroism is a case of preferential absorption of left- or right-circularly polarized light, which occurs when there's a broken inversion symmetry or, in our case, a break of time-reversal - the material then exhibits a magnetic ordering. By analyzing the spectra for opposite polarizations, one can obtain information on both the spin S_Z and orbital L_Z ground-state operators. The amount of information, however, depends on the probed edge, as from the K-edge, one retrieves only the L_Z . [53, 60]

To probe the magnetic properties of the material, we invoke excitations from core to valence states. In our case, to the semi-filled $3d$ orbitals, which carry the magnetic moment. The basic principle is illustrated in Figure 3.6. Photons of circularly polarized light carry angular momentum, depending on its helicity μ . The transition must then follow a set of selection rules, explained in section 3.1.2. The occupancy of the valence state thus determines whether the certain photon with its specific helicity can be absorbed and what intensity will be observable in an experiment.

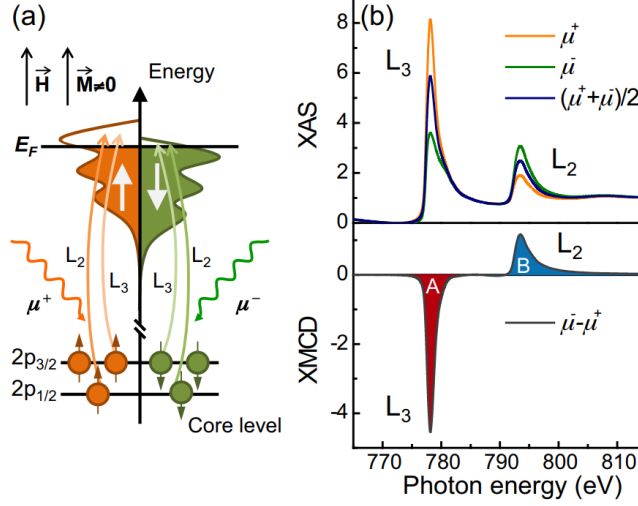


Figure 3.6: (a) XMCD principle and (b) the resulting spectra at L edges [54].

The XMCD signal in a magnetic field H will be calculated as

$$XMCD = \mu^-(H) - \mu^+(H) = \mu^+(-H) - \mu^-(-H). \quad (3.3)$$

The sign above the measured signal μ denotes the helicity, and the sign in front of H denotes the orientation of the applied field with respect to the photon beam direction. [54, 61]

We also need to define the XAS (X-ray Absorption Spectroscopy) signal as [61]

$$XAS = \frac{\mu^-(H) + \mu^+(H)}{2} = \frac{\mu^+(-H) + \mu^-(-H)}{2}. \quad (3.4)$$

In this thesis, we will focus on the transitions L₂ ($2p_{1/2} \rightarrow 3d$) and L₃ ($2p_{3/2} \rightarrow 3d$) in the soft X-ray region and K ($1s_{1/2} \rightarrow 4p$) and its pre-edge ($1s_{1/2} \rightarrow 3d$) for hard X-rays. The L-edges origin in dipole transitions, discussed in section 3.1.2. K-edges, on top of that, manifest different effects and are given a separate section 3.1.3. [53, 54]

3.1.2 Selection rules

The transition of a single electron from a core level to an empty valence state is due to an electric multipole transition operator, which contains magnetic and electric multipole operators. At the L-edges, the dipole transitions are prevalent; however, at higher energies, the quadrupole transitions also come into effect, as will be seen at K-edges. They are described by a multipole operator $T_q^{(Q)}$ of rank Q and components $q = -Q, -Q + 1, \dots, Q$. We can view it as an angular momentum operator of photons since the components behave similarly to the angular momenta of electrons - they follow the same commutation relations and transformations. For the dipole transition: $Q = 1$, for quadrupolar: $Q = 2$. [54]

The effect on the orbital momentum eigenstates $|\alpha'l'\rangle$ of the core state and the unoccupied state $|\alpha l\rangle$ satisfies the Wigner-Echart theorem. [54]

$$\langle l m_l | T_q^{(Q)} | l' m_l' \rangle = (-1)^{\ell - m_l} \begin{pmatrix} l & Q & l' \\ -m_l & q & m_l' \end{pmatrix} \langle \ell || T_q^{(Q)} || l' \rangle. \quad (3.5)$$

$\langle \alpha \ell \| T_q^{(Q)} \| \alpha' l' \rangle$ is the reduced matrix element, which is independent of m_l , m_l' and q . For simplicity, other quantum numbers, namely the radial quantum number, were left out. [54]

The 3- j symbol, denoted by the parentheses, is nonzero for certain conditions, two of which are [54]

$$l + Q + l' = \text{even}, \quad (3.6)$$

$$q = m_l - m_l'. \quad (3.7)$$

When we consider the SO L-S coupling of the core level, we can write the probability of the transition $|l' j' m_j'\rangle \rightarrow |l j m_j\rangle$ as

$$|T_{qm_l m_s}^{(Q)}|^2 = \sum_{m_j} (2j+1) \begin{pmatrix} l & Q & l' \\ -m_l & q & m_l' \end{pmatrix}^2 \begin{pmatrix} l' & s' & j' \\ m_l' & m_s' & -m_j' \end{pmatrix}^2. \quad (3.8)$$

The SO coupling, expressed in the second 3- j symbol, gives a condition $m_j' = m_l' + m_s'$. In combination with the transition condition for the orbital moment components, we get for each combination of q , m_l , m_s' only one transition to [54]

$$m_j' = m_l - q + m_s'. \quad (3.9)$$

3.1.3 K-edges of 3d TMs

The K-edge represents a dipole transition from $1s$ to a $4p$ SO-split doublet $p_{1/2}$ and $p_{3/2}$. Unlike L-edges, the XMCD signal can't come from the SO-coupling of the ground state since it's the $1s$ orbital with $L = 0$ and thus only one J state. The sole source of the XMCD signal is the split $4p$ levels, which need to be spin-polarized (the population of spin-up and spin-down differs) to stand behind the asymmetrical absorption. Spin-polarization naturally occurs in ferromagnets and can be induced by the $3d$ states. It can also be achieved with external field. [54, 62, 63, 55]

At the foothill of the K-edge lies a weak signal called the pre-edge. It arises from a transition ($1s \rightarrow 3d$). This transition can't be dipolar because the selection rule regarding orbital momentum l is prohibited for the dipolar $Q = 1$. The Q needs to be 2, implying a quadrupolar transition. [54, 55]

However, the pre-edge can also contain a dipolar signal from $4p$ when the transitions are superimposed or when the $3d$ and $4p$ hybridize. The most important changes in pre-edge are driven by the crystal field and the oxidation state, which changes both the position and the intensity of the pre-edge. Higher oxidation states reduce core electron screening, shifting the peak to higher energy. Pre-edges thus require a more demanding interpretation but give us a deeper insight into the environment and electronic state. [54, 55, 64, 65]

K-edges lie in the hard X-ray part of the spectrum. The high-energy rays penetrate deeper into samples, unveiling bulk properties. This contrasts the L-edge spectroscopy, whose sensitivity is heavily dependent on the surface. [56, 55]

It is worth noting that a negative peak in the XMCD corresponds to the spin polarization of $4p$ states being antiparallel to the net magnetization. Multiple peaks of different signs are often observed, indicating opposing microscopic polarizations. [62, 56]

3.1.4 Sum rules

To retrieve the information on the magnetic moment of the ground state from both the XAS and XMCD data, one uses sum rules.

The intensity of XAS is proportional to the number of holes n_h in the $3d$ state, the integrated XMCD to a projection of the orbital moment along the X-ray beam $\langle L_z \rangle$.

The sum rules are following [61, 54, 60]:

$$\langle S_{\text{eff}} \rangle = \langle S_z \rangle + \frac{7}{2} \langle T_z \rangle = \frac{3p - 2q}{r} n_h, \quad (3.10)$$

$$\langle L_z \rangle = \frac{4q}{3r} n_h, \quad (3.11)$$

$$\frac{\langle L_z \rangle}{\langle S_{\text{eff}} \rangle} = \frac{4q}{9p - 6q}. \quad (3.12)$$

Definitions of q , r and p for L-edges are in Figure 3.7.

The first equation (3.10) gives us information about the effective spin moment, where we take into account the magnetic dipole term

$$\mathbf{T} = \sum_i \mathbf{s}_i - 3\hat{\mathbf{r}}_i \frac{(\hat{\mathbf{r}}_i \cdot \mathbf{s}_i)}{r_i^2}. \quad (3.13)$$

The term depends on the SO coupling, which in turn depends on the strength of the exchange field. In $3d$ metals, $\langle T_z \rangle$ can be considered negligible with respect to $\langle S_z \rangle$ and disappears in weakly SO-coupled systems. [54, 60]

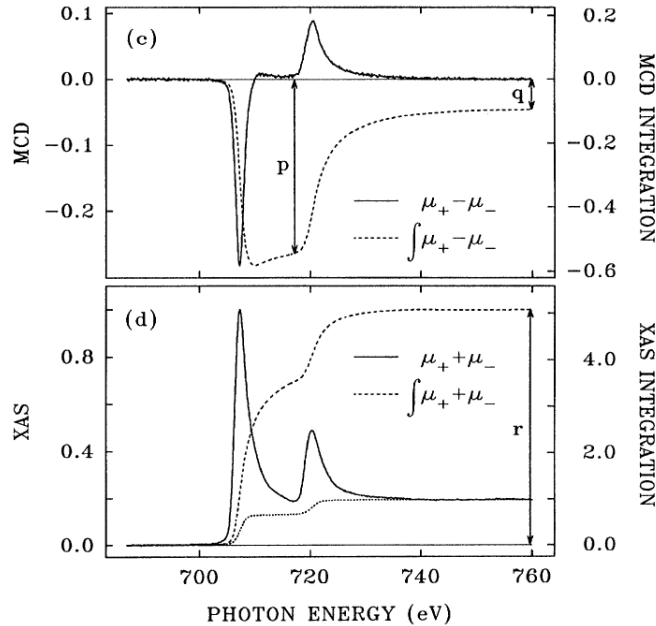


Figure 3.7: $L_{2,3}$ -edge XMCD and XAS spectra (full lines) and their integrals (dashed) of Fe/parylene films, defining the parameters of sum rules in (3.10), (3.11), (3.12) [61].

r is the Integral of both peaks in XAS and q in XMCD. However, an issue arises with p , the Integral value of the single L_3 peak. In light $3d$ metals, such as

V, the SO splitting of the p -orbit is not big enough not to have the peaks overlap. As a result, one can not separate the peaks completely. [60, 61, 54]

The XAS graph in Figure 3.7 contains a dotted line corresponding to the step function. Before calculating the XAS Integral and q , one must, in fact, remove a signal coming from the excitations into higher unoccupied states or the continuum. These effects are represented by the step function. The formula of the step function used for our calculations can be found in the experimental section 3.2. [61, 54]

3.2 Experimental results

3.2.1 L-edges: VI_3

The measurement was carried out at the X-treme beamline of the Paul Scherrer Institute (PSI) [66]. The sample was mounted to have the beam perpendicular to the crystal basal plane. We had around 10 scans for both photon helicities in a field of -5 T (the field was antiparallel to the beam direction). The studied temperatures ranged from 2 K to 60 K.

First, all obviously damaged scans were removed, and the rest were averaged and used for the calculation of XAS and XMCD defined in (3.4) and (3.3).

From XAS spectra, we calculated the normalization factor equal to the value at the L_3 peak, which we then used to normalize the XAS to have the peak reach 1. Afterwards, the XMCD spectrum was divided by this factor, too. From the normalized XMCD, the cumulative Integral was calculated. All normalized XAS, XMCD and the Integral are displayed in Figure 3.8 for temperatures between 40 K and 65 K. The positions of the edges were retrieved as inflex points of the slopes and were highlighted using vertical lines.

In order to calculate the $\langle L_z \rangle$, one needs to know the XAS Integral. To obtain it, we need to subtract the absorption jump, which can be modelled using a step function following

$$\begin{aligned} \text{stepFunction} = & \left\{ \frac{2}{3} \cdot \left[\tan^{-1}\left(\frac{E - E_3}{\text{width}}\right) + \frac{\pi}{2} \right] \right. \\ & \left. + \frac{1}{3} \cdot \left[\tan^{-1}\left(\frac{E - E_2}{\text{width}}\right) + \frac{\pi}{2} \right] \right\} \cdot \frac{\text{fullStep}}{\pi}. \end{aligned} \quad (3.14)$$

The fullStep is usually set to a XAS value at the further post-edge region; however, we observe an oxygen K-peak at this region, especially at low temperatures, leading to an unwanted signal. Because of this disturbance, we normalized the step function right above the L_2 edge at 527 eV [1]. An exception is the 2 K spectrum. Because of the oxygen pre-edge, we normalized the step function to a value at 525 eV - in the little valley. The fractions $2/3$ and $1/3$ correspond to the probabilities of the transitions [54], thus their contribution to the full step. E is the energy and $E_{2,3}$ are the corresponding energies of the edges. Other parameters are there to make the $\tan^{-1}$ function start at zero and end at the desired value. To adjust the steepness of the step function, we set the width to $1/3$.

The XAS cumulative Integral was calculated from the XAS lowered by the step function. All XAS, step function, XAS corrected for edge jumps and the Integral are displayed in Figure 3.9 at 2 K as an example.

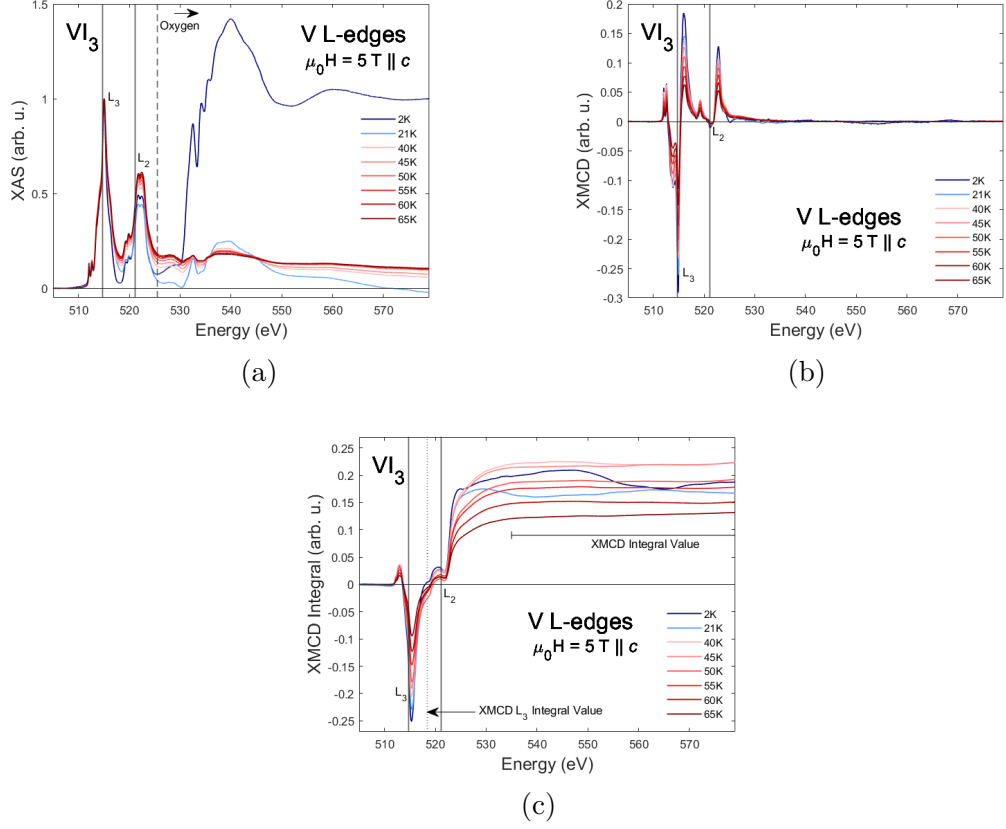


Figure 3.8: (a) XAS, (b) XMCD and (c) XMCD Integral of VI_3 at V L-edges. The vertical lines indicate the L-edges, the dashed line is the beginning of the Oxygen signal. The energy range over which the XMCD signal is averaged to obtain the Integral value is indicated. The XMCD Integral of the L_3 edge is indicated by a dotted line.

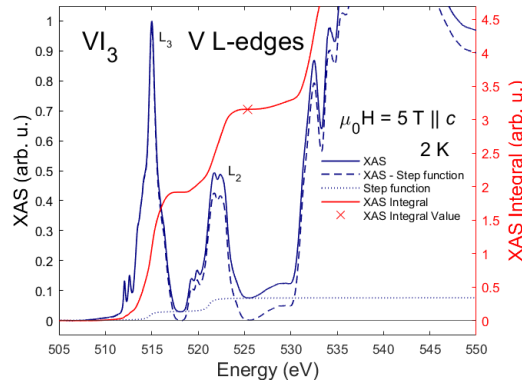


Figure 3.9: XAS Integral of VI_3 at V L-edges at 2 K, including the XAS spectrum, step function and XAS with the subtracted background. The value of the XAS Integral is marked by a cross.

Using both XMCD and XAS Integrals, we managed to calculate the values of $\langle L_z \rangle$ and $\langle L_z \rangle / \langle S_{\text{eff}} \rangle$ in all measured temperatures using the sum rules (3.11) and (3.12). We used $n_h = 8$, the number of holes in the $3d$ orbital or the V^{3+} valence state [1]. Results are shown in Figure 3.10.

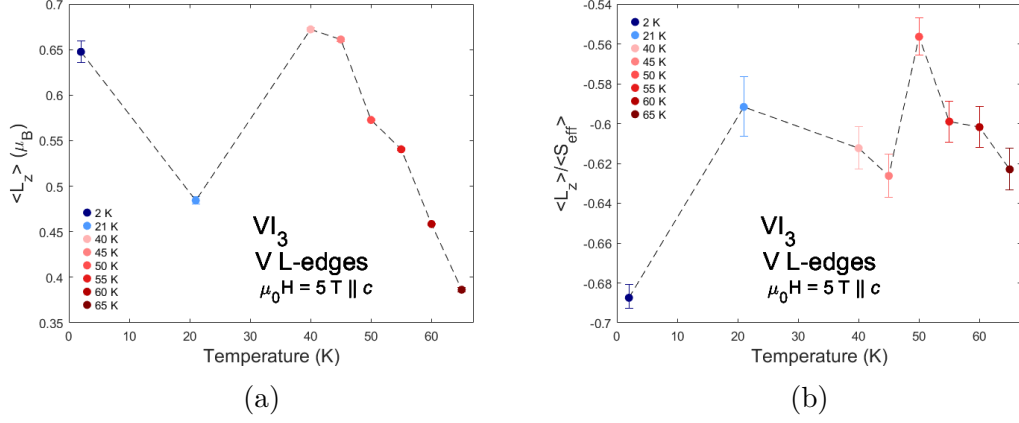


Figure 3.10: (a) $\langle L_z \rangle$ and (b) the ratio $\langle L_z \rangle / \langle S_{eff} \rangle$ of VI_3 at V L-edges.

As discussed in the previous section 3.1.4, the $L_{2,3}$ edges overlap. Hence, one can't avoid an error deducting a value of the Integral of a single L_3 peak (variable p in (3.12)). A border value around 518 eV was chosen, where the XAS has a valley before the L_2 starts. The value of the L_3 Integral was taken at this border, shown in Fig. 3.8c.

To account for the uncertainty of choosing the border energy, we added an error bar, which symbolizes a change in p as the border shifts by 0.2 eV. We can see in Figure 3.10b that the shift doesn't play a significant role. However, the overlap still leads to a significant error, as the XMCD signal for the Integrals in spin sum rules (3.10) and (3.12) cannot be assigned properly. This should shift the results from all temperatures by approximately the same amount. The relationships between different temperatures should thus be correct, but the absolute values must be viewed with caution.

The value of the XMCD Integral over the whole spectrum (variable p in (3.12),(3.11)) is the average of the post-edge region, highlighted in Fig. 3.8c.

As seen in Figure 3.10a, the out-of-plane orbital momentum doesn't diminish, not even for said 40 K. Moreover, the orbital momentum at 40 K is the biggest out of the dataset. The previously measured orbital moment at 2 K using this procedure was $0.67 \mu_B$ [1] (in the SI), which we confirm. Since the ratio in Figure 3.10b is negative, the orbital momentum points opposite to the spin moment, just as expected.

We must point out that zero orbital moment corresponds to zero XMCD Integral (as seen in (3.11)). De Vita et al. conducted the XMCD experiment in a field of 0.5 T, claiming it is enough to reach saturation. The magnetization curves measured by Son et al. [41] show that at 50 K, the magnetization and, thus, the XMCD signal can increase to almost double the value in 5 T, which we used. A small fluctuation in the spectra with worse overall signal could thus influence the final Integral. A sample-dependent effect or signs of degradation could also play their roles. Frankly, a similar scenario happened in our K-edge measurement (see section 3.2.2), where an XMCD Integral of one sample almost reached zero at the pre-edge end.

Table 3.1: Table of XAS and XMCD Integral values, along with the calculated orbital moment L_z and the ratio L_z/S_{eff} for VI_3 at the Vanadium L-edges.

Temperature (K)	XMCD L_3 Integral (arb. u.)	XMCD Integral (arb. u.)	XAS Integral (arb. u.)	L_z (μ_B)	L_z / S_{eff}
2	0.004	0.19	3.16	0.65	-0.69
21	-0.014	0.17	3.68	0.48	-0.59
40	-0.013	0.22	3.51	0.67	-0.61
45	-0.009	0.22	3.51	0.66	-0.63
50	-0.025	0.19	3.52	0.57	-0.56
55	-0.013	0.18	3.49	0.54	-0.60
60	-0.011	0.15	3.50	0.46	-0.60
65	-0.006	0.13	3.49	0.39	-0.62

3.2.2 K-edges: VI_3 and VBr_3

K-edges of V of both VI_3 and VBr_3 were measured at the hard X-ray beamline ID12 at ESRF (European Synchrotron Radiation Facility).

Differently from the L-edge PSI measurement, we obtained spectra for both opposite orientations of the magnetic field. Data from respective orientations were processed the same way as for L-edges: spectra of respective helicities were averaged, XAS and XMCD were calculated and normalized, the XMCD Integral was calculated. On top of that, we averaged the resulting spectra over the field orientation.

The data were gathered in two measuring sessions. The first session focused mainly on VBr_3 spectra and their evolution with temperature. Nonetheless, we managed to measure two VI_3 spectra at 2.5 K and 40 K.

The second, shorter session focused on the alleged quenching of the orbital moment at 40 K in VI_3 .

VI_3 spectra will be shown first, followed by VBr_3 , ending with a comparison of both at 2.5 K.

VI_3

Outcomes of both hard X-ray sessions regarding VI_3 are displayed in Fig. 3.11. Scans of the sample belonging to the first session (further called Sample 1) are drawn as dashed lines. The vertical dashed lines define the pre-edge area.

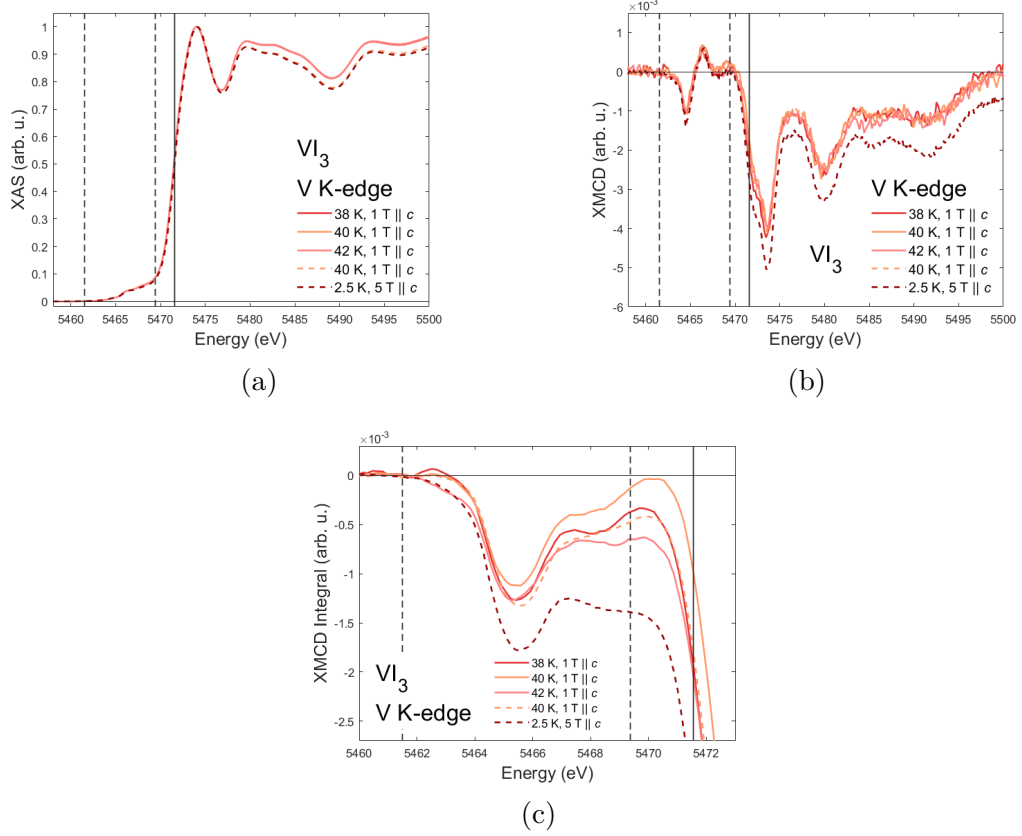


Figure 3.11: (a) XAS, (b) XMCD and (c) pre-edge XMCD Integral of VI_3 at V K-edge of Sample 1 (dashed lines) and Sample 2 (full lines). The vertical dashed lines indicate the boundaries of the pre-edge region, while the solid vertical line marks the Vanadium absorption edge.

In Figure 3.11a, one can see the XAS differs between the two samples, especially in the EXAFS area. Fortunately, we are mainly interested in the pre-edges, where the differences are not so significant. However, since the signal is weak, even small deviations in XMCD (Fig. 3.11b) are reflected in a notable change in the XMCD Integral in Fig. 3.11c. Fortunately, we obtained two spectra at 40 K in the same magnetic field of 1 H and can thus deduce the sample dependence. The said small change in XMCD resulted in the XMCD Integral of Sample 1 being $-0.47 \cdot 10^{-3}$ at the end of the pre-edge region, whereas the Integral of Sample 2 resulted in $-0.13 \cdot 10^{-3}$.

Such results might have come from slight sample degradation, which occurs exceptionally quickly on air. The samples were attached to the sample holder in glovebox; however, the ESRF provided us with only a temporary glovebox with insufficient quality of inner atmosphere, which might have led to a small contact with air. Moreover, the samples were exposed to air when being put into the device. All manipulation was done as quickly as possible. Still, there might have been slight signs of degradation.

Secondly, scans of Sample 2 were of lower resolution than those of Sample 1, increasing the likelihood of a statistical error. Such an error, though seemingly small, might have resulted in an XMCD error on the order of 10^{-4} .

Nevertheless, the spectra did not shift in energy with temperature - the oxidation state remained the same. In contrast, the XMCD, proportional to the

orbital moment [67], did evolve according to Figure 3.14, with the largest being at 2.5 K.

VBr₃

All VBr₃ spectra were collected in the first session and are of the same sample. We also managed to increase the magnetic field up to 17 with a much better resolution. The results are shown in Figure 3.12.

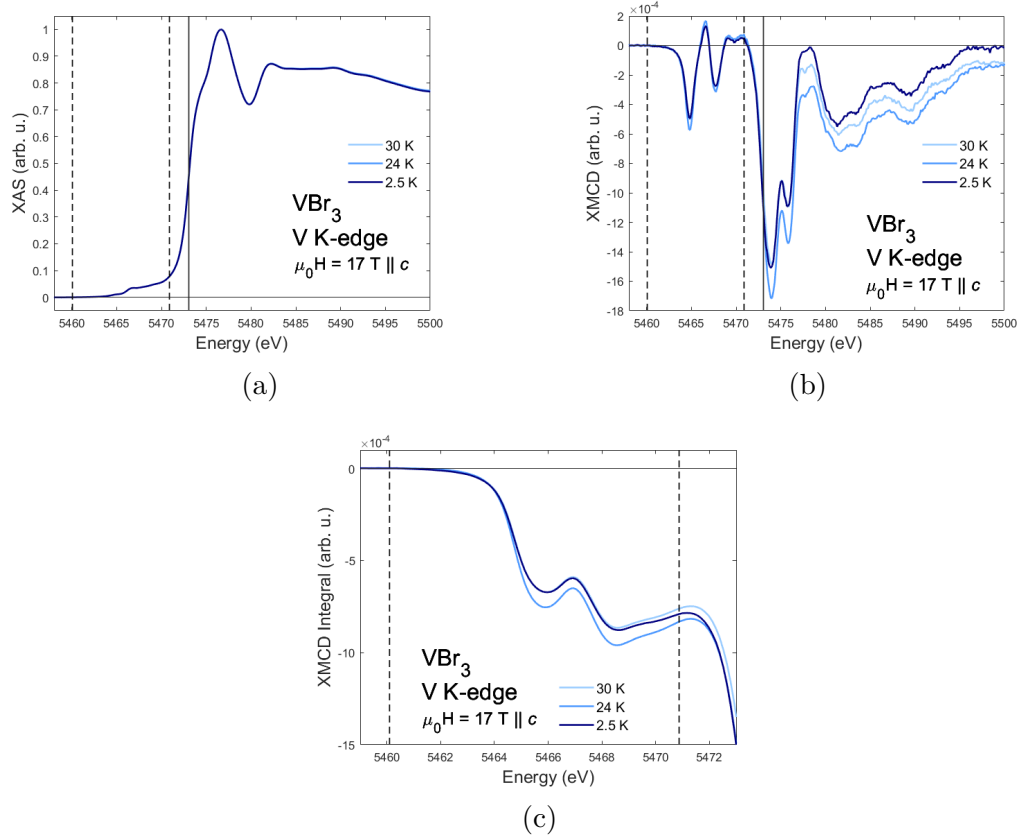


Figure 3.12: (a) XAS, (b) XMCD and (c) pre-edge XMCD Integral of VBr₃ at V K-edge. The vertical dashed lines indicate the boundaries of the pre-edge region, while the solid vertical line marks the Vanadium absorption edge.

In the pre-edge, all scans behave similarly, resulting in an almost identical XMCD Integral value.

We are now able to compare the spectra of both materials at 2.5 in Fig. 3.13.

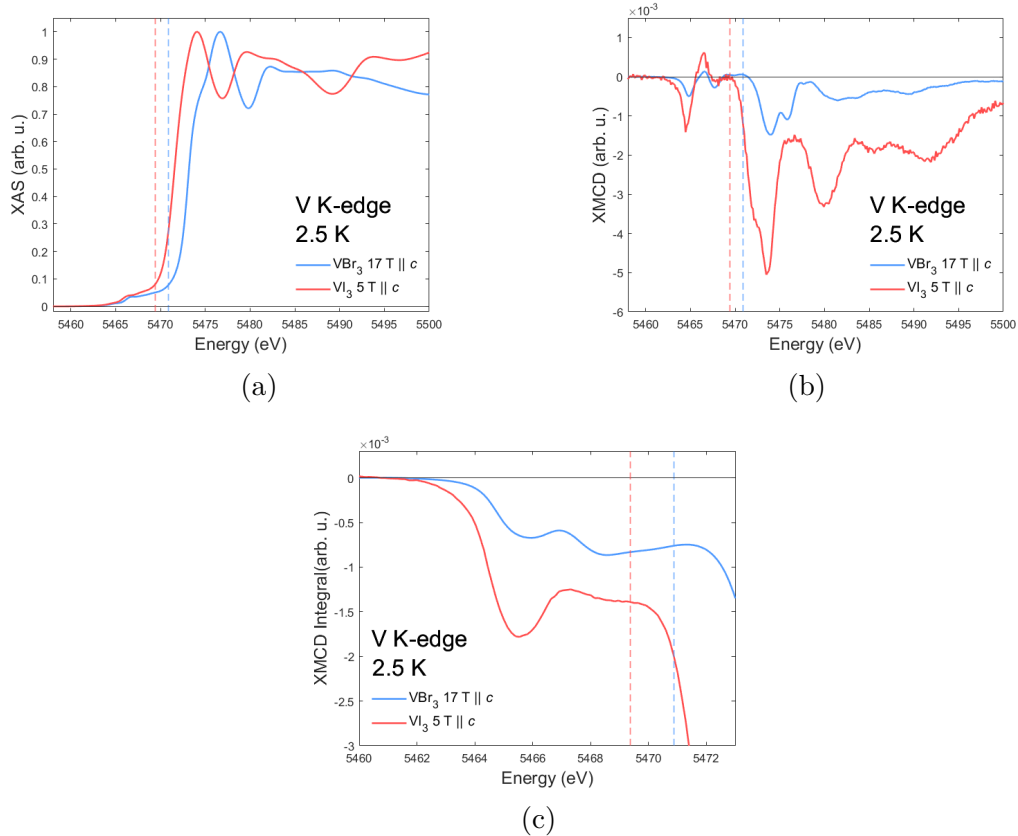


Figure 3.13: (a) XAS, (b) XMCD and (c) pre-edge XMCD Integral of VI_3 and VBr_3 at V K-edge at 2.5 K. The dashed vertical lines indicate the end of the corresponding pre-edge region.

First, we see an energy shift of the XAS edge. Shifts are mostly connected with bond lengths and valence states [54, 55, 64, 65, 68]. In Vanadium-based compounds, shorter chemical bonds and a higher oxidation state usually meant a shift of both the XAS edge and a pre-edge peak to higher energies [68, 65, 64]. Having said that, we must warn that it is not a general case.

The effect of the oxidation state can be explained by the fact that losing an electron (i.e., a higher oxidation state) increases the binding energy, even for core levels, causing the XAS peak to shift to higher energies. This relationship between the Vanadium oxidation state and binding energy has been confirmed by XPS measurements [69]. We have already discovered at least a bivalent occurrence of V in VCl_3 with V^{2+} and V^{3+} states, and we can assume the same for other Vanadium trihalides.

Bromine has a higher electronegativity than Iodine. Vanadium thus experiences a stronger pull for electrons in VBr_3 . This pull could possibly increase the mean oxidation state of Vanadium, meaning the relative content of V^{3+} is higher in VBr_3 , causing the shift.

The covalent radius of Br is also smaller, which is reflected in the lattice parameters shown in Fig. 2.5. From that, we expect the Br-V bond to be shorter than the I-V bond. A shorter bond in Vanadium compounds mostly led to an energy increase of the XAS-edge and the opposite effect in the pre-edge [64]. This would make sense in our case, as the VBr_3 pre-edge peak around 5466 eV is more extended from the main edge.

XAS intensities of the pre-edge peaks differ only slightly, meaning that the possible mixing of $3d$ and $4p$ states is similar for both materials.

All XMCD Integral values at the pre-edge ends of both materials are summarized in Fig. 3.14 with error bars representing a shift of the end of the pre-edge region by 1 eV.

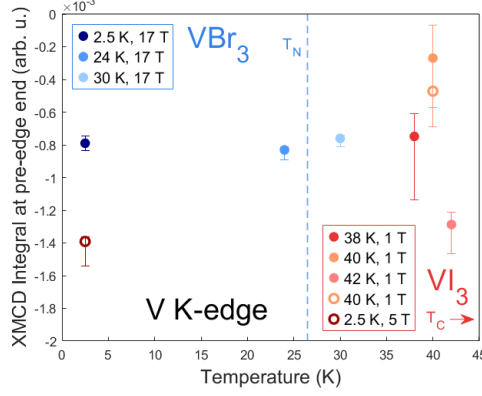


Figure 3.14: XMCD Integral values of VI_3 (shown in red) and VBr_3 (blue) at the V K-pre-edge end. The error bars indicate a shift of the end of the pre-edge by 1 eV.

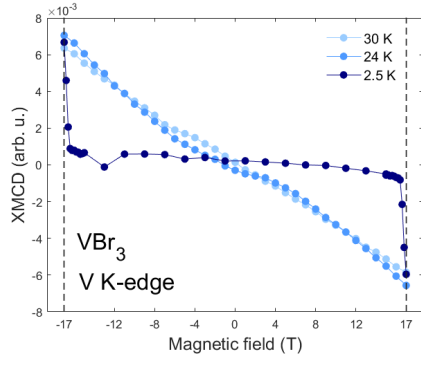
To account for the uncertainty in selecting the pre-edge region, we included error bars representing a 1 eV shift in the region's endpoint.

Apart from the differences in the two VI_3 samples at 40 K, we see a dramatic decrease (an increase in the magnitude of $\langle L_Z \rangle$) at 2.5 K, whereas the value in VBr_3 decreases only slightly, even when crossing the Néel temperature T_N . At 2.5 K, the expected orbital moment of VBr_3 is 0.57(7) times the value in VI_3 . The error was calculated from the relative errors:

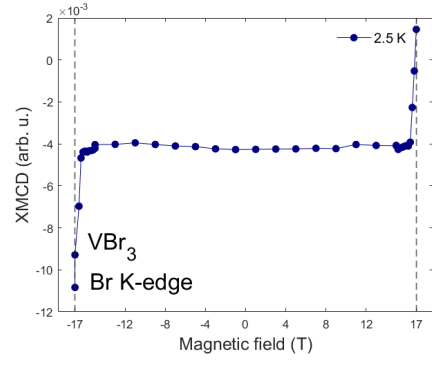
$$\sigma = \frac{\text{Integral}(\text{VBr}_3)}{\text{Integral}(\text{VI}_3)} \sqrt{\left(\frac{\sigma(\text{VBr}_3)}{\text{Integral}(\text{VBr}_3)}\right)^2 + \left(\frac{\sigma(\text{VI}_3)}{\text{Integral}(\text{VI}_3)}\right)^2}. \quad (3.15)$$

Using XMCD, we also managed to measure hysteresis loops of VBr_3 , depicted in Fig. 3.15. Figure 3.15a shows the loops at the V K-edge in three temperatures. The curve at 30 K reflects the paramagnetic state, while the one at 24 K—just below the Néel temperature $T_N = 26.5$ K—shows a slight change in the curvature to an S shape arising from a metamagnetic transition, fully developing at 2.5 K. The curve at 2.5 K shows a steep increase in the signal in the vicinity of 17 T. This behaviour exactly coincides with the spin-flip metamagnetic transition of first-order type to the polarized paramagnetic state [46].

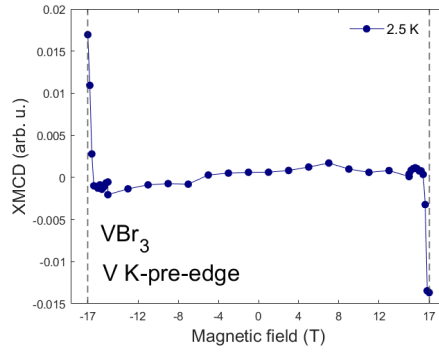
The transition appeared also in the signal from the pre-edge (Fig. 3.15c) and, surprisingly, from the Br K-edge (Fig. 3.15b). The signal from the non-magnetic Br thus suggests a possible magnetic polarization coming from V.



(a)



(b)



(c)

Figure 3.15: XMCD hysteresis loops of VBr_3 measured at (a) the V edge, (b) the Br edge, and (c) the V pre-edge.

4. Infrared spectroscopy

4.1 Vibrational spectroscopies

The most common techniques to probe the vibrational spectra are infrared (IR) and terahertz (THz) absorption, supplemented by Raman scattering. Raman spectroscopy was not explored in this work; however, it is too important not to mention it, especially since the Raman scattering is complementary to the absorption methods. [70, 71]

The infrared spectrum is said to cover the electromagnetic frequencies from 0.3 THz (300 GHz) to 400 THz. Terahertz radiation is thus a subset of the so-called far infrared range (FIR), which ranges from 0.3 THz to 3 THz and, in some sources, even to 30 THz. [72, 73, 71]

This range corresponds to the energies of molecular vibrational excitations. In order to be absorbed, photons need a wavelength corresponding to an energy gap to a higher rotational or vibrational state - a condition known as resonance. One can thus measure the absorption spectra and deduce at which wavelength the molecule changed its vibrational state. There is a rule that the absorption must be accompanied by a change in a dipole moment of the molecule p , which is expressed as a product of the atomic charges q_i and their positions r_i [70]

$$p = \sum_i e_i r_i. \quad (4.1)$$

In a polar diatomic molecule, an incident electromagnetic field induces opposite forces on the two atoms, reducing/increasing the interatomic distance and changing the dipole moment p . If the wavelength also corresponds to the excitation energy, the molecule can absorb it.

The key takeaway is that not all vibrations are accessible through absorption. In such a case, the Raman scattering comes into play. This inelastic scattering is not limited by the same resonant condition and can thus unveil different off-resonant transitions. Nevertheless, it has its own limitations. In this case, the transition must be connected to a change in polarizability, the tendency to deformation of the electron cloud about the molecule, thereby inducing the dipole moment [70].

The working principles are illustrated in Fig. 4.1. While IR absorption induces a transition to a real higher vibrational or rotational state, Raman scattering involves excitation to a virtual state. The subsequent relaxation can lead to a higher-energy state (Stokes branch), a lower-energy state (Anti-Stokes branch), or a return to the initial state, resulting in scattered light at multiple wavelengths. [70]

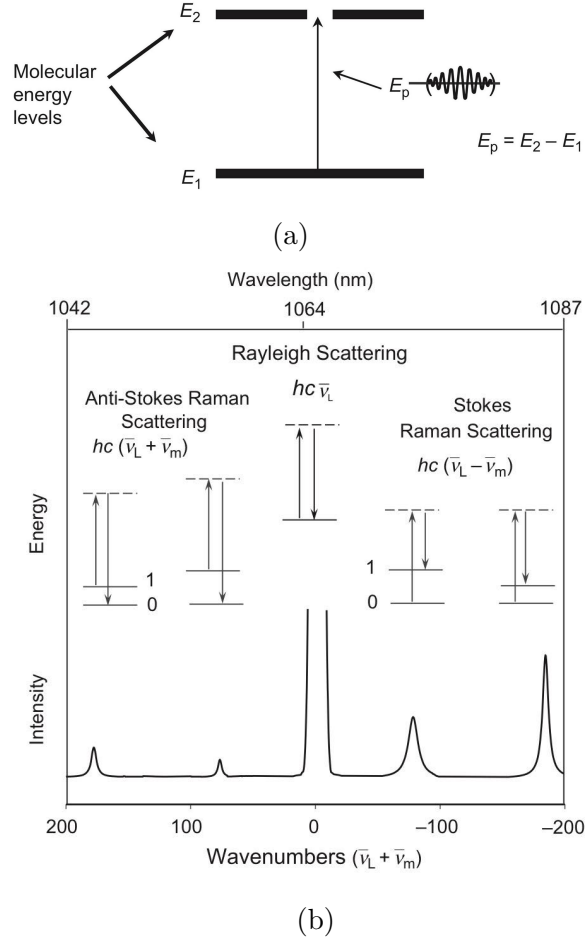


Figure 4.1: A principle of (a) absorption and (b) Raman scattering [70].

Whether the vibration is Raman or absorption active is highly determined by the molecular structure. Some vibrations may be active in both. However, when dealing with molecules with the centre of symmetry, there is a great exclusion rule: If the vibration retains the centre of symmetry, it's Raman active. The mode is then denoted as "gerade". If not, it's IR active and called "ungerade". To measure the whole phonon spectrum, both methods must be utilized. [70]

Even though the techniques were explained on vibrational states, they can also be useful in studying magnons, which was the primary goal for which we used them. [74, 71].

4.2 Experimental details

The infrared spectra were gathered using the BRUKER IFS113v in the Dielectric and infrared spectroscopy laboratory of the Physical Institute of the Czech Academy of Sciences (FZU AV) [75].

Thin VCl_3 layers were chosen for a measurement in a transmission mode at normal incidence. Even though the bulk crystals appear thin to the human eye, they do not let through the slightest signal. To thin the crystals, a careful exfoliation using Scotch tape inside a glovebox with Ar inert atmosphere was necessary. [76]

Exfoliated samples, that were transparent in a bright visible light have proven to be suitable. On the other hand, layers too thin had various cracks and inhomogeneities that let through unwanted signal. [76]

The exfoliated layers were stuck to the Scotch tape. Fortunately, the Scotch tape gave only an incoherent signal, which we used as a reference in the data normalization

$$T_{normalized} = \frac{T_{sample}}{T_{reference}} \cdot 100, \quad (4.2)$$

where T_{sample} is the spectrum obtained by shining through the sample stuck on the tape and $T_{reference}$ is a spectrum of the sole tape. All spectra were collected for approximately 7 minutes until they no longer drastically improved with additional scans.

Mounted samples are shown in Figure 4.2. During the first few measurements, the samples were only stuck to the holders with the duck tape. However, when we reached low temperatures (below 50 K), the duck tape cracked, fell off and took the sample with it. Securing the Scotch tape with Kapton tape resolved this problem and allowed us to measure down to 7 K with no issues. Exfoliation using only the Kapton tape was not successful; thus, both tapes were used.

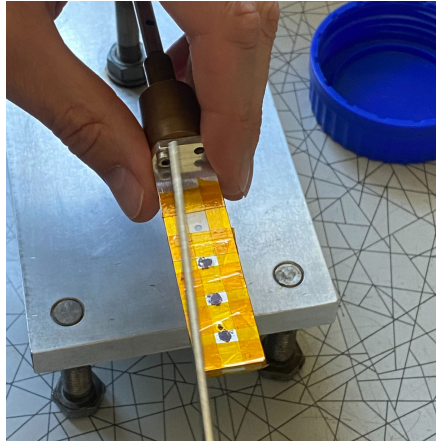


Figure 4.2: VI_3 samples for IR transmittance measurements, mounted on a holder using Scotch and Kapton tapes.

4.3 Experimental results

Spectra of three samples are displayed in Figures 4.3 and 4.4. The Figures show a temperature evolution of the spectra, ranging from room temperature down to 7 K. The samples are named based on their relative thickness: thick, middle, and thin. However, one must bear in mind that all the samples were exfoliated and transparent, their thickness presumably in the order of $10 \mu\text{m}$.

The thin sample exhibited the sharpest peaks, as shown in Figure 4.3a. Additionally, we observed a splitting in the Reststrahlen band between 270 and 360 cm^{-1} , which remains opaque in the thick sample (Figure 4.4a). To emphasize the peaks and their evolution, we drew Figure 4.3b, which contains the deviations of each spectrum from their average.

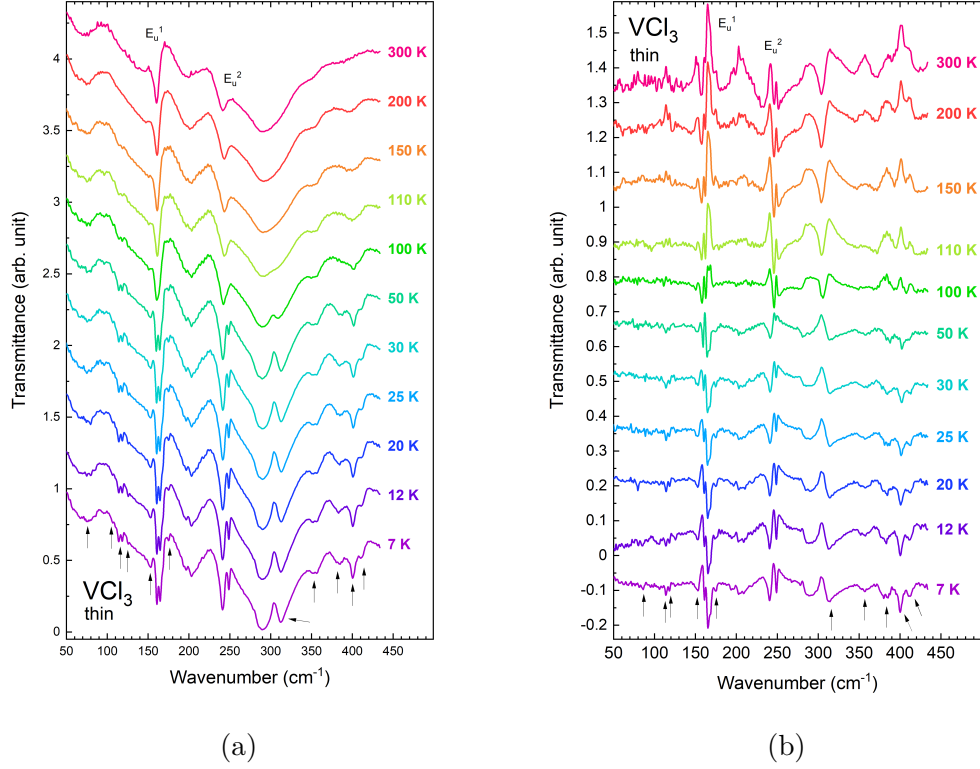


Figure 4.3: (a) VCl₃ IR spectra of a thin sample and their (b) deviation from an average spectrum. Arrows mark peaks suspected to originate from phonon modes.

Since there are 8 atoms in the unit cell, we expect 24 phonon modes, 3 of which are acoustic. The rest should be visible as absorption peaks in IR and THz spectroscopies or Raman scattering. The assignment between spectroscopies and Raman scattering depends on the point group of the crystal structure. [77].

VI₃ IR spectra have been interpreted using a rhombohedral point group C_{3i} , for which the corresponding irreducible representations of optical modes are [77]

$$\Gamma_{C_{3i}} = 4A_g + 4E_g + 3A_u + 3E_u, \quad (4.3)$$

where E denotes a doubly degenerate mode, A is non-degenerate. The subscript u means "ungerade" mode, which behaves antisymmetrical under inversion and thus is active in IR. g is "gerade" - Raman active.

In low temperatures, a monoclinic point group C_{2h} with

$$\Gamma_{C_{2h}} = 6A_g + 6B_g + 4A_u + 5B_u, \quad (4.4)$$

is expected. The B modes are also non-degenerate. Hence, the structural transition forces a splitting of the degenerate phonons. The splitting was, in fact, observed in our spectra. Two phonon modes in Figure 4.3 are marked $E_u^{1,2}$ since they split visibly below the $T_S \approx 105$ K. The splitting gets even more pronounced as the peaks sharpen with cooling. There are many more peaks, which hint at the existence of phonons. The candidates are marked by arrows at the bottom part of Figures 4.3a and 4.3b.

Figure 4.4 contains spectra of thicker samples, where some peaks are slightly more visible. The medium sample fell off the holder upon reaching the low temperatures, thus the incomplete evolution.

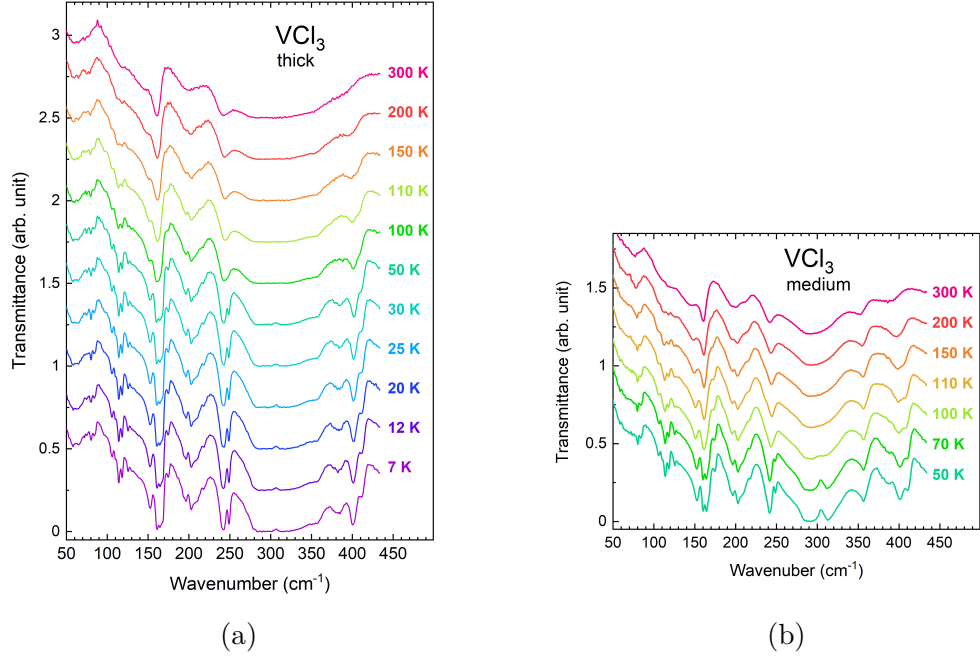


Figure 4.4: VCl_3 IR spectra of (a) a thick sample and (b) a medium sample.

To be confident about the assignment to specific phonon modes, the spectra must be accompanied by simulations of the vibrational states. The calculations use the crystal structure as a vital input, as it heavily determines the phonons. A room-temperature comparison of calculated phonon modes and the candidates observed in the experiment are summarized in Fig. 4.5. Unfortunately, the exact low-temperature structure is not yet known, so we can't compare the low-temperature results.

The lines on the left side of Fig. 4.5 correspond to the calculated phonon modes; their height correlates with their wavenumber. The right side shows all candidates observed in the experiment. Blue colour signals degenerate modes; the non-degenerated states are depicted in pink.



Figure 4.5: The comparison of calculated phonon modes and measured IR peaks for the R-3 structure at room temperature.

The experiment showed 14 possible phonons, whereas the calculation assigned only 6 likely IR active modes, as explained in (4.3). Some of the experimental peaks, especially in the lower area, may thus only be a noise. The same applies to the phonons with the highest wavenumbers.

The degenerate E_u modes calculated at 248 and 155 cm^{-1} have a good correspondence to the experiment. However, the third E_u mode is off by 26 cm^{-1} . On top of that, an A mode in the region doesn't have an experimental counterpart. This area lies within the Reststrahlen band. Because it split, we assigned it to an E_u mode. In reality, one peak might belong to the A mode and the second signs the remains of the Reststrahlen band. In such case, we are missing an E_u mode and need to consider the experimental E_u mode at 390 cm^{-1} , which is even more remote. There is also a likely possibility of a hidden weak E_u mode in the Reststrahlen band.

Surprising is that the experimental peaks between 150 and 201 cm^{-1} don't have their calculated twin since the peaks are clearly visible in all of the samples.

To properly distinguish the noise from the experimental peaks might require us to measure with a device possessing a better resolution. A more brilliant source might also help - we could use thicker samples, without the necessity of exfoliating and thus deforming the crystals.

All spectra of multiple samples combined, we drew a diagram 4.6 showing the splitting and temperature evolution of the phonon modes. Positions of the phonons were assigned from the bottoms of their peaks. Since the information was read from the spectra, some splittings were not clear right below the T_S but in lower temperatures instead. Nevertheless, we assume the splitting arising from

the structural transition.

The non-degenerate states mostly manifested hardening (shift to higher wavenumbers) with cooling, the shift ranging from 1 eV up to 3 eV. This is the case for the phonons below 180 cm^{-1} . The non-degenerate phonons above 180 cm^{-1} didn't move.

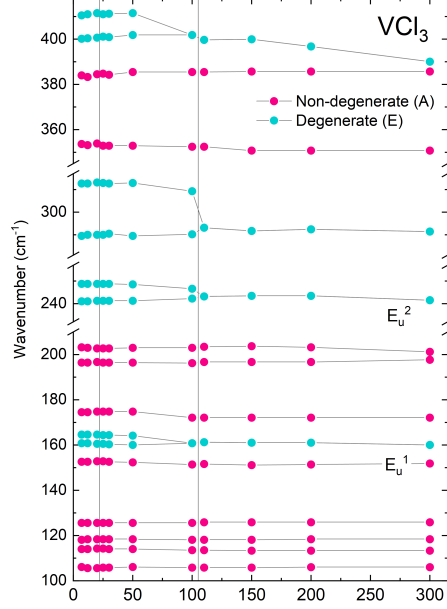


Figure 4.6: Temperature evolution of peaks observed in the VCl_3 IR spectra.

Apart from knowing the phonon evolution with temperature, we wanted to observe possible magnons, who would appear as peaks below the ordering temperature $T_N \approx 22 \text{ K}$. Sadly, no unambiguous peaks appeared. This doesn't mean they do not occur, but they may return too small a signal to be observed with the device used. They also might have appeared out of the working range of the used bolometer - below 50 cm^{-1} or above 450 cm^{-1} , where the signal gets noisy.

Related IR with different detectors or THz and Raman measurements may thus be further probed to unveil the expected magnons.

Conclusion

In this thesis, we investigated the Vanadium trihalide triad — VI_3 , VBr_3 , and VCl_3 — using XMCD and infrared absorption techniques.

These compounds are known for their intriguing potential in future applications, particularly due to their magnetic ordering in low-dimensional systems, combined with unique crystalline and magnetic structures. This magnetic ordering arises from an unquenched orbital moment, a rare and exciting property among $3d$ transition metal compounds.

To probe this orbital moment in VI_3 and VBr_3 , we measured their XAS and XMCD spectra at various temperatures. From the L-edge spectra of VI_3 , we could directly calculate the orbital moment. A previous low-temperature study reported a value of $0.6(1)\mu_B$ [1], based on an average across multiple analytical approaches. In this work, we applied one of those methods and obtained a result of $0.65(1)\mu_B$, closely matching their value of $0.67\mu_B$ derived using the same approach.

K-pre-edge XMCD spectra provided a qualitative comparison of the orbital moments in VI_3 and VBr_3 . While VBr_3 generally exhibited a smaller XMCD integral — proportional to the orbital moment — its temperature dependence was more flat. In contrast, VI_3 displayed a stronger variation with temperature, although the results carried larger uncertainty due to greater sensitivity of the Integral to the choice of the pre-edge region.

Additionally, we contrasted our data with a previous study suggesting a sudden quenching of the orbital moment in VI_3 at 40 K [3], using both L-edge and K-edge data. In the study, De Vita et al. [3] attribute this quenching to the reorientation of spins in the vicinity to the order-to-order ferromagnetic transition at $T_{FM2} = 36$ K [44]. Below the temperature, two inequivalent magnetically ordered sites exist, one of which quenches the orbital moment. Above, only one exists [44]. Because of the transition, a significant change in orbital moment would be reasonable. However, we did not see such a change in our data. Therefore, a prominent evolution is likely to happen at the site with the quenched orbital moment, which doesn't manifest itself in the XMCD signal. Nevertheless, both sites must adapt to form one site and keep the value of the orbital moment the same. The sudden quenching can thus be a result of a fluctuation in the measurement, which is highly susceptible to the sample degradation and the resolution, increased with the size of the magnetic field.

The final part of this thesis focused on the infrared spectra of thin VCl_3 crystals prepared via dry exfoliation. We observed the temperature evolution of the spectra from room temperature down to 7 K, revealing peak splittings that indicate a lowering of phonon mode degeneracy, a natural result of a structural transition. However, comparison with calculated phonon modes for the R-3 space group at room temperature yielded unsatisfactory agreement. Further refinement of the calculation parameters will be necessary to reach confident phonon mode assignments.

One of our goals was to identify magnon excitations. Unfortunately, no clear magnon features were observed in the range of 50–450 cm^{-1} . Further measurements on detectors sensitive to different wavelengths can be conducted. THz spectroscopy will also be a subject of our future interest.

In summary, this work provides new insights into the orbital magnetism and lattice dynamics of Vanadium trihalides. Through a combination of X-ray and infrared spectroscopy, we have advanced the understanding of their magnetic behaviour and structural properties. These results lay the groundwork for future studies, particularly those exploring the role of the orbital moment and excitations in low-dimension environments.

Future perspectives

Up until recent years, the research regarding Vanadium trihalides focused mainly on their complex structure and the unquenched orbital moment - the source of their valuable anisotropy and magnetic ordering in low dimensions. However, new interesting studies have emerged, offering even more promising features these materials possess.

One of the novel studies was done by Mastrippolito et al. [5], who claim to have proven a 2D polaronic state in VCl_3 .

Principally, polarons are quasiparticles describing an interaction between electrons and the ions in the lattice. A moving electron displaces the atoms from their equilibrium, which increases the electron's effective mass and lowers its mobility, possibly leading to a trapping of the electron [78].

Prior to the study, the electronic properties of VCl_3 had not been thoroughly experimentally studied. Calculations suggested VCl_3 to be either metal [79] or an insulator [80]. The existence of a polaron thus shifts the narrative toward a Mott insulator, which opens up new doors for its electronic applications.

Another exciting study regarding VCl_3 was recently done by Camerano et al. [4]. Their calculations revealed a multiferroic order in the orbital and spin order of freedom, intertwining their excitations. On top of that, they suggest an anti-ferro-orbital ordering (the preferentially occupied orbitals alternate between atoms) [4]. In combination with antiferromagnetism, this added spatial symmetry could possibly make VCl_3 a host to altermagnetism.

Multiferroicity has also been predicted in VI_3 [81]. In this case, the ferromagnetic order should coexist with ferroelectricity (spontaneous electric polarization). This combination of magnetic and electric responses is highly requested in technical applications. Since it's quite rare, scientists usually have to come up with artificial devices, such as heterostructures, to fulfil the demand. [81]

Even though the Vanadium trihalides have been studied extensively for the past few years, new exciting properties are still being discovered, demonstrating their versatility in a wide range of applications. These discoveries not only reveal their unique potential but also predict a rich and promising future in which the Vanadium trihalide triad plays a significant role in modern devices.

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List of Abbreviations

- **(A)FM** - (anti-)ferromagnetic
- **EDX** - Energy Dispersive X-ray Spectroscopy
- **EPFL** - École Polytechnique Fédérale de Lausanne
- **ESRF** - The European Synchrotron Radiation Facility
- **IR** - Infrared
- **PSI** - Paul Scherrer Institute
- **SO** - Spin-orbit interaction (coupling)
- **SQUID** - Superconducting quantum interference device
- **vdW** - van der Waals
- **XAS** - X-ray absorption spectroscopy
- **XMCD** - X-ray magnetic circular dichroism
- **XPS** - X-ray photoelectron spectroscopy