

## ABSTRACT

Title of dissertation: SITE AND SYMMETRY DEFINED MAGNETIC  
GROUND STATES OF INTERCALATED  
DIVALENT TRANSITION METAL  
DISELENIDES

Héctor Cein Mandujano Canales, Doctor of  
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Dissertation directed by: Professor Efrain E. Rodriguez  
University of Maryland Department of Chemistry  
and Biochemistry

Transition metal dichalcogenides (TMDs) are a vast family of compounds with various structural types. In this thesis, we focus on the 2H-type TMD structure. The number “2” describes the number of two-dimensional layers needed to describe the hexagonal unit cell, which is denoted by the letter “H”. We exploit the versatility of the interstitial site between the two TMD layers to introduce magnetic cations – specifically cobalt. While the 2H-phase is the most stable structure for the host TMD, we find that the intercalant can have many site arrangements leading to distinct superlattice arrangements. These superlattices will have severe implications on the symmetry of the crystal, where at low intercalation ratios we find that centrosymmetry of the host is preserved; further increasing the intercalant, this symmetry operation is broken, leading to a non-centrosymmetric structure. Each of these symmetries has direct implications on both observed electronic and magnetic properties.

The host lattice made of TMD has partially filled electronic states, leading to various electronic properties and instabilities. Filling these available states through intercalation

leads to an intricate interplay between the host electronic properties and the “guest’s” (intercalated cation) magnetism. Here, we explore the conditions under which particular symmetry (centrosymmetric or non-centrosymmetric) crystalize and map the magnetostructural phase diagram producing each magnetic phenomena. These magnetic properties are mainly anti-ferromagnetic for the present case of intercalating cobalt, and include altermagnetism at low cobalt densities, and spin density waves at higher occupations. We particularly focus on the effects of intercalating within NbSe<sub>2</sub> and TaSe<sub>2</sub>, as we have found them to be underexplored at the time of this study, while being canonical examples of exhibiting electronic instabilities.



SITE AND SYMMETRY DEFINED MAGNETIC GROUND STATES OF  
INTERCALATED DIVALENT TRANSITION METAL DISELENIDES

by

Héctor Cein Mandujano Canales

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Advisory Committee:  
Professor Efrain E. Rodriguez, Chair/Advisor  
Professor Johnpierre Paglieone  
Professor YuHuang Wang  
Professor Hong-Zhou Ye  
Professor Zhiwei Li

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2026

## Foreword

The following is a list of all the manuscripts I have contributed to during my period as a Ph.D. graduate student at the University of Maryland, College Park. Manuscripts marked with an asterisk belong to the work that comprises this thesis.

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## Dedication

To my love, G. G. S. S., my family, and those who shaped my character.

## Acknowledgments

This has been a long and fast-paced segment of my career, making it difficult to recall everyone who's been involved in shaping this work. I have been among many lab mates and unofficial advisors to whom I am very grateful, and although some interactions may seem trivial, their contributions to my progress are not negligible.

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I thank Timothy Diethrich and Matthew Leonard for showing me the ropes in the lab. From sealing tubes to changing oil, I wouldn't have gone far without doing maintenance in the lab. Furthermore, Matt convinced me to join the group. Were it not for him, I may have landed elsewhere. From the past members, I thank Tianyu Li for inspiring me to have independent ideas. He taught me not to wait to be given a task, but rather, to create a task to be done. Conversations with Tianyu served as fuel to the fire of my scientific curiosity. On a personal note, I was accompanied by Stephanie J. Hong during my Ph.D. journey in Rodriguez's group. I thank her for keeping the lab environment warm and making me feel accompanied through the hard times. Midway, Tyler Romig joined and made dreadful tasks an adventure each day. I am grateful to Captain Romig for serving as a social mediator in the group facilitation tasks.

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## List of Abbreviations

|       |                                        |
|-------|----------------------------------------|
| 2D    | two-dimensional                        |
| AFM   | antiferromagnetic                      |
| AM    | altermagnetic                          |
| CDW   | charge density wave                    |
| CIF   | crystallographic information file      |
| CVT   | chemical vapor transport               |
| DFT   | denisity functional theory             |
| DM    | Dzialoshinskii-Moriya                  |
| EDS   | energy dispersive X-ray spectroscopy   |
| FC    | field-cooled                           |
| FFM   | forced ferromagnet                     |
| FM    | ferromagnetic                          |
| MPMS  | magnetic properties measurement system |
| NPD   | neutron powder diffraction             |
| PDF   | pair distribution function             |
| PDOS  | partial density of states              |
| PPMS  | physical property measurement system   |
| RKKY  | Ruderman-Kittel-Kasuya-Yosida          |
| RMC   | reverse Monte Carlo                    |
| SDW   | spin density wave                      |
| $T_C$ | Curie temperature                      |
| $T_N$ | Neél temperature                       |
| TMD   | transition metal dichalcogenide        |
| vdW   | van der Waals                          |
| XPS   | X-ray photoelectron spectroscopy       |
| XRD   | X-ray diffraction                      |
| ZFC   | zero field-cooled                      |

## Chapter 1: Introduction

Transition metal dichalcogenides (TMDs) are a fertile system for emergent quantum phenomena, including superconductivity, charge density waves (CDWs), and complex magnetism .[2] Two of the most extensively studied materials of this family are 2H-NbSe<sub>2</sub> and 2H-TaSe<sub>2</sub>. This particular TMD alone exhibits both superconductivity and CDW phases at low temperatures and other topological phenomena due to its itinerant character.[3–5] Furthermore, due to the sufficiently wide van der Waals gap that these two-dimensional materials pose, it is possible to intercalate magnetically active ions, giving access to a great variety of magnetic properties.[6] Throughout this work, we focus on cobalt intercalated tantalum and niobium diselenide with different cobalt-to-host TMD ratios to characterize the magnetic properties associated with the structure of these low-dimensional systems.

### 1.1 Two-dimensional Transition metal dichalcogenides

As the name implies, a TMD unit is composed of a transition metal ( $M$ ) of groups 4 to 10 from the period table, and two chalcogens ( $Q$ ).[7] However, only those from groups 4 to 7 will commonly form layered systems, while those from groups 8 to 10 will not, such as pyrite (cubic FeS<sub>2</sub>).[8] Of those that form layered structures, the coordination environment can be either octahedral (point group  $O_h$ ) or trigonal prismatic (point group  $D_{3h}$ ), in which six chalcogens surround the transition metal (Figure 1.1(a and c)). The layered polymorphs are considered to be two-dimensional (2D) despite their monolayer limit being comprised of



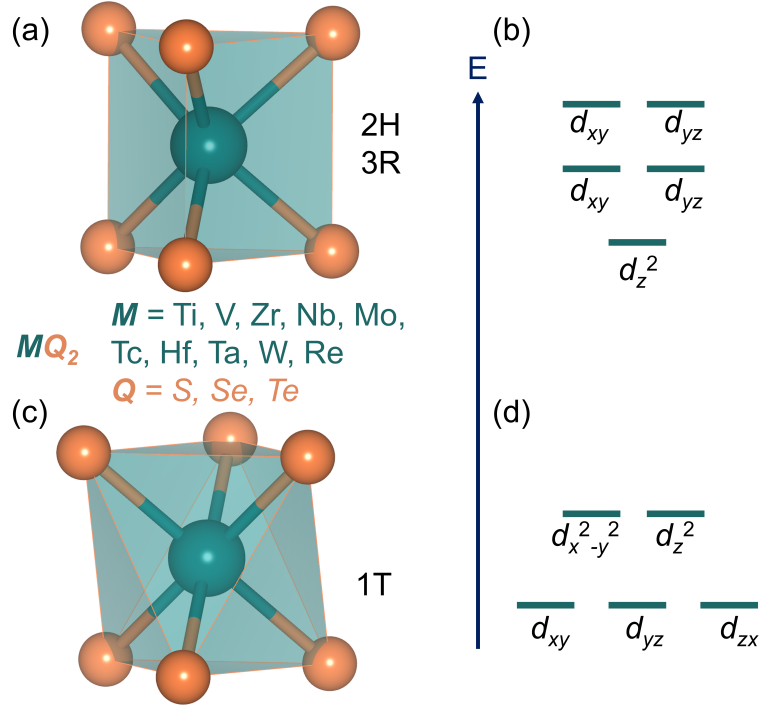


Figure 1.1: TMD unit local structure with its corresponding crystal field diagram.

three atomic layers along the vertical direction. As we later illustrate, these materials are considered to be van der Waals (vdW) compounds due to their weak layer-to-layer bonding forces and strong interlayer bonding. As already stated, this family of compounds can have two crystal field configurations. Crystallographically, these are denominated as 1T, 2H, and 3R, where the number indicates the number of layers that it takes to describe the unit cell and the letter to the crystal system; T is trigonal, H is hexagonal, and R is rhombohedral. An example of a TMD crystallizing in all these polymorphs is TaSe<sub>2</sub>.<sup>[9]</sup>

Depending on how their crystal field, their respective electronic structures will change due to the molecular orbital energies depicted in Figure 1.1 (b and d). This is why, in summary, MoS<sub>2</sub> can be conducting or semiconducting. The electronic properties of each TMD, of course, depend on the  $d$ -electron count along with the coordination environment. A molybdenum TMD, for example, will have a  $d^2$  low-spin configuration, for which the 2H will be in a trigonal prismatic environment and the electron will pair in the  $d_{z^2}$  orbital, and is

below the Fermi level, leading to a semiconducting phase. In contrast, in a 1T phase where the crystal field splitting is octahedral, the electrons partially occupy the triply degenerate  $d$ -orbitals, which generate a partially filled Fermi level, and produce its metallicity.[10–12] In this context, TMDs from group-V and VII will predictably be metallic, while the rest will be semiconducting.

In this thesis, we focus on the effects of intercalating low-dimensional 2H transition metal diselenide phases. It is henceforth useful to first describe the electronic properties of 2H-TaSe<sub>2</sub> and 2H-NbSe<sub>2</sub>.

### 1.1.1 Hexagonal Group-V Transition Metal Dichalcogenides

As stated in the previous section, when orbitals are partially filled, the system exhibits metallic conductivity. In the case of group-V TMDs, there is an  $d^1$  electron count, which indicates that the system will be metallic in either trigonal prismatic or octahedral coordination environment.

This group of TMDs in the 2H phase all exhibit similar electronic band structures. Therefore, they all undergo two electronic instabilities at low temperatures. First, a charge density wave (CDW) and then a superconducting phase upon cooling below room temperature.[13] An exception to these features in this group is 2H-NbS<sub>2</sub>, which does not exhibit a CDW transition under normal conditions.[14] The critical temperature of the superconducting phase does not have a clear trend, as the highest onset temperature is observed in NbSe<sub>2</sub> at 7.2 K, then NbS<sub>2</sub> at 5.7 K, TaS<sub>2</sub> at 0.8 K, and finally TaSe<sub>2</sub> at  $\sim 0.2$  K.[13–16] This phase is understood to be mediated by electron-phonon coupling, making them conventional superconductors.

Competing with the superconducting phase, the CDW has different modulation vectors and stabilizing temperatures.[17] CDW are generally linked to Peierls distortions, inducing

Table 1.1: Phase and Phenomena Summary of Group-V TMD

| Phase | TMD               | $T_c$ (K) | $T_{CDW}$ (K)                      | $q_{CDW}$                                         | ref.         |
|-------|-------------------|-----------|------------------------------------|---------------------------------------------------|--------------|
| 2H    | NbS <sub>2</sub>  | 5.7       | -                                  | -                                                 |              |
|       | TaS <sub>2</sub>  | 0.14      | 75                                 |                                                   | [16]         |
|       | NbSe <sub>2</sub> | 7.2       | 33                                 | (1/3,0,0)                                         | [5, 17]      |
|       | TaSe <sub>2</sub> | 0.8       | 122 <sup>i</sup> , 90 <sup>c</sup> | (0.323,0,0) <sup>i</sup> , (1/3,0,0) <sup>c</sup> | [16, 17, 19] |

nesting in the Fermi surface.[18] In this picture, the periodicity of the lattice changes, opening a gap in the zone boundary. This then leads to a gap formation in the electronic band structure. This is why the resistivity tends to increase at the transition temperature. The change in periodicity generates a lattice modulation resulting in a structural transition observable through satellite reflections indexed by a vector  $q_{CDW}$  in the diffraction pattern.

In the case of 2H-NbSe<sub>2</sub>, the CDW phase structure has been solved with single-crystal X-ray diffraction. The structure solution indicates that the Nb–Nb bonds and network shift from their ideal position to produce such modulations while the Se atoms remain minimally disturbed.[5, 20] This scenario is similar to that of 2H-TaSe<sub>2</sub>, although under pressure the Se atoms shift in-plane.[19] A key difference between these two analogs is that the Ta TMD has a stronger interacting incommensurate CDW transition at 122 K and then locks into a commensurate modulation at 90 K, thus making this phenomenon much more complex[21]. A probe sensitive to this phenomenon is magnetic susceptibility. As metallic systems, these compounds are not expected to exhibit a Curie paramagnetic behavior; however, the overall susceptibility can be deconvoluted into contributions from three parts: diamagnetism ( $\chi_D$ ), Pauli paramagnetism ( $\chi_P$ ), and Van Vleck paramagnetism ( $\chi_{VV}$ ).[22] The diamagnetic term comes from the core electrons of the compound, while the Van Vleck paramagnetic term comes from the coupling of occupied  $d$ -states. The only term sensitive to the CDW is  $\chi_P$  as it is proportional to the conduction electrons or density of states at the Fermi level ( $g(E_F)$ ).

The Pauli paramagnetic term can be expressed as:

$$\chi_P = \mu_0 \mu_B g(E_F) \quad (1.1)$$

where  $\mu_0$  is the vacuum magnetic permeability, and  $\mu_B$  is the Bohr magneton. Once the Fermi surface is gapped, the available states at the Fermi level change, thereby affecting this term and the overall susceptibility.

## 1.2 Intercalated Transition Metal Dichalcogenides

In light of all the rich electronic properties that hexagonal TMDs have, it is of great interest to explore their magnetism. A readily available way to do this is to exploit the vdW gap found between each hexagonal (1H) layer to introduce a magnetically active *3d*-metal. For the host TMDs discussed above, this must be done using metals from vanadium to zinc, which exhibit a wide range of magnetic properties.

Intercalated TMDs are generally described by the  $T_xMQ_2$  chemical formula, where  $T$  is an intercalated metal in between the  $MQ_2$  layers, where  $M$  is either Nb or Ta, and  $Q$  is S or Se. The rich phases emerging from metal-ion-intercalated TMDs can be attributed largely to the distinct structure and symmetry they adopt. When intercalated, these layered materials will form superlattices of  $2a_h \times 2a_h$  for  $x=1/4$  and a  $\sqrt{3}a_h \times \sqrt{3}a_h$  for  $x=1/3$  in dimension, where  $a_h$  corresponds to the *a*-axis lattice constant of the host TMD (see Figure 1.2 (a) and (b)).[23, 24] Such superlattices will have direct implications on the observed bulk electronic and magnetic structures, leading to a great diversity in physical properties. This structural difference is reflected in the space groups used to describe the crystal structure of each, as shown in Figure 1. When  $x < 1/3$ , the symmetry is centrosymmetric ( $P6_3/mmc$ ), while for  $x = 1/3$ , the symmetry is chiral and non-centrosymmetric ( $P6_322$ ).

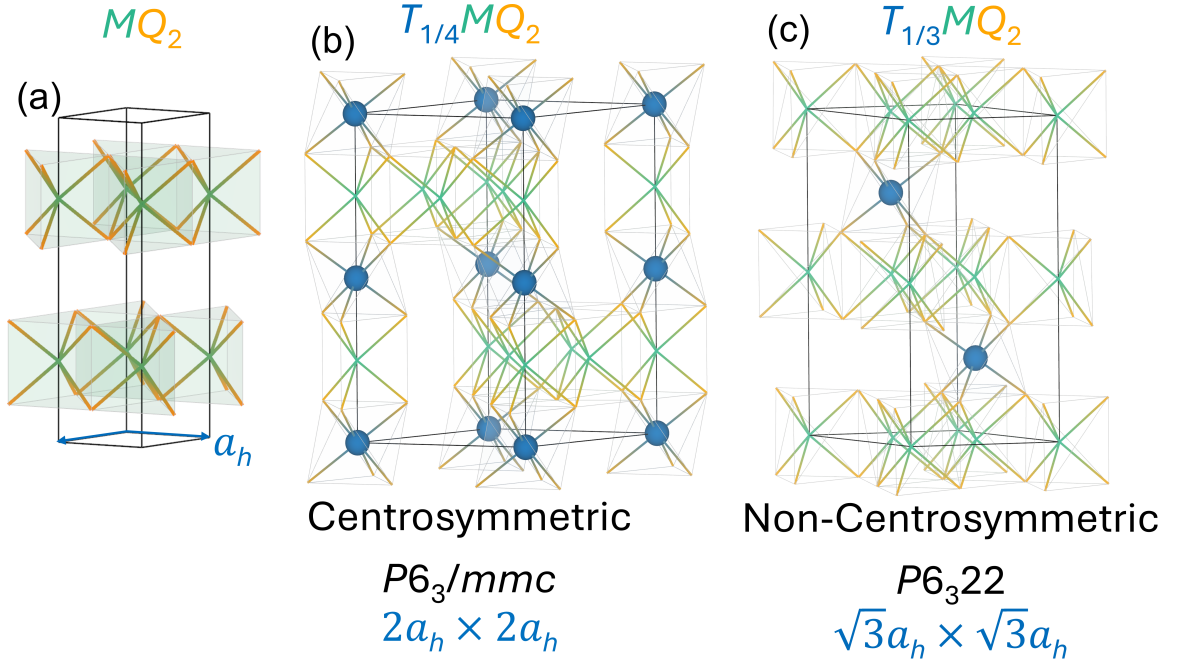


Figure 1.2: Structure of 2H-TMD (a) and intercalated  $x = 1/4$  (b) and  $x = 1/3$  (c) phases

In most cases, the intercalated cation will enter an octahedral coordination environment within the TMD interstitial site. However, this site can either be rigid or susceptible to undergoing a trigonal distortion. This distortion occurs when the intercalate can be trivalent, such as Cr and Fe[25]. Hence, the crystal field can either be octahedral with three degenerate  $t_{2g}$  and two  $e_g$  orbitals or split the  $t_{2g}$  orbitals into the doublet  $d_{xy}$  and  $d_{x^2-y^2}$ , and an elevated in energy  $d_{z^2}$  singlet while maintaining the degenerate  $e_g$ . [26] The splitting of these orbitals is highly correlated to the angle made by the intercalated metal with the neighboring chalcogen anion with respect to the  $c$ -axis. In an ideal octahedra, all angles are  $90^\circ$ , whereas in the distorted environment, the angle along the  $c$ -direction will be extended beyond  $90^\circ$ . This distortion can have multiple effects and may originate from various causes.

The more intercalant is inserted into the host, the more the vdW gap expands due to coulomb repulsion[27, 28]. This expansion is proportional to the magnetic ordering transition temperature to a certain extent. The more intercalant is present, the more octahedral

sites are occupied, and long-range magnetic ordering may be established. However, once the  $2a_h \times 2a_h$  intercalant lattice is established, in-plane nearest-neighbor avoidance due to charge repulsion becomes relevant if more intercalant is inserted. Thus, the  $\sqrt{3}a_h \times \sqrt{3}a_h$  motif arises, which will change the magnetic exchange pathways affecting the overall properties.[29]

### 1.2.1 Itinerant Magnetism: Host-Guest Interaction

Before diving into the survey of known intercalated TMDs and their properties, it is useful to understand the driving mechanisms behind the electronic and magnetic properties that these systems have in common. Since the host is metallic, meaning that magnetic moment is not necessarily produced by localized magnetic moments, but itinerant moments; the magnetism of these systems is generally explained by the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange mechanism. Furthermore, the symmetry, as already explained, can break inversion symmetry, which would change the long-range orbital interactions and also enable the asymmetric exchange interaction, allowing for spin canting.

As we already established, 2H-NbQ<sub>2</sub> and 2H-TsQ<sub>2</sub> have a partially filled  $d_{z^2}$  orbital with one electron. The intercalant electrons are thus donated to the host to fill the conduction band, making the host anionic and the intercalant cationic.[30, 31] This electron configuration is exemplified in Figure 1.3 for cobalt intercalated (Nb/Ta)Q<sub>2</sub>. In Figure 1.3(a), we see how the intercalated ions forming the  $2a_h \times 2a_h$  lattice form a continuous chain along the vertical axis. Aligned along this same axis is the half-filled  $nd_{z^2}$  orbital of the host. Figure 1.3(b) ten marks where the 3d electrons of the intercalated guest incorporate into the energy landscape to hybridize (Figure 1.3(c)). This hybridization of orbitals then allows for new states to form near the Fermi level, making the magnetic phenomena of these systems itinerant.[32] This property is evidenced by the observation of a magnetic moment smaller than what is

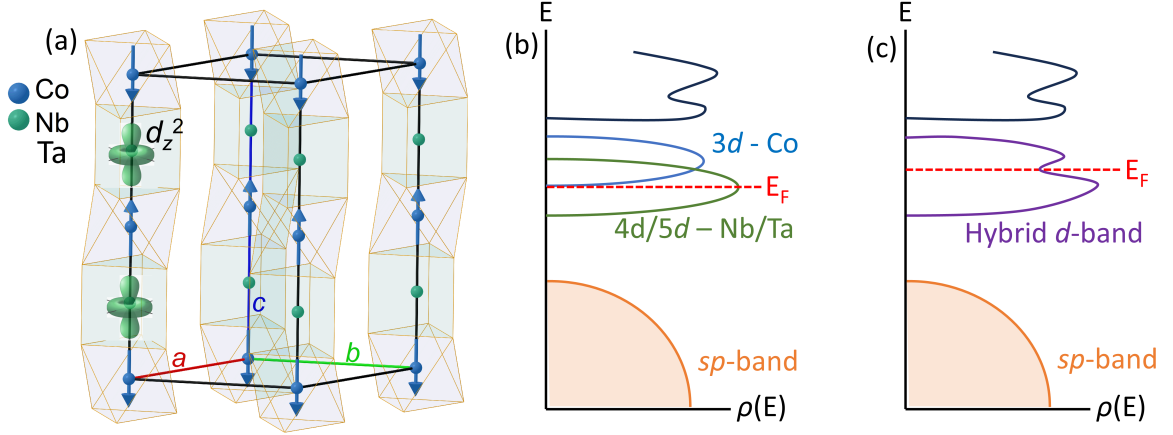


Figure 1.3: (a) Magnetically ordered  $\text{Co}_{1/4}\text{MSe}_2$  and (b) a schematic representation of its density of states leading to (c) an illustration of orbital hybridization.

expected of the intercalated  $3d$ -ion.

## RKKY Exchange Mechanism

As elucidated in the previous sections, the host is metallic and nonmagnetic, while the intercalant presents localized magnetization. The exchange coupling between magnetically active ions embedded in such a sea of electrons has been addressed by Ruderman, Kittel, Kasuya, and Yosida.[33–35] When the localized magnetization of the ion polarizes the surrounding electron gas, the next-nearest ion responds to this alignment, thereby establishing an indirect exchange interaction mediated by the itinerant electrons.[36] This mechanism is called RKKY interaction and has an oscillatory term that depends on the distance between local moments ( $r$ ), dictating ferromagnetic or antiferromagnetic interactions. Since most Fermi surfaces are rarely spherical, the expression for the spatial spin polarization can vary according to the dimensionality of the system. [37] When the system has interactions along all three dimensions, the exchange energy ( $J$ ) expression has the following proportionality:

$$J_{\text{RKKY}}(r) \propto \frac{\cos(2k_F r) - \sin(2k_F r)}{r^3} \quad (1.2)$$

where  $k_F$  is the Fermi wave vector in reciprocal space. In a two-dimensional system, this proportionality expression changes to:

$$J_{RKKY}(r) \propto J_0(k_F r)Y_0(k_F r) + J_1(k_F r)Y_1(k_F r) \quad (1.3)$$

where  $J_n$  and  $Y_n$  are Bessel functions of the first and second order.[37–39] Alternatively, Fischer and Klein[40], simplify both dimensional RKKY functions to be proportional to  $[\text{xcos}(x) - \sin(x)]/x^4$  in three dimensions and  $\sin(x)/x^2$  in two dimensions; here  $x = 2k_F r$ .

The dimensionality of these systems is often addressed qualitatively. Quantitative interpretation of the exchange interactions is rarely performed and is beyond the work of this thesis. Determining the dimensionality of the intercalated TMDs seems trivial, and one would assume to be intuitively treated as two-dimensional, as the host implies. However, the following crystal chemistry should be considered. When the 2D-host is intercalated at  $x = 1/3$ , the intercalant is staggered along the  $c$ -direction, increasing its distance along this axis. This filling in reduces the nearest-neighbor distance within the layer. Hence, the 2D character is preserved. When the intercalant is at  $x = 1/4$  ratio, the in-plane distances are larger, but establish the  $3d\text{-}nd_{z^2}$ -orbital hybridization. This interaction would almost seem vertical, one-dimensional, and embedded in the already established horizontal 2D network of the host, generating a complex higher-dimensional network. Evidently, the dimensionality will is not so straightforward and would require more careful analysis.

## Dzyaloshinskii-Moriya and Heisenberg exchange interactions

The distances between neighboring intercalated ions make the contributions from direct exchange mechanisms minimal and thus not a relevant interaction in this work. Bringing the in-layer distances of the intercalant closer, however, breaks spatial inversion symmetry as shown in Figure 1.2. Along with spin-orbit coupling, this asymmetry allows for spin canting



relative to each other and chiral magnetic ground states. This effect is explained by the Dzyaloshinskii-Moriya (DM) interaction.[41, 42] The energy between two DM interacting spins ( $S$ ) is expressed as:

$$H_{DMI} = - \sum_{i \neq j} \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j) \quad (1.4)$$

where  $D_{ij}$  is the DM vector. In this model, spin canting is favored from the cross product ( $S_i \times S_j$ ), which is a vector perpendicular to both  $S_i$  and  $S_j$ . Because of the negative sign, the energy is then minimized when  $D_{ij}$  is parallel to this cross product. For clarity, this can be seen more easily if we rewrite the expression in terms of the dot product:  $D_{ij} \cdot (S_i \times S_j) = |D_{ij}| |(S_i \times S_j)| \cos \theta$ , where in the parallel case, the angle between  $D_{ij}$  and  $(S_i \times S_j)$  is  $\theta = 0$  leads to minimum energy. For this to happen, the spins must rotate such that they are not parallel nor antiparallel to each other for  $(S_i \times S_j) = |S_i| |S_j| \sin \phi_{ij} \hat{n}$ , where  $\phi_{ij}$  is the angle between spins, and  $\hat{n}$  the normal vector. This rotation will then lead to a chirality and is proportional to the magnitude of  $D_{ij}$ .

The key concept of broken inversion symmetry comes from the fact that  $H_{DMI}$  does not remain invariant under the inversion operation:  $T$ . [42] Inversion means that for every atom, or in this case, spin with coordinates  $x, y, z$ , (or position  $r$ ), there must not be another with coordinates  $\bar{x}, \bar{y}, \bar{z}$  ( $-r$ ). Since  $S_{i,j}$  are axial vectors, they will remain unaffected under inversion. The vector  $D_{ij}$ , however, is a polar vector and must therefore change signs such that  $T(D_{ij}) = -D_{ij}$  when the path  $r_{ij}$  is inverted. We see that in a centrosymmetric environment, to obey the inversion requirement, the only way that the condition  $T(D_{ij}) = D_{ij}$  is met is when  $D_{ij} = 0$ . Hence, this term is absent when a TMD preserves the  $2a_h \times 2a_h$  centrosymmetric arrangement, but is non-zero when symmetry is broken due to the  $\sqrt{3}a_h \times \sqrt{3}a_h$  ordering. In this case, the DM vector is parallel to the  $c$ -axis and is composed of three individual vectors from the three  $r_{ij}$  paths taken from one octahedral site to the next nearest-neighbor from the upper layer (Figure 1.4). The out-of-plane vector then leads to the

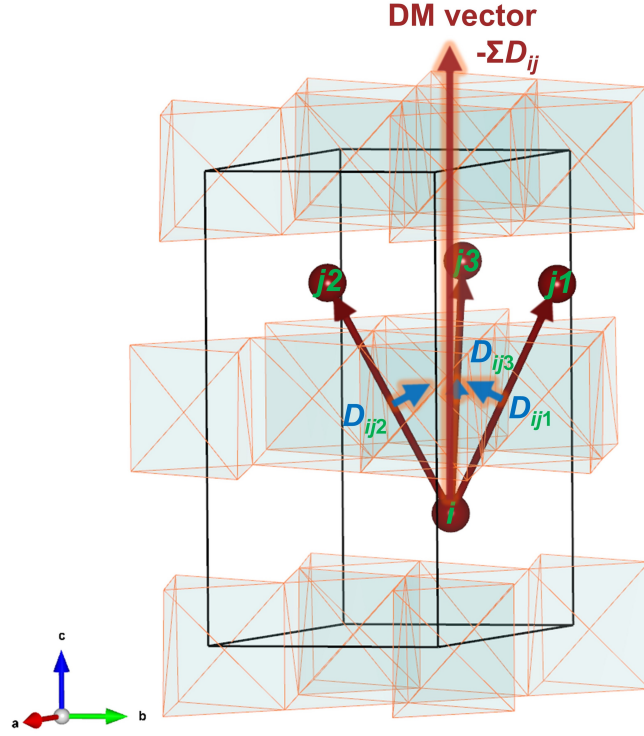


Figure 1.4: Dzyaloshinskii-Moriya vectors in  $x = 1/3$  intercalant.

preferred in-plane orientation of the spins.[25, 43]

The other competing interaction in the intercalated TMDs is the Heisenberg exchange interaction. This interaction comes from the antisymmetric wavefunction of electrons, which then induces a spin polarization. This interaction is expressed as:

$$H = - \sum_{i \neq j} \mathbf{J}_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (1.5)$$

where  $H$  is the Hamiltonian and  $J$  is the exchange constant. If the exchange  $J > 0$ , the interaction is ferromagnetic, and if  $J < 0$ , it is antiferromagnetic. This interaction will then generate parallel or antiparallel spin alignments. Competition between DM and Heisenberg interactions is then largely responsible for complex ground states such as spin spirals or waves.

Table 1.2: Existing intercalated TMDs and their magnetic transitions. Antiferromagnetic (**AFM**), ferromagnetic (**FM**), helimagnetic (HM), and spin-density wave (SDW) transition temperatures are in parentheses. Those marked with ‘\*’ are proposed altermagnets or helimagnets accordingly.

| Guest            | $x$ | NbS <sub>2</sub>           | NbSe <sub>2</sub>      | TaS <sub>2</sub>                  | TaSe <sub>2</sub>                          |
|------------------|-----|----------------------------|------------------------|-----------------------------------|--------------------------------------------|
| V <sup>3+</sup>  | 1/3 | <b>AFM</b> (50 K) [44, 45] | -                      | <b>AFM</b> (32 K) [44]            | -                                          |
|                  | 1/4 | -                          | -                      | -                                 | -                                          |
| Cr <sup>3+</sup> | 1/3 | HM (130 K)[46]             | <b>FM</b> (97 K)[47]   | HM (150 K)[46]                    | -                                          |
|                  | 1/4 | <b>AFM*</b> [48]           | <b>FM</b> (79 K)[49]   | <b>AFM</b> (145 K)[50]            | -                                          |
| Mn <sup>2+</sup> | 1/3 | HM (45 K)[48, 51]          | <b>FM</b> (22 K)[49]   | <b>FM</b> (70 K) [26]             | -                                          |
|                  | 1/4 | <b>FM</b> (104 K)[52]      | HM*(27 K)[53]          | <b>FM</b> /HM* (75 K) [48, 54]    | -                                          |
| Fe <sup>2+</sup> | 1/3 | <b>AFM</b> (45 K) [55]     | <b>AFM</b> (60 K)[56]  | <b>FM</b> (38 K)[57]              | -                                          |
|                  | 1/4 | <b>AFM*</b> (150 K)[58]    | <b>AFM</b> (130 K)[59] | <b>FM</b> (160 K)[60]             | <b>FM</b> / <b>AFM</b> (60/130 K) [61, 62] |
| Co <sup>2+</sup> | 1/3 | <b>AFM</b> (28 K)[63]      | SDW (36 K)[1]          | <b>AFM</b> (26-38) K[63, 64]      | -                                          |
|                  | 1/4 | -                          | <b>AFM*</b> (169 K)[1] | <b>AFM</b> / <b>FM</b> (26 K)[65] | <b>AFM*</b> (173 K)[66]                    |
| Ni <sup>2+</sup> | 1/3 | HM (84 K) [67]             | -                      | <b>AFM</b> (158 K)[67]            | -                                          |
|                  | 1/4 | -                          | -                      | -                                 | <b>FM</b> (58 K)[68]                       |

### 1.3 Properties of ordered $T_{1/4}MQ_2$ and $T_{1/3}MQ_2$

Now that we have discussed how a 3d-metal is incorporated in the metallic 2H- $MQ_2$  host to generate an itinerant-localized magnetic hybrid, we can review the known intercalant-TMD permutations compiled in Table 1.2 to the best of our knowledge. For simplicity, I divide these known compositions according to the magnetic structures and properties they entail. When centrosymmetric, the magnetic structures are predominantly collinear and can exhibit parallel (ferromagnetic) or antiparallel (antiferromagnetic) spin-spin alignment. When it is noncentrosymmetric, the structure has access to DM interactions, and this leads to misalignment of the spins from one to another that can form complex structures such as spin-spirals with long propagation vectors.

#### 1.3.1 Collinear magnetic order

##### Ferro- and antiferromagnetism

As seen in Table 1.2, out of the 29 known intercalant-host permutations, 9 are ferromagnetic. Out of these, 6 are centrosymmetric, and the AFM-FM interactions should come

from the metal ion to metal ion distance as dictated by the RKKY and Heisenberg exchange mechanisms. In this scenario, we can split the interaction between in-plane and out-of-plane. The resulting magnetic ground state is thus dictated by the interaction, ratio, and balance of these two interactions. In-plane distances within the triangular sublattice do not appreciably change across the first row of transition metals. The  $c$ -axis, however, generally contracts from left to right with Mn and Fe breaking the trend as they are much larger than the others.[26, 53] Thus, we can loosely see the trend where, at maximum separation from ions, we find preferred FM interactions as most of the known Mn-intercalated TMDs have FM ground states. Mn, however, might be exceptional in some cases, as it has shown a strong anisotropic character and interplay between AFM and FM states.[53] Focusing on TaS<sub>2</sub> we see that the largest unit cell (Mn) is FM. Shrinking the unit cell slightly, we see it is still FM for Fe, but going lower to Co or Cr, the ground state is then AFM. Similarly, the intercalant-intercalant distances can be modified by changing the host or intercalant ratio.

For those phases with intercalation amounts of  $x = 1/3$ , the magnetic order, although summing to a ferromagnetic preference, may actually be a helical structure with an extremely small propagation vector.[47, 51] This, in a neutron diffraction pattern, would seemingly appear as a regular ferromagnet but with a very small peak deviation with respect to the nuclear Bragg reflections. This deviation would be small enough that it may be overlooked by instrumental resolution. Hence, revisiting the ferromagnetically ordered  $T_xMQ_2$  for  $x = 1/3$  in search for novel magnetic textures would be of interest.

The case of Fe<sub>1/3±δ</sub>NbS<sub>2</sub> is an example where the DM interactions are unobserved, thus producing collinear AFM ground states.[55] However, due to disorder, this compound has competing stripe ( $x < 1/3$ ) and zigzag ( $x > 1/3$ ) AFM orderings. The stripe structure refers to FM aligning along a defined path, with the neighboring path being anti-aligned; the zigzag phase is a similar case, but interrupted lines stagger along the  $a$ -direction.

## Altermagnetism – the proposed new 3<sup>rd</sup> magnetic state

Conventional teachings on magnetism generally describe two primary collinear orders: FM and AFM. However, in recent years, altermagnetism (AM) has attracted significant attention as a new manifestation of time-reversal symmetry breaking in collinear AFM structures. In reciprocal space, FM order exhibits a net magnetization with spin-split electronic bands, whereas collinear AFMs display zero net magnetization and degenerate bands. AM combines features of both: it has no net magnetization yet exhibits non-degenerate spin-resolved electronic bands. In real space, FM and AFM states typically show isotropic spin-density distributions, while AM states develop chiral distributions due to their crystal field environment. Importantly, although collinear AFM structures are common, only certain crystal symmetries permit altermagnetism, as predicted by Smejkal et al.[69, 70]. Since this phenomenon arises from symmetry rather than spin-orbit coupling, it is also known as non-relativistic spin splitting.

In summary, AM must have the following three structural and symmetry requirements: (1) an even number of magnetic atoms per unit cell; (2) lack of inversion center between opposing spin sublattice sites; (3) each spin site must be connected by a rotation plus a translation.

Many of the intercalated TMDs have these symmetry requirements to be an AM. For the  $x = 1/3$  stoichiometries, this may be more obvious as the space group  $P6_322$  already indicates that the structure does not have a center of inversion. AM has been proposed to occur in the in-plane collinear AFM structure phase of  $V_{1/3}\text{NbS}_2$ [71] and  $\text{Ni}_{1/3}\text{MS}_2$ . [72] When the composition is at  $x = 1/4$ , the system is centrosymmetric, so there is no local inversion center between the spin-up and spin-down sublattices. However, this symmetry requirement is imposed between magnetic atoms from the opposite-spin sublattice. Figure 1.5 shows the A-type antiferromagnetic structure of  $\text{Co}_{1/4}\text{NbSe}_2$ , which is common in other

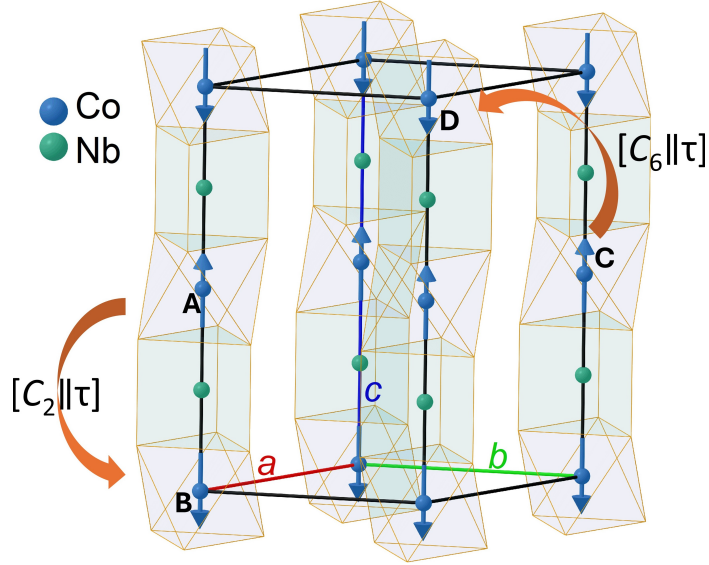


Figure 1.5: Antiferromagnetic structure of  $\text{Co}_{1/4}\text{NbSe}_2$  depicting the two-fold and six-fold rotation operations relating the spin sublattice

collinear AFM TMDs. In this structure, we find that going from spin site A to B or vice versa, the  $\text{CoSe}_6$  octahedra need to perform a  $C_2$  rotation plus a  $c/2$  translation. The spin sublattice is also connected by a  $C_6$  rotation plus a  $c/2$  and  $a$  translation to go from site C to D.[73, 74]

Having properties similar to a FM in reciprocal space with a net zero magnetization, it is not hard to imagine what AM may be used for. Especially when the electronic band of these materials may vary from insulators to metallic systems. In TMDs, this property is interesting to explore as the band splitting may occur near the Fermi level by which may be observable or have a response to electronic transport properties, yielding the anomalous Hall effect.[69, 75] AM have been proposed as alternatives to make more efficient magnetic random access memories (MRAM), memories through electronic tunnel junctions, and fast switching spintronic devices, to name a few.[73]

### 1.3.2 Non-collinear magnetic order

As we have already established, Heisenberg interactions are responsible for collinear ordering, whereas the DM allows for canting. Hence, all the non-collinearly ordered TMDs have the non-centrosymmetric nuclear structure with  $x = 1/3$ . The only possible exception to this may be  $\text{Mn}_{1/4}\text{MQ}_2$ , which would require detailed magnetic structural studies with neutrons.[52–54]

The distances between magnetic ions dictate the delicate balance of all exchange interactions. Any alteration in the paths, such as vacancies or additional occupied interstitial sites, may lead to different magnetic ground states. This, in fact, poses a synthetic challenge for consistency from one sample to another (see section 1.4). Wu and Park *et. al.* make an exemplary in-depth study of the collinear and non-collinear ground states that emerge from such local composition disorders.[55, 64, 76]

$\text{Co}_{1/3\pm\delta}\text{TaS}_2$  has a strong magnetic transition temperature and structure dependence. For intercalant ratios where  $x < 1/3$ , the system has two transitions, the first one at a higher Néel temperature ( $T_N = 38$  K) has a stripe AFM structure. At a lower temperature, the structure enters a triple- $q_m$  structure state. The sum of these vectors results in a tetrahedral-type structure in which one layer of triangular intercalated Co has moments pointing inwards and the next layer outwards. This second lower-temperature phase is absent for ratios where Co is  $x > 1/3$ . In this ratio, the structure is helical propagating along the  $a$ - or  $b$ -axis with moments in the  $ac$ - or  $bc$ -plane.[64, 76]

Another composition presenting multiple magnetic phases is  $\text{Cr}_{1/3}\text{NbS}_2$  and  $\text{Cr}_{1/3}\text{TaS}_2$ . However, in this compound, the magnetic phases are not stabilized by composition variations, but rather by the applied magnetic field. These Cr intercalated TMDs have a chiral helimagnet ground state with moments in-plane, which gradually evolves to a chiral soliton lattice under field, and eventually a forced ferromagnetic phase.[25, 43, 77, 78] Both Nb and

Ta analogs of these disulfides have very similar properties. Their phase diagrams suggest that the main difference between these two is the strength of the spin-orbit coupling. The Ta analog susceptible to stronger spin-orbit coupling (with a large  $Z$ ) has a higher  $T_C = 150$  K compared to Nb with  $T_C = 130$  K. Additionally, the metamagnetic transitions tend to the soliton lattice and force the ferromagnetic state are about an order of magnitude higher for Ta than Nb. Lastly, this stronger magnetic coupling can be inferred from the larger magnetic propagation vector  $q_m$  leading to a shorter helimagnetic wave pitch.

Predicting the magnetic properties is notably complicated. It mostly seems to depend on lattice size and electron count, as all the other effects, such as spin-orbit coupling, trigonal distortions, and intercalation proximity. All this is to say that the chemistry of these systems dictates the rich physics and varied magnetism. The contrasting example is the phase diagrams of non-collinear  $\text{Co}_{1/3}\text{TaS}_2$  compared to collinear  $\text{Fe}_{1/3}\text{NbS}_2$ . Both have access to DM interactions, but only one of these two systems has it readily displayed.

## 1.4 Crystal phase stability

Complications in obtaining a pure  $x = 1/4$  phase arise from competing factors and phases. In a chemical vapor transport crystal growth, the halogen sequesters the intercalant, reducing the ratio when  $\text{MX}_2$  is formed ( $X = \text{I}, \text{Br}, \text{or Cl}$ ).<sup>[57]</sup> A good starting point to choose the halogen transport agent is to look at the formation enthalpy of the competing salt and select whichever corresponds to the least favorable  $\text{MX}_2$  phase.

In a molten-salt flux, the salt used for the flux can also intercalate through an ion exchange, resulting in undesired inclusions. In solid-state synthesis, the intercalant can directly react to form the common binary  $TQ$ , or  $TQ_2$ , phases.<sup>[79]</sup> Furthermore, as we explained earlier, the  $1/4$  and  $1/3$  ratio phases do not have the same properties nor interactions. It is always possible to have  $1/3$  phase domains competing with the  $1/4$  phase, or vice versa.



Clearly, synthesizing the exact stoichiometry of intercalated TMDs is an open challenge, as accessing these phases can be a kinetic, thermodynamic, and stoichiometric battle.

As already stated in section 1.3.2, disorder in the intercalant leads to different exchange pathways consolidating distinct magnetic ground states. This disorder, although not easy to manipulate, can be exploited to access specific and even new phases with particular properties.[80] When the disorder is high enough, the long-range magnetic order can be disrupted, leading to a spin-glass state. This state of disorder may be desired as it presents phenomena called the exchange bias effect.[81] This effect is an observation of the hysteresis loop shifting its center from the origin. The direction of the shift is decided by the direction of the applied field in which the sample is cooled. Thus, this effect is a kind of memory induction effect and can be achieved in disordered TMDs.[82] Furthermore, disorder can also lead to anisotropic charge currents.[83, 84]

## 1.5 Objectives and Outline

The previous section of this chapter described the fundamentals and background that motivated this thesis. The work presented here is notably interdisciplinary at the interface between solid-state chemistry and condensed matter physics. In this thesis, we describe the synthesis, nuclear and magnetic structures, and the associated bulk physical properties of cobalt-intercalated transition-metal diselenides.

In Chapter 2, we detail the methods implemented to produce and perform the materials and measurements in this thesis. Methods used range from crystal structure solving and determination to temperature and field-dependent physical property measurements.

Chapter 3 presents the magnetic behavior and resulting transport properties of  $\text{TaSe}_2$  when intercalated by magnetically active cobalt cations. Acting as the layered host,  $\text{TaSe}_2$  is a transition metal dichalcogenide (TMD) that adopts the 2H-polytype. We find through

our single crystal and powder diffraction studies that we can prepare the stoichiometry  $\text{Co}_{1/4}\text{TaSe}_2$ , which crystallizes in the centrosymmetric space group  $P6_3/mmc$ . From magnetic susceptibility and x-ray photoelectron spectroscopy measurements, we find a transition consistent with antiferromagnetic order below the temperature  $T_N = 173$  K and  $\text{Co}^{2+}$  in the high-spin state. Neutron powder diffraction and specific heat measurements, however, point to a much smaller than anticipated ordered moment in this sample. From the neutron results, the magnetic structure can be described as an A-type antiferromagnet with an ordered moment size of  $1.35(11) \mu_B$  per Co cation. The direction of the moments are all long the c-axis, which is consistent with the magnetization and susceptibility studies showing this direction to be the easy axis. Interestingly, we find that a weak and subtle ferromagnetic component appears to exist along the *ab*-plane of the  $\text{Co}_{1/4}\text{TaSe}_2$  crystals. We place the results of this work in the context of other magnetic-ion intercalated TMDs, especially those of Ta and Nb.

We then look at  $\text{Co}_x\text{NbSe}_2$  in Chapter 4, where we find that the crystal symmetry and cobalt site occupation drive the formation of two distinct magnetic phases. At  $x = 1/4$ , the centrosymmetric structure ( $P6_3/mmc$ ) promotes Co-Co interactions leading to the formation of an A-type antiferromagnetic structure phase with a transition temperature of  $T_N^A = 169$  K. At  $x = 1/3$ , the non-centrosymmetric structure ( $P6_322$ ) induces a lower-temperature magnetic phase with  $T_N^S = 28$  K. We report the coexistence of both substructures within a superlattice, with a nuclear propagation vector of  $(1/3, 1/3, 0)$  relative to the host lattice. Single crystals of  $\text{Co}_{0.28}\text{NbSe}_2$  exhibit both magnetic transitions, with  $T_N^A$  corresponding to the  $x \sim 1/4$  phase and  $T_N^S$  corresponding to the  $x \sim 1/3$  phase. Magnetic susceptibility and specific heat measurements confirm these transitions, although only the high-temperature  $T_N^A$  phase significantly affects resistivity. We successfully isolate each phase in powder samples, while single crystals with an intercalation ratio of  $x = 0.28$  display the coexistence of both phases in a single sample. Using single-crystal neutron diffraction,

we solved the magnetic structure of the high-temperature centrosymmetric phase ( $T_N^A$ ), and neutron powder diffraction revealed the double- $q$  magnetic structure of the low-temperature noncentrosymmetric phase ( $T_N^S$ ).

In Chapter 5, we broaden the scope of the context of intercalated TMD to all group-V transition metal dichalcogenides (TMD) exhibiting a variety of magnetotransport phenomena arising from diverse nuclear and magnetic structures. We find that a comprehensive mapping of the magnetic, thermodynamic, and structural phases is lacking. Thus, we investigate  $\text{Co}_x\text{NbSe}_2$  for  $x = 0.29 - 0.36$ , using quenching and controlled cooling to tune structural order and map the resulting magnetic phases. We find that the altermagnetic states ( $x = 1/4$ ) and the spin density wave ( $x = 1/3$ ) remain robust under both synthesis conditions. In contrast, intermediate compositions give rise to spin-glass-like behavior or magnetic phase coexistence, producing two distinct phase diagrams depending on the thermal history of the synthesis process. To identify the underlying drivers of each ground state, we applied reverse Monte Carlo modeling to diffuse neutron scattering data, revealing the presence of local  $\sqrt{3}a_h \times \sqrt{3}a_h$  sublattice domains in all samples independently of the synthesis conditions. As the intercalant concentration decreases, the Co ions preferentially adopt the  $2a_h \times 2a_h$  sublattice, where dominant magnetic interactions emerge, stabilizing the altermagnetic phase. We evaluated these interactions through first-principles calculations for  $x = 1/4$  and  $1/3$ , where each domain interaction type is structurally and magnetically well defined. The resulting exchange reveals spin-glass and spin density wave phases driven by frustration from tighter intercalant arrangement and altermagnetism from  $2a_h \times 2a_h$  domains. Overall, we present local structure-driven magnetic phases across  $\text{Co}_x\text{NbSe}_2$  compositions, demonstrating how synthesis impacts local order of the Co atoms and thereby the overall magnetic properties.

Finally, Chapter 6 summarizes the results from this work and provides insight to future projects and research directions for intercalating group-V TMDs.

## Chapter 2: Methods

### 2.1 Synthetic Methods

This section describes the synthesis methods used to obtain polycrystalline  $T_xMSe_2$  and crystal growth parting from the obtained powders. We first describe the limitations and principles of solid-state synthesis, which are mainly diffusion-related. We then provide an overview of chemical vapor transport and how, with a heat gradient, a charge powder becomes a crystal.

#### 2.1.1 Solid-state synthesis

One of the most common approaches to obtaining new inorganic crystalline compounds is solid-state synthesis. This method usually implies mixing the elemental constituents in powder form, adding energy, commonly in the form of heat, and allowing the reaction to proceed through the energy landscape. The reaction is then allowed to reach the global minimum (generally considered the thermodynamic product) or a local minimum (accessible *via* kinetic pathways). This method is often regarded as a ‘black box’ as the obtained product is, in many cases, not what we desire due to competing and more thermodynamically stable phases. One of the greatest limiting factors inducing side phase formation is the diffusion rates. To achieve a successful solid-state synthesis of desired compounds is necessary to have reasonable diffusion rates or shorten the diffusion path lengths each species needs to travel to form the target composition.[85]

In the synthesis of the title compounds of this work, we deal with the diffusion of three elements to obtain  $M_xTQ_2$  where  $M$  is any 3d-transition metal,  $T$  is either Nb or Ta, and  $Q$  is S or Se. Fortunately, for the combination of  $T + 2Q$ , the desired stoichiometry is thermodynamically favored, although polymorphs do exist. This would only pose a challenge if we were to target a particular polymorph of the host TMD (see section 1.1). Once an intercalant is introduced, the structure becomes the desired 2H-type structure. The fact that the desired phase does not change means that diffusion is not an issue. Impurity phases such as any of the binary  $MQ$ ,  $M_2Q$ , and  $MQ_2$  still appear due to low diffusion rates in the solid-state. Multiple heating with grinding and mixing in between each heating is still required to help promote the phase formation. Despite multiple heating steps, these phases might be as stable as the desired TMD phase and will hardly dissociate to incorporate into the target phase. A simple way to discourage the formation of any of the undesired binary phases is to pre-react  $T + 2Q$  to make the host and use this as a precursor in  $xM + TQ_2$  reactions. However, diffusion is once again a barrier as the host lattice now has a reduced surface reaction area, and the 3d-metal will only diffuse through the vdW gap. This means that only in-plane metal-ion hopping has a low diffusion energy, which would take long periods of time to reach intercalation saturation as depicted in the top image structure of Figure 2.1. The greatest competing factors in intercalated TMDs are vacancies, domains, and disorder. As explained in section 1.2, the intercalant can be arranged in a  $2a_h \times 2a_h$  and/or  $\sqrt{3}a_h \times \sqrt{3}a_h$  superlattice. Furthermore, other sites can be occupied that are not necessarily the thermodynamic ground state. Figure 2.1 depicts the starting materials and heating profile used to make the compounds in this thesis. At the highest reaction temperature (900 °C), the intercalant has high mobility and diffusion proceeds inside the interstitial site. When cooling, however, due to this mobility, if the cooling rate is fast or the sample is quenched, disorder can be induced by kinetically trapping or ‘freezing’ the high-mobility state of the intercalant into a random site. If the heating profile is slow, the thermodynamically preferred

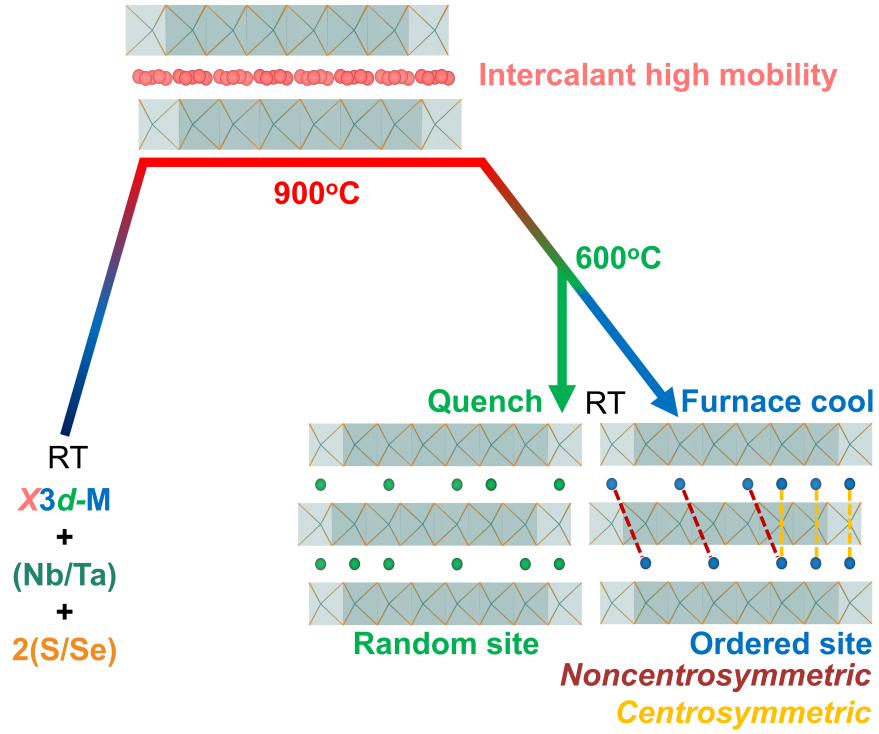


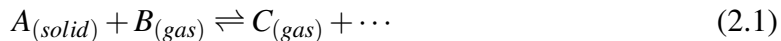
Figure 2.1: Solid-state synthesis heating profile diagram with quenching cooling profile promoting intercalation disorder and control-cooled (furnace-cooled) profile with preferred sublattice site arrangements.

state is obtained. In chapter 5, we address the synthetic challenges and structural details of obtaining these intercalated TMDs under different cooling profiles.

The next barrier we encounter is to grow bigger particles or sizable single-crystals. This step is limited by the nucleation.[86] In this scenario, a molten-salt flux can be used to increase the dynamics and promote crystal growth. A common molten-salt flux is KCl:NaCl mixture, which has a eutectic point at 660 °C. This melting point is reasonably low to promote single-crystal growth of this family of materials.[87] This method is not reported in this thesis; however, it was attempted but not continued due to the smaller crystal size in comparison to those obtained by CVT.

### 2.1.2 Chemical vapor transport (CVT)

A CVT reaction is a reversible reaction in which the charge powder ( $A$ ) reacts with a transport gas agent ( $B$ ) to form a vapor, to form a vapor complex product ( $C$ ) or products.[88] This reaction is then reversed at a different location within the environment. This reaction equilibrium is generally expressed as:



In this work, this reaction takes place in a closed vacuum-sealed tube with a known length and a known amount of transport agent ( $B$ ). The transport agent is typically a halogen molecule or halogen-based compound, such as molecular iodine ( $I_2$ ) or  $NH_4Cl$ . We typically choose to use transport agents that are solid at room temperature but readily evaporate at a relatively low temperature. For example, the boiling point of  $I_2$  is around 184 °C. This makes it easy to quantify and handle during preparation.

The sealed tube containing a set amount of charge powder and transport agent is then set on a tube furnace that has a heat gradient. The goal is for one side of the reaction tube to be at a higher temperature than the other, as depicted in Figure 2.2. One side is therefore set at  $T_{hot}$  and the opposite end at temperature  $T_{cold}$ , where the heat gradient  $\Delta T$  should be the difference between the two ( $T_{hot} - T_{cold}$ ). This heat gradient, along with the ideal gas law, will then promote gas motion as the system attempts to achieve equilibrium. In this sense, Le Chatelier’s principle can be used to get a general intuition of the reaction. Because there is a temperature dependence on the equilibrium constant, the driving forces behind a CVT are the Gibbs free energy ( $\Delta G$ ) and enthalpy ( $\Delta H$ ). [89] With the use of the van’t Hoff equation, we can determine the direction of the reaction. For an endothermic reaction,  $\Delta H > 0$ , the equilibrium constant increases as the temperature increases, in which case,

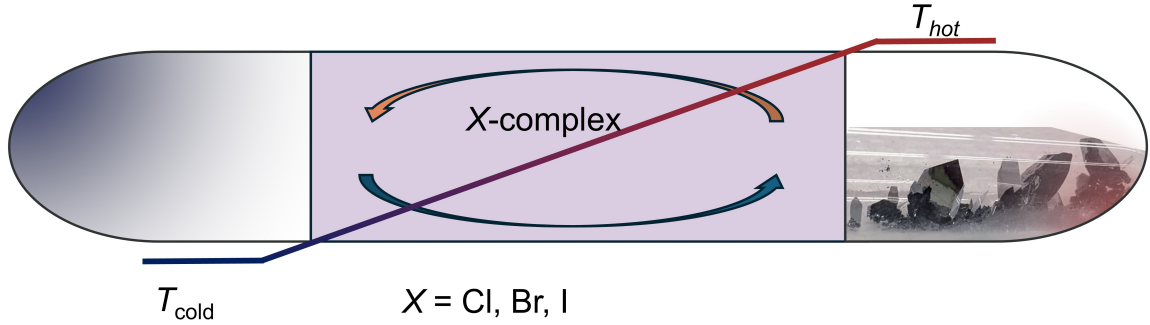


Figure 2.2: Chemical vapor transport diagram. Vacuum sealed ampoule tube with temperature gradient (left:  $T_{cold}$ , and right:  $T_{hot}$ ) depicting how a transport agent of any halogen forms a complex with the charge powder and deposits on the crystallization end.

the charge powder will be transported from the hot end to the cold end. In an exothermic reaction,  $\Delta H < 0$ , the equilibrium constant decreases as temperature increases, changing the reaction flow from cold to hot. In summary:

$$\text{Endothermic} : T_{cold} \leftarrow T_{hot} \quad (2.2)$$

$$\text{Exothermic} : T_{cold} \rightarrow T_{hot} \quad (2.3)$$

We have so far described the working principles of a CVT reaction. These principles, if thermodynamic data is available on the formation enthalpies, the ideal reaction temperatures, and hence the heat gradient may be calculated; this is rarely done. Furthermore, we have yet to describe what determines the rate at which a crystal grows and the amount of transport agent required. Both of these two concepts are linked by Schäfer's transport equation that indicates the amount of transport rate ( $n_A$ ) as[88]:

$$n_A = \frac{i \cdot D \cdot c \cdot t \cdot \Delta P}{j \cdot L \cdot P_{total} \cdot R \cdot T} \quad (2.4)$$

where  $i$  and  $j$  are stoichiometric factors,  $D$  is the diffusion coefficient,  $c$  is the cross-sectional area of the tube,  $L$  is the tube length,  $t$  is the duration of the growth,  $P$  is the respective



total and partial pressures at each heating  $T$  (for  $T_{hot}$  and  $T_{cold}$ ), and  $R$  is the universal gas constant. Notably, this equation has many variables, and we can practically manipulate all of them directly or indirectly. The most important thing to notice is that the transport rate is inversely proportional to the total pressure. This pressure will be dominated by the transport agent; hence, the moles of select halogens can be calculated using the ideal gas law. This is assuming we know the average temperature ( $\frac{T_{hot}-T_{cold}}{2}$ ), as well as the internal volume of the sealed tube.

For the present work, the general tube lengths used have ranged between 12 cm and 15 cm, with temperature gradients of  $\sim 70$  °C. This allowed us to try various halogen concentrations ranging from 2 mg/mL to 4 mg/mL. In our experience, increasing the temperature in the hot end while reducing the amount of transport agent will make the crystal grow on the cold end of the tube with a thick  $c$ -axis. Doing the opposite will, in general, produce thinner crystals, although wider area and much cleaner surface with fewer stacking defects.

CVT has long been used to grow layered materials, and TMDs single-crystals readily grow with this method[90, 91]. However, as we will see in Chapter 4, the CVT reaction (2.1) is not always reversible for certain transport agents. When the reaction is not reversible, looking at formation enthalpies of probable competing phases formed with the halide is a good starting point. Some of the most common transition metal salts are tabulated in the CRC Handbook of Chemistry and Physics.[92] Some of the relevant formation enthalpy values are given in Table 2.1. Selecting a transport agent that can potentially produce a less stable metal halide is ideal to ensure the reversibility of the CVT transport reaction. The more negative the enthalpy (exothermic) is, the more stable the product is. These values then provide another useful degree of freedom we can use to tune the reaction vector and thermodynamic landscape.

Table 2.1: Standard enthalpy of formation ( $\Delta H_f^\circ$ ) for selected metal halides.

| Compound           | State | $\Delta H_f^\circ$ (kJ/mol) | Trend                                                                           |
|--------------------|-------|-----------------------------|---------------------------------------------------------------------------------|
| CoF <sub>2</sub>   | s     | -672.0                      | Decreasing stability as halogen electronegativity and lattice energy decreases. |
| CoCl <sub>2</sub>  | s     | -312.5                      |                                                                                 |
| CoBr <sub>2</sub>  | s     | -221.3                      |                                                                                 |
| CoI <sub>2</sub>   | s     | -89.5                       |                                                                                 |
| MnCl <sub>2</sub>  | s     | -481.3                      | High stability of divalent state.                                               |
| NbCl <sub>5</sub>  | s     | -797.5                      | Stability increases with higher oxidation state in Niobium chlorides.           |
| NbCl <sub>4</sub>  | s     | -705.4                      |                                                                                 |
| NbCl <sub>3</sub>  | s     | -554.4                      |                                                                                 |
| NH <sub>4</sub> Cl | s     | -314.6                      |                                                                                 |

## 2.2 Diffraction

To fully comprehend the properties of matter, it is crucial to understand the atomic structural arrangement. The periodic arrangement of atoms or motifs enables the interpretation of causality regarding anisotropic properties and phase transitions. To this end, we employ diffraction and crystallography to determine crystal structures. This section provides an overview of the crystallographic methods used to describe nuclear and magnetic structures.

### 2.2.1 Crystallography

Crystalline solids can be defined as the periodic arrangement of atoms, motifs, or any arbitrary basis that remains invariant after translation. Such periodic arrangement can be represented mathematically by a *lattice*:  $\mathbf{l} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ . Where  $\mathbf{l}$  is a lattice point with respect to an arbitrary origin,  $n$  is an integer, and  $\mathbf{a}$  are non-coplanar lattice vectors.

Depending on whether a crystal is described by a single lattice point, a primitive unit cell can be constructed using such vectors. If the shape is too complicated, conventional, larger unit cells are preferred. The volume of the unit cell is then described as  $v = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$ , where  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  are the lattice parameters. These parameters can be used to classify the

crystal symmetry among the seven crystal systems and fourteen Bravais lattices depending on their value and the angles between them ( $\alpha$ ,  $\beta$ , and  $\gamma$ ). For example, a crystal is cubic if  $\mathbf{a} = \mathbf{b} = \mathbf{c}$ , and  $\alpha = \beta = \gamma = 90^\circ$ . Since many TMDs crystallize in a hexagonal system, a hexagonal lattice is delimited by  $\mathbf{a} = \mathbf{b} \neq \mathbf{c}$ , and  $\alpha = \beta = 90^\circ$ , while  $\gamma = 120^\circ$ .

Due to the periodic arrangement of crystals, the atoms will arrange in planes that are ideally equally spaced by a distance  $d$ . Hence, any electromagnetic wave with a wavelength ( $\lambda$ ) of the order of this spacing will constructively or destructively interact according to Bragg's Law:

$$n\lambda = 2d_{hkl}\sin(\theta). \quad (2.5)$$

Here,  $n$  is an integer,  $h$ ,  $k$ , and  $l$  denote the Miller indices, and  $\theta$  the scattering angle.

By using a diffractometer, we can then determine this inter-planar  $d$ -spacing and determine the unit cell with:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}, \quad (2.6)$$

which applies to orthorhombic, tetragonal, and cubic unit cells. For hexagonal unit cells:

$$\frac{1}{d_{hkl}^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}. \quad (2.7)$$

A close inspection of the position and extinctions of the diffraction spots can then be used to determine the space group, a set of symmetry operations that fully describe the crystal. A description of elements of symmetry can be found in the crystallography literature; I will not dwell on the description of each operation.[93] In summary these are: rotation axis (1, 2, 3, 4), mirror plane ( $m$ ), identity (1), center of inversion/symmetry ( $\bar{1}$ ), and improper rotation axis also known as rotatory inversion axis or roto-inversion ( $\bar{1}$ ,  $\bar{2}$ ,  $\bar{3}$ , and  $\bar{4}$ ). Notation in parentheses is the Hermann-Mauguin symbol convention. The reflection conditions and rules to determine or select the cell centering, as well as the presence of symmetry

operations, have been well established, documented, and tabulated in the International Tables for Crystallography.[94]

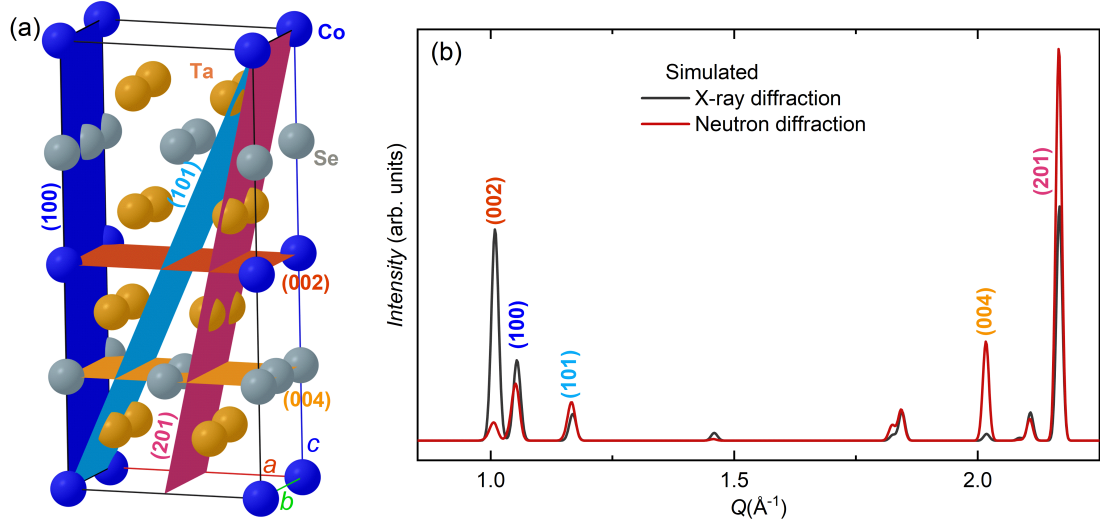


Figure 2.3: (a) Crystal structure and diffraction planes of  $\text{Co}_{1/4}\text{TaSe}_2$  along with (b) simulated X-ray and neutron powder diffraction.

One of the most valuable pieces of information that diffraction yields is the atomic positions and coordinates. Such information is contained in the intensity of the observed Bragg reflections. The intensity will depend on the incident source, which we will discuss in the next section. The Bragg reflections are indexed by the Miller indices  $h$ ,  $k$ , and  $l$ , which are used to specify the orientation of the planes in reciprocal space by their reciprocals. For example, in Figure 2.3(a) we have hexagonal  $\text{Co}_{1/4}\text{TaSe}_2$  with (002), (100), (101), (004), and (201) Miller planes. These reflections will provide information about what is inside the unit cell. For example, the (002) and (004) reflections will be scattered from the plane at half and quarter of the unit cell along the  $c$ -direction. The (101) and (102) diffract of what is perpendicular to the  $b$ -axis, and so on. The case of (002) and (100) provides direct information on the unit cell dimensions.

The relationship between the observed momentum or  $Q$ -space (as plotted in Figure

2.3(b)),  $d$ -space, and the diffracting angle is given by the Laue condition, such that:

$$Q = 4\pi \frac{\sin(\theta)}{\lambda} = \frac{2\pi}{d}. \quad (2.8)$$

This plotting convention is convenient as it is wavelength-independent and allows for the overplotting of different diffraction sources.

Notably, in Figure 2.3(b), the peak intensities vary from one to another, and what is more, they are different depending on the source. This leads us to the final concept that is yet to be introduced for this section: the structure factor. Before getting into that, we must define the reciprocal lattice. The set of all reciprocal lattice vectors can be generated by  $\mathbf{G} = ha^* + kb^* + lc^*$ , where  $a_i^*$ ,  $b_i^*$ , and  $c_i^*$  are the reciprocal lattice basis vectors. We will need this as the integrated intensity of an elastic diffraction peak is directly proportional to structure factor squared ( $I_{hkl} \propto |F_{hkl}|^2$ ). The structure factor is defined as:

$$F_{hkl} = \sum_r \bar{b}_r e^{i\mathbf{G} \cdot \mathbf{r}}, \quad (2.9)$$

where for neutron diffraction,  $\bar{b}_r$  is the bound coherent scattering length of element  $\mathbf{r}$ . For X-rays, this term would represent the form factor of the electron density, typically written as  $f(Q)$ . For  $\mathbf{r} = x_r a + y_r b + z_r c$ :

$$F_{hkl} = \sum_r \bar{b}_r e^{2\pi i(hx_r + ky_r + lz_r)}, \quad (2.10)$$

One could then apply this equation to the example in Figure 2.3 to determine the relative intensities for each  $(hkl)$  reflection. In practice, however, the intensity depends on many other factors, such as scale, peak-shape parameters, absorption corrections, and others.

The non-powder-averaged structure factor from 2.9, is also written as:

$$S(Q) = \sum_{i,j} b_i b_j e^{iQ \cdot (r_i - r_j)} e^{-W_d}, \quad (2.11)$$

where  $S(Q)$  is used interchangeably with structure factor, but is most commonly used when referring to total scattering. The first exponent of this expression describes the diffraction between the scattering centers found between  $r_i$  and  $r_j$ . The second exponent depends on the thermal displacement parameter given by the Debye-Waller term  $W_d$ , and is the reason why a scattering experiment benefits from low temperatures, as this would minimize thermal oscillations.

### 2.2.2 Diffraction Sources

As long as the radiation wave is in the order of atomic spacing distances, almost any source may be employed to obtain information about crystalline matter. Such a requirement comes from the diffraction condition established by Bragg's Law. As expressed in equation 2.9, X-rays are scattered from the electron density cloud of the crystal's atoms, while neutrons interact with the nucleus of the atom. Unlike X-rays (where the scattering interaction decreases at high- $Q$ ), neutron scattering lengths do not depend on the scattering vector, but depend on the type of nucleus and specific isotope. This property of each source interaction with a crystal makes both sources complementary. X-rays have a strong interaction with matter, and intensity is proportional to the atomic number ( $Z$ ), making it ideal to solve a structure but difficult to distinguish between elements with similar electron count. Neutrons interact much less, but since the scattering length does not have a linear dependence on  $Z$ , it is often used to determine the occupation ratios of neighboring atoms in the periodic table.

To solve crystal structures, single-crystal X-ray diffraction is regarded as essential. In a single crystal diffraction experiment, we aim to collect the position and intensities of

Bragg reflections. The accessible reflections are determined by the instrument's reach in  $Q$ . With a 2D detector, it is possible to change the accessible  $Q$ -range by either changing the distance of the detector from the sample (to modify the diffraction angle) or by shifting the diffraction peaks by changing the wavelength ( $\lambda$ ). Thus, using a short wavelength such as a molybdenum X-ray source ( $\lambda_{\text{Mo}} \approx 0.71 \text{ \AA}$ ) is useful to access a higher  $Q$ -space.

In many cases, obtaining a single crystal is difficult, whereas a polycrystalline powder is readily available. In these situations, due to the random orientations of the crystallites in a powder, the diffraction pattern in a two-dimensional detector will appear as rings from all equivalent  $d$ -spaced Bragg reflections. Integrating these intensities from a 2D detector or scanning the angle with a line detector, then gives a one-dimensional profile plot of the diffraction pattern. The pattern can then be fit to a known crystallographic model using the Rietveld method to obtain detailed information about the sample in question.

Powder X-ray diffraction experiments are most commonly performed using a copper source ( $\lambda_{\text{Cu}} \approx 1.54 \text{ \AA}$ ) in a Bragg-Brentano setup. This geometry consists of rotating a flattened powder sample while the X-ray source and detector scan the angle in tandem by moving from wide to narrow (meeting at the middle). This scan will typically range from  $\sim 3^\circ$  to  $\sim 140^\circ$  in  $2\theta$  depending on the instrument specifications.

On special occasions, either a shorter wavelength (or higher energy) or a brighter source is needed. Synchrotron sources providing user accessibility, such as the Advanced Photon Source at Argonne National Laboratory, are used. Such facilities have a variety of instruments with distinct sample environments, detectors, monochromators, and other specifications depending on the specialty of each beamline. Synchrotrons produce X-rays as a byproduct of accelerating electrons in a ring. By means of optics and a crystal monochromator, it is possible to select a specific wavelength from the X-ray energy distribution provided by the source. In a powder experiment, the instrument setup in a synchrotron will typically be a Debye-Scherrer configuration. In this geometry, the incident beam does not move

while the sample rotates in a capillary tube. The detector is then positioned depending on the  $Q$ -range sought. Reasons to use a synchrotron include specific sample environmental conditions, in-situ experiments with fast dynamics, a need for high resolution, a small sample, or even to change the X-ray absorption of the incident sample.

X-rays are electromagnetic radiation, and as we already pointed out, they are a complementary probe to neutron scattering, which is a subatomic particle and wave simultaneously. As such, producing a neutron beam is more complex, and its flux is much lower. Neutrons are emitted at reactors from the nuclear fuel, such as Uranium-235. Such sources are constantly producing neutrons and are thus called continuous wavelength (CW) sources. Alternatively, neutrons can be produced by colliding accelerated protons with a heavy metal (such as Hg) target in pulses. These facilities are called spallation neutron sources and are a time of flight (t.o.f.) source. Due to the pulsing nature of the neutron production, the time of production of a neutron pulse is known, as well as when it is received at the detector after scattering from the sample. The time scales of these events are in microseconds ( $\mu\text{S}$ ), and once scattered, this time axis can be converted to  $d$ -spacing by the following expression:

$$t.o.f. = \text{DIF}(C) \cdot d + \text{DIF}(A) \cdot d^2 + \frac{\text{DIF}(B)}{d} + \text{zero}, \quad (2.12)$$

where DIF A, B, and C, and *zero* are instrument parameters. Isolating  $d$  we can then convert to  $Q$  from 2.8.

In the work presented in this thesis, we rely on both X-ray and neutron diffraction. Instruments such as POWDER (HB-2A), DEMAND (HB-3A), and POWGEN (BL-11A) were used, located in the High Flux Isotope Reactor (HFIR) and the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory.



### 2.2.3 Rietveld method

The peak position and shape of the collected diffraction pattern contain information about the crystal structure. Provided with a known crystal structure, it is possible to match the diffraction pattern to such a model.[95] The Rietveld method is the standard least squares fitting method to model the full profile expressed as:

$$Y^{\text{obs}} = \sum_{i=1}^n b_i + K \sum_{j=1}^m y_j(x_j) I_j, \quad (2.13)$$

where  $b_i$  is the background at the  $i^{\text{th}}$  data point,  $K$  is the scale phase factor,  $m$  is the number of Bragg reflections contributing to the intensity of  $i^{\text{th}}$  data point,  $y_j(x_j)$  is the peak shape, and  $I_j$  is the integrated intensity of the  $j^{\text{th}}$  Bragg reflection. The integrated intensity is proportional to the structure factor (2.9) squared and other peak shape terms taking the form:

$$I_{hkl} = p_{hkl} \times L_{\theta} \times P_{\theta} \times A_{\theta} \times T_{hkl} \times E_{hkl} \times |F_{hkl}|^2, \quad (2.14)$$

where  $p_{hkl}$  is the multiplicity factor,  $L_{\theta}$  is a Lorentz multiplier,  $P_{\theta}$  indicates the polarization factor,  $A_{\theta}$  corrects for absorption,  $T_{hkl}$  scales the preferred orientation, and  $E_{hkl}$  accounts for extinctions. The goal of the Rietveld method is then to minimize the full profile modeling ( $\Phi$ ), which is the square of the observed intensity minus the calculated, written as the function:

$$\Phi = \sum_{i=1}^n (Y^{\text{obs}} - Y^{\text{calc}})^2. \quad (2.15)$$

Notably, minimizing this function will produce detailed information of the powder sample, where for our purposes, the most relevant information is the atomic position and occupancies. The metric we generally use to determine the quality of the refinement is given

Table 2.2: Common Rietveld refinement parameters and peak profile contribution

|            | Peak position                                                | Peak shape                                             | Peak intensity                                                                                                        |
|------------|--------------------------------------------------------------|--------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|
| Instrument | Zero                                                         | Gaussian ( $u, v, w$ ),<br>Lorentian ( $A, B, C$ )     | Scale factor                                                                                                          |
| Sample     | Unit cell parameters<br>( $a, b, c, \alpha, \beta, \gamma$ ) | Microstrain, surface<br>roughness,<br>crystallite size | Preferred orientation,<br>occupancies, atomic<br>coordinates ( $x, y, z$ ), atomic<br>displacement parameters ( $U$ ) |

by the  $R$ -factors or residuals. One of the most common residuals is the weighted profile residual given by:

$$R_{wp} = \sqrt{\frac{\sum_{i=1}^n w_i (Y^{\text{obs}} - Y^{\text{calc}})^2}{\sum_i w_i (Y^{\text{obs}})^2}}, \quad (2.16)$$

with the values given in percentage. The lower the percentage, the better the refinement is considered to be.

When performing a Rietveld refinement, peak position, shape, and intensity are generally considered to tell first hand whether a phase is fitting to the observed data or not. Table 2.2 has a compilation of parameters we generally refine depending on what needs to be improved in the model.

#### 2.2.4 Neutron diffraction from magnetic structures

Neutrons have a magnetic moment due to them having a spin of 1/2. Thus, they can interact and diffract off of an atom's local magnetic moment. The neutron diffraction is proportional to the sum of the nuclear structure factor squared plus the magnetic structure factor squared ( $|F_N|^2 + |F_M|^2$ ), where the nuclear structure factor,  $|F_N|$  as given by 2.11 can be written as:

$$F_N(Q) = \sum_r b_r e^{iQ \cdot r} e^{-W_d} \quad (2.17)$$

and the magnetic part as:

$$F_M(Q) = p \sum_r \mu_r f_r(Q) e^{iQ \cdot r} e^{-W_d} \quad (2.18)$$

where  $p = \gamma r_0 / 2\mu_B$  ( $\gamma$  is a constant equal to 1.913, and  $r_0$  the classical radius of the electron),  $f_r(Q)$  is the magnetic form factor, and  $\mu_r$  the magnetic moment on site  $r$ . The magnetic component will only diffract off of spin perpendicular to  $\hat{Q}$  and is given by:

$$F_{M\perp} = \hat{Q} \times \{F_M \times \hat{Q}\}, \quad (2.19)$$

squaring to get  $|F_M|^2$ :

$$F_{M\perp} \cdot F_{M\perp} = (\hat{Q} \times \{F_M \times \hat{Q}\}) \cdot (\hat{Q} \times \{F_M \times \hat{Q}\}), \quad (2.20)$$

which we can then follow through using identities  $F_{M\perp} = M - (M \cdot \hat{Q})\hat{Q}$ ,  $M \cdot \hat{Q} = |M||\hat{Q}|\cos(\theta)$ , and  $\sin^2(\theta) = 1 - \cos^2(\theta)$  we arrive at the simplified expression:

$$I_M(Q) \propto M^2 \sin^2(\theta). \quad (2.21)$$

This  $\sin^2(\theta)$  term, known as the orientation factor, is useful for obtaining an intuitive sense of the magnetic moment direction. In the case where  $M \parallel \mathbf{Q}$ ,  $\theta = 0^\circ$ , then  $\sin^2(0^\circ) = 0$ , making the magnetic moment invisible; if  $M \perp \mathbf{Q}$ , then  $\theta = 90^\circ$ , and  $\sin^2(90^\circ) = 1$ , maximizing the observed intensity.

For example, in the simplest case of a commensurate magnetic structure, where the magnetic lattice coincides with the nuclear lattice, if we observe a magnetic Bragg reflection with index (101), we can anticipate that the magnetic moment  $M$  will be either along the  $a$ -axis or the  $c$ -axis. The vector  $\mathbf{G}_{101}$  has components in both  $a^*$  and  $c^*$ . To determine the

preferred orientation of the spins, we look to see if the  $(00l)$  or  $(h00)$  magnetic reflections are absent. In such a case where the  $(00l)$  reflections are absent, it would indicate that  $M \parallel \mathbf{G}_{00l}$ , hence the moment would be along the  $c$ -direction. If  $M \perp \mathbf{G}_{00l}$ , then the  $(00l)$  reflections would be present and prominent.

Magnetic structures may be more complex, however. Magnetic reflections may appear elsewhere from the nuclear Bragg peaks at integer intervals, which would require a commensurate propagation vector  $q_m$  (or  $k_m$ ). If these reflections do not appear at integer values with respect to the nuclear cell, the magnetic unit cell is said to be incommensurate.

To construct a magnetic structure using any propagation vector, we must consider the moment distribution  $M_r$  associated with atom  $r$ . [96] This is expressed by the summation of basis vectors  $\Psi_j$  at the atomic site  $j$  translated by the vector  $r$ :

$$M_j = \sum_{q_m} \Psi_j^{q_m} e^{-2\pi i q_m \cdot r}. \quad (2.22)$$

A basis vector is a projection operation describing the moment in terms of the crystallographic axes. For example,  $\Psi = (100)$  would describe a moment aligned only along the  $a$ -axis. In most cases, the magnetic moment requires multiple basis vector components, which would then expand:

$$\Psi_j = \sum_i C_i \psi_i. \quad (2.23)$$

where  $C_i$  are the weighting coefficients for basis vector  $i$ .

From equation 2.22, we see that the structure can even be described by multiple magnetic propagation vectors (multi- $q_m$ ). For commensurate  $q_m = (0,0,0)$ , it is easy to see that the magnetic lattice matches the nuclear lattice and for any integer fraction vector, the magnetic lattice is multiplied by the reciprocal of the vector in its respective directions. For example, a  $q_m = (1/2,0,0)$  will be twice as large along the  $a$ -direction and equally sized along the other

two as the nuclear cell. Incommensurate propagation vectors, however, are better understood when the exponent is expressed by the Euler expansion as:

$$M_j = \Psi_j^{q_m} [\cos(\eta) + i\sin(\eta)] \quad (2.24)$$

where  $\eta = -2\pi i q_m \cdot r$ . This then divides the magnetic moment into a real component and an imaginary component. When both components are non-zero, the structure forms a helimagnetic structure, but when either component is nullified, the structure will only form a cosine or sine wave, also known as a spin density wave.

Whatever formalism is used, the recipe to determine a magnetic structure is more or less the same. In general, the procedure is as follows: (1) find propagation vector ( $q_m/k_m$ ), (2) understand magnetic Bragg reflections qualitatively, (3) refine proposed models to the data, and (4) determine the magnitude of magnetic moments.

### 2.2.5 Magnetic structure determination

There are several formalisms to describe magnetic structures.[97, 98] Two of the most common are irreducible representation analysis (IRA), also known as the Bertuat method, and magnetic space groups (MSG).[99, 100] Each formalism has its advantages and disadvantages; the goal is the same: to describe a magnetic structure. Deciding which formalism comes down to simplicity and the overall aim of understanding properties determined by symmetry. IRA is a group-theory-based approximation, whereas MSG applies a time-reversal symmetry-breaking operation to the already established nuclear space groups. For example, the magnetoelectric or magnetic tensor relationship

## Irreducible representation analysis

To use the IRA formalism, the first step is to identify the little group  $G_{q_m}$ , which is the set of symmetry elements of the parent space group (represented as  $G_0$ ) that leave the propagation vector unchanged or produce an equivalent one. The full star, or the other operations that do not leave the vector invariant, are used when the system is multi- $q_m$ . In this case, it is said to use the full ‘star’. Once  $G_{q_m}$  is known, the magnetic representation ( $\Gamma$ ) is decomposed:

$$\Gamma = \sum_{\nu} n \Gamma_{\nu} \quad (2.25)$$

where  $n$  is an integer, and  $\Gamma_{\nu}$  the irreducible representation (IR). These IRs describe the possible ways the spin dipoles can be arranged. Using the projection operators, the basis vectors ( $\Psi$ ) are then calculated.[101] Since,  $M_j = \Psi_j$ , refining the  $C_i$  coefficient of equation 2.23 will give the magnetic moment. Here, the basis vectors produced from the irreducible representations determine the spin orientations.

In many cases, more than one basis vector may produce a better residual when fitting a model to neutron data. In these cases, we can lean on Landau’s theory of phase transitions. Second-order phase transitions have only one irreducible representation associated with them. This then limits the possible ways to implement the allowed representations.

## Magnetic space groups

While IRA will represent the structure based on the allowed modes of spin-dipole configurations, the MSG formalism will produce the magnetic order based on the invariance of the already established paramagnetic space group.[102] The resulting magnetic space groups are also known as Shubnikov Groups.

To produce the MSG, a time reversal operation is implemented over the paramagnetic

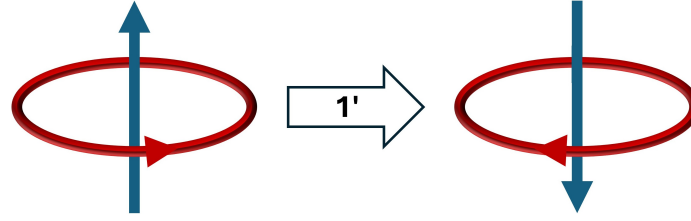


Figure 2.4: Time reversal operator ( $1'$ ) acting on a spin current to invert its direction.

space group. This operation is denoted by  $1'$  (primed operation). This operator flips the direction of the magnetic moment. The magnetic moment or spin is an axial vector that is typically represented by a rotating current. If this current is reversed, based on the right-hand rule, the direction of the moment will change as shown in Figure 2.4. Hence, this operator is also known as the spin reversal operator.

Notably, if we apply this operator to the 230 paramagnetic space groups, we would end up with a very large number of MSG. To be exact, 1651 non-equivalent Shubnikov groups.

The generic way to represent an MSG is  $\{R, \theta, t\}$ , where  $R$  is a proper or improper rotation,  $\theta$  is the time reversal operator, which can take the form  $-1$  or  $+1$ , and  $t$  is translation.[100] The MSG are then categorized into four types (I-IV). Type-I are the original 230 parent space groups with no time reversal; type-II (grey groups) explicitly contain the time reversal operator; type-III (black and white) have  $q_m = 0$ ; and type-IV (black and white) have  $q_m \neq 0$ . In this formalism, when refining the magnetic moment, we refine only three components such that  $M = (m_x, m_y, m_z)$ . Here, the constraints are all given by the space group symmetry elements.

## 2.3 Pair distribution function analysis

Scattering from a highly ordered material, i.e., crystalline, results in sharp Bragg reflections from diffraction. Scattering from a less ordered material broadens these peaks due to the loss of long-range periodicity. An amorphous or even a liquid would then give no

Bragg reflections, but diffuse components that would appear as rings in a powder diffraction experiment and would seem like a broad background. Taking the Fourier transform of scattering data produces a real space interpretation of the diffuse features. This results in producing the radial distribution function ( $G(r)$ ) of the species contained in the scattering material.[103] The radial distribution is then obtained by integrating the total scattering data (2.11) over a large  $Q$  range, and is obtained by the sine Fourier transform:

$$G(r) = \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} Q[S(Q) - 1] \sin(Qr) dQ, \quad (2.26)$$

Figure 2.5 shows a simulated example of the pair distribution of  $\text{Co}_{1/4}\text{TaSe}_2$ . The gray curve in Figure 2.5(a) corresponds to the total atom pairs composed of each partial atomic pair (colored lines). From this data, we can determine atomic pair distances from peak position, coordination number from peak area, disorder from peak width, and even average particle size from the maximum  $r$ -peak denoting the particle boundary. We can visualize this information as the shortest peak in  $r$  corresponds to the shortest atomic pair distance. For  $\text{Co}_{1/4}\text{TaSe}_2$  in Figure 2.5(b), Co-Se (red bond) and Ta-Se (purple bond) are the shortest bonds. Any distortion or bond length modification would lead to peak broadening or even splitting as observed by the teal Ta-Ta and orange Se-Se bond lengths. Notably, some pair distribution peaks have different intensities and areas despite the coordination number being the same. To understand this, we first invoke the total radial distribution function expressed as:

$$G(r) = \sum_{i,j=1}^n c_i c_j b_i b_j [g_{ij}(r) - 1], \quad (2.27)$$

where,  $c$  is the self part of the structure factor ( $S(Q)$ ),  $b$  is still the bound coherent



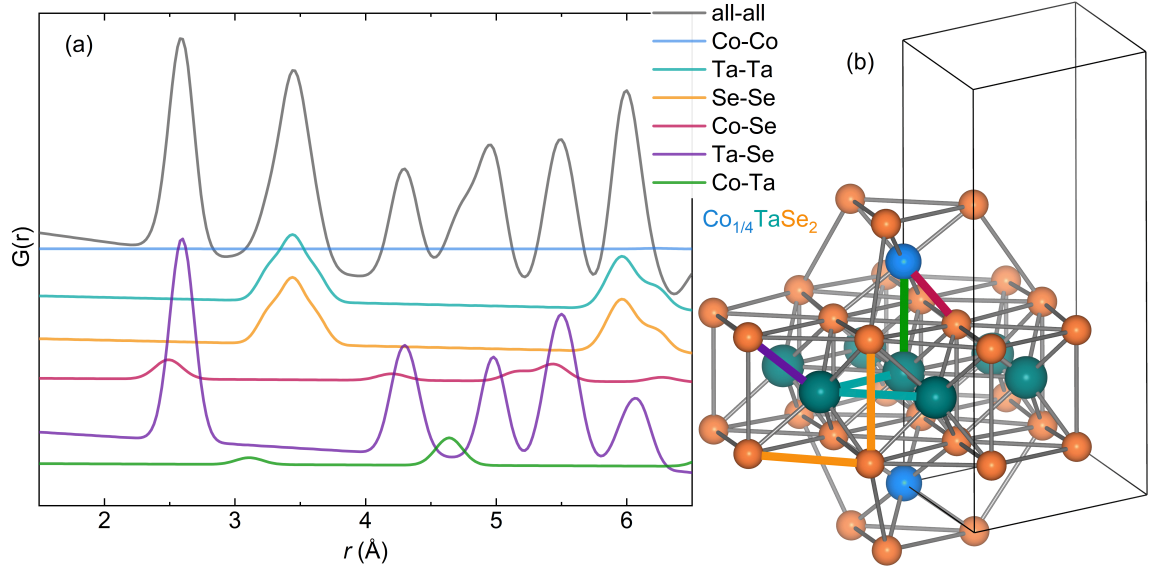


Figure 2.5: (a) Simulated pair distribution function (PDF) of  $\text{Co}_{1/4}\text{TaSe}_2$  and bon pair partials. The curves are color-coded to the corresponding atom pair in the local structure of  $\text{Co}_{1/4}\text{TaSe}_2$ (b).

scattering length, and  $g_{ij}(r)$  is the partial pair distribution:

$$g_{ij}(r) = \frac{n_{ij}}{4\pi r^2 dr \rho_j}, \quad (2.28)$$

which contains the number of particles of type  $i$  and  $j$  between  $r$  and  $r + dr$ . From equation 2.27, we see that the radial distribution depends on the bound coherent scattering lengths, where in the current example, these are: for Co (2.49 fm), Nb (7.054 fm), Ta (6.91 fm), and Se (7.97 fm). Notably, cobalt's scattering length is smaller than that of the other two, and, considering that it is in a 1:4:8 or even 1:3:6, Co:(Nb/Ta):Se, the contribution is very small. Thus, in Figure 2.5 (a), although the Co-Co pair distance is approximately  $r \approx c/2 \approx 6.2$  Å, there is little to no contributed intensity to the full distribution curve. Analyzing the disorder of the intercalant can then provide challenges, as the general tool to model PDF data, PDFFIT[104], and PDFgui[105, 106] could allow for human bias to take over. These tools are considered to be small-box modeling, as the model consists of the contents of a single unit cell.

To overcome any bias, a statistical approach where random atomic movements within a supercell several times larger than the unit cell are used to model the PDF data (big-box modeling). RMCprofile[107, 108] is one software suite that is capable of simulating and fitting multiple data sets by means of the reverse Monte Carlo (RMC) method. Unlike traditional least-square fits, RMCProfile can fit neutron total scattering, X-ray total scattering, Bragg profiles, and Extended X-ray Absorption Fine Structure (EXAFS) data simultaneously, exhausting all the information available from the sample and diffraction.

From equation 2.27, we see that the total scattering data is multiplied by  $Q$  before performing the Fourier transform, which amplifies the noise at high- $Q$ ; however, the most relevant information regarding the local structure is found at very low- $d$  spacings, meaning that the maximum obtainable  $Q$ -range will determine the resolution of the resulting PDF data.[109] Therefore, the PDF data performed for this thesis was thus collected at POWGEN, which has the required  $Q$ -range and resolution.

### 2.3.1 Big-box modeling data pre-processing

Reducing the raw scattering data for small-box and big-box modeling requires different treatments. While for small-box modeling,  $G(r)$  can simply be obtained by 2.27 from normalized  $S(Q)$ , big box modeling must assume an un-normalized structure factor  $F(Q)$ . To distinguish each data representation apart, it is easiest to simply plot the data and inspect the low- $Q$  region. If the data is at a low-level in the low- $Q$  region and then tends to a value of 1, the total scattering structure factor is in an adequate form for big-box modeling. If the data has a slope, it is likely due to the multiplying  $Q$  from the  $Q[S(Q) - 1]$  term. Keen[110] provides clarifications for the notation of each data representation.

Once the data is ensured to be in the correct  $F(Q)$  representation, the next step is to rebin the data. This means to make the data array equally spaced for the Fourier transform

step. The scaling of the data and the Fourier transform can be performed with the ‘stog-new’ function built into RMCprofile; “stog” stands for “ $S(Q)$  to  $G(r)$ ”. To do this, Table 2.3 shows an example of an input file with parameters used in the work for this thesis.

Table 2.3: Example of stog input text file

|                        |                                      |
|------------------------|--------------------------------------|
| 1                      | Number of files                      |
| Name-SQ-File.dat       | Input file name                      |
| 0.92 30.0              | $Q_{min}$ and $Q_{max}$              |
| -0.21 0.87             | $y_{offset}$ and $y_{scale}$         |
| 0                      | $Q_{offset}$                         |
| scale.sq               | scaled $S(Q)$                        |
| scale.gr               | scaled $G(r)$                        |
| 50                     | $r_{max}$                            |
| 5000                   | Number of points                     |
| N                      | smoothing function                   |
| 0.051407               | number density ( $\text{\AA}^{-3}$ ) |
| 0                      | $y_{offset}$                         |
| N                      | Try again                            |
| Y                      | Fourier filter                       |
| 1.0                    | rcutoff for Fourier filter           |
| scale-ft.sq            | Fourier filtered $S(Q)$              |
| scale-ft.gr            | Fourier filtered $G(r)$              |
| 0.378865               | Faber-Ziman coefficient              |
| scale-ft-rmc-qmax30.fq | $F(Q)$                               |
| scale-ft-rmc-qmax30.gr | $G(r)$                               |
| 2.25 0 0               | cutoff, $r_{min}$                    |

The output files, along with a supercell model generated preferentially from a Rietveld fit and saved into an rmc6f file, can be used to run reverse Monte Carlo modeling.

## 2.4 Physical property measurements

While the methods used in this work are bulk measurements, the diffraction and scattering methods discussed previously provide insight into the structure. To better understand the physical properties that accompany these materials, it is useful to examine their magnetization, specific heat, and electrical transport properties. Furthermore, we often make use of

these techniques before performing structural analysis. We study the magnetic susceptibility to search for magnetic anomalies and transition temperatures; specific heat to derive the magnetic entropy or to search for other phase transitions that are not magnetic in nature, such as structural transitions; and resistivity measurements to understand the electrical conductivity as a function of field and temperature, which provides insight into the Fermi surface of the sample. The following sections briefly describe these methods.

### 2.4.1 Magnetic susceptibility and magnetization

Temperature-dependent magnetic susceptibility  $\chi$ , as the name suggests, is the field susceptibility of a material to an externally applied field.[111] In other words, it is the magnetic force a material experiences within the field. This quantity is given by:

$$\chi = M/H, \quad (2.29)$$

relating the magnetization ( $M$ ) of a material to the externally applied field ( $H$ ). This quantity can be measured under two magnetic field circumstances: using a direct current magnet for static magnetic properties ( $\chi_{DC}$ ), or an alternating current magnet ( $\chi_{AC}$ ) to get information on magnetic dynamics. In this work, we only collected susceptibility under a direct current magnet.

Equation 2.29 implies the need for a magnetic field, which we already established can be DC or AC, and a manner in which to detect the magnetization of the material. Historically, this began with the Gouy balance to determine the sample's weight within the magnetic field. Currently, however, we have the vibrating sample magnetometer (VSM) and the superconducting quantum interference device (SQUID). The VSM consists of attaching the sample to a rod and oscillating the sample within the magnetic field at a fixed frequency. A coil then detects the currents generated from these vibrations to determine the magnetization.

The core elements of the SQUID, in contrast to a coil, are two Josephson junctions connected in parallel in a superconducting loop. This device can detect very small magnetic fields.

These magnetometers used in this work are built within a magnetic property measurement system (MPMS) from Quantum Design, which can cool or heat the sample chamber between 1.8 K and 350 K. To measure the magnetization in this instrument, powders are loaded into plastic gel capsules fixated onto a straw. Conversely, single-crystal samples are mounted in a quartz rod. For this work, the single crystal can easily be aligned in such a way that the applied magnetic field can be parallel or perpendicular to the  $c$ -axis ( $H||c$  and  $H||ab$ ). Within the instrument, the magnetic field is vertical; thus, if we wanted to measure the in-plane magnetization, we would mount the crystal flat on the rod as the field is parallel to the rod.

There are two common ways to collect temperature-dependent magnetic susceptibility data: (1) zero-field-cooled (ZFC) and (2) field-cooled (FC). The sequence in which the data was collected is to cool the sample with no magnetic field applied. Once the sample is at base temperature (typically 1.8 K), a small magnetic field is applied; usually 0.1 T, although a higher field can be applied to probe for any field-induced magnetic phenomena. The data is then collected with the applied field fixed while warming the sample at a steady rate. This is the first step of the sequence that collects the ZFC part. The FC part can then be measured either while cooling again after the ZFC step, simply by not turning off the magnetic field. Alternatively, the data can be collected while warming, the only condition being that the magnetic field not be modified from cooling to warming. When the sample is in a paramagnetic state, the magnetic susceptibility is expected to behave inversely proportional to the temperature ( $T$ ) times a constant:

$$\chi \propto \frac{C}{T} \quad (2.30)$$

This is known as the Curie-Weiss law, where  $C$  is the Curie constant.

Field-dependent magnetization measurements ( $M$  vs.  $H$ ) can also be collected under isotherm conditions. These magnetization measurements are limited by the maximum magnetic field achievable by the magnet. In this case, we were able to collect magnetization data from - 7 T to 7 T.

Both susceptibility and magnetization measurements provide useful information regarding the magnetic phenomena of the sample. Temperature dependent susceptibility is dependent on many factors, but for a traditional paramagnet, the susceptibility will rise as a function of field. This gradual rise will experience a discontinuity if there is a magnetic phase transition. If the system is ferromagnetic, the magnetization will have a saturation point when all the spin are aligned. If the system is antiferromagnetic, the magnetization will decrease as the moments cancel out within the material. Similarly, in a magnetization curve, the moment will saturate at a certain field for a ferromagnet. Furthermore, it may provide information regarding the hardness of the magnetic moments, meaning if there is a coercive field due to a hysteresis loop formation. If the system is antiferromagnetic, the slope is expected to decrease below the transition temperature.

For a ferromagnet, the transition temperature is denoted by  $T_C$ , which stands for Curie temperature. In an antiferromagnet, the transition temperature is known as the Néel temperature, written as  $T_N$ .

#### 2.4.2 Low-temperature specific heat

Heat capacity is defined as the change in temperature ( $T$ ) as a function of added heat ( $Q$ ) at constant pressure ( $p$ ) or volume  $v$ :

$$C_{p,v} = \left( \frac{dQ}{dT} \right)_{p,v}, \quad (2.31)$$

where for solids we can consider  $C_p \approx C_v$ . Specific heat is then obtained by dividing by the sample mass ( $m$ ). Measuring specific heat as a function of temperature is particularly useful to inspect phase transitions and obtain quantitative information regarding the sample. In this work, we used a physical property measurement system (PPMS) from Quantum Design to measure specific heat capacity. This instrument uses the two tau ( $\tau$ ) method, which is a time constant. This constant works as a function of a nonlinear first-order differential equation.[112] By mounting the sample onto a platform as in Figure 2.6, the specific heat in this model, in simple terms, is obtained by solving:

$$C_{total} = \frac{dT}{dt} = -K_w(T - T_b) + P(t) \quad (2.32)$$

where  $K_w$  is the thermal conductance of the wires,  $T_b$  is the temperature of the bath, and  $P(t)$  is the power input to the platform, which is a function of time  $t$ . The Specific heat of the sample is then:  $C_{sample} = C_{total} - C_{addenda}$ ; where the addenda is the platform itself with the grease. This measurement resembles that of a resistor-capacitor circuit, where the heat pulse in will rise exponentially and turn into a exponential decay once the power feed is off. Thus, in a two- $\tau$  model, we have:

$$\Delta T = -Ae^{-t/\tau_1} - Be^{-t/\tau_2}, \quad (2.33)$$

where  $A$  and  $B$  are constants,  $\tau_1$  delineates the relaxation of the sample platform into the bath, and  $\tau_2$  is the relaxation from the sample onto the platform. Each specific heat data point is therefore obtained from fitting the thermal relaxation time constants. At low temperatures, this measurement is relatively fast, taking less then a second at very low temperatures, but it becomes more time-consuming at higher temperatures as the time to achieve thermal equilibrium gets slower. At higher temperatures, a data point collection

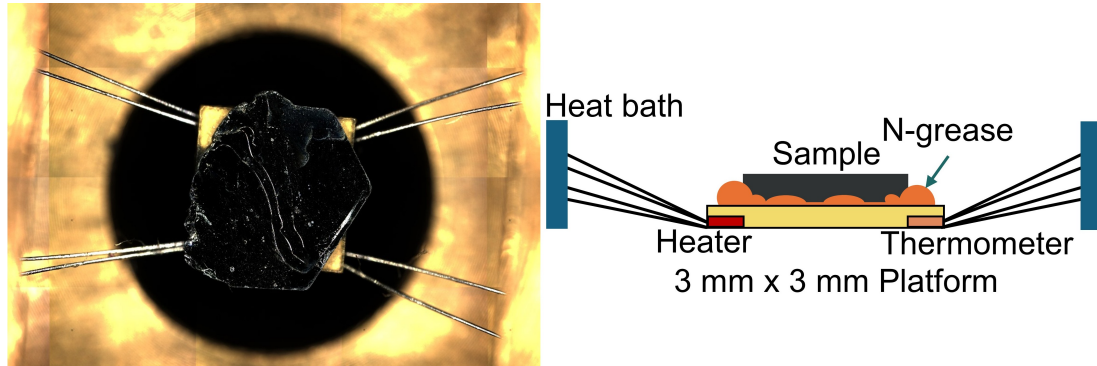


Figure 2.6: Flat crystal on specific heat measuring platform and schematic diagram of measuring platform and components.

may take up to one hour.

To perform a specific heat measurement, we must know the thermal conductance of the grease, which is later used to ensure good thermal contact and conductivity with the sample (aside from serving as a fixation). Hence, we must measure the platform with the grease alone. This gets us the addenda table, which must be measured in the same temperature range and conditions as the sample. Once the addenda are obtained, the sample can be mounted onto the platform as shown in Figure 2.6.

### 2.4.3 Electrical transport

Electrical transport measurements provide valuable information on how electrons or holes flow through the Fermi surface of metals. The flow of electrons can easily be measured by resistivity ( $\rho$ ) measurements. By placing four point contact on a crystal, as shown in Figure 2.7, using either solder or silver paste, the longitudinal resistance ( $R$ ) can be measured with Ohm's law by applying a constant ( $I$ ) current and measuring the voltage ( $V$ ). The resistance is then converted to the intrinsic resistivity unit by taking into account the



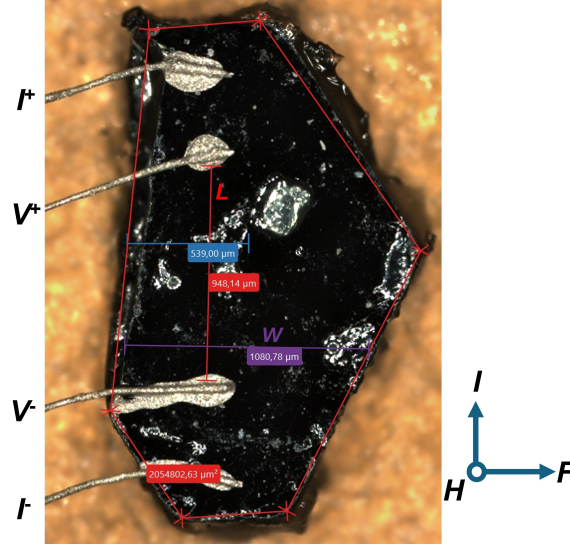


Figure 2.7: Four-point wire contacts for longitudinal resistivity measurement

geometric factors of the crystal sample, such that:

$$\rho_{xx} = R_{xx} \frac{W \times h}{L} = \frac{V_{xx}}{I} \cdot \frac{A}{L} \quad (2.34)$$

where the width ( $W$ ) times the height ( $h$ ) gives the cross-sectional area and  $L$  is the distance between the leads. Here,  $R_{xx}$  stands for the longitudinal resistance along the  $x$ -direction. This is noted as it is possible to add two more contacts for a total of six-point contacts. These other two contacts would lie between  $V^+$  and  $V^-$ , where one would typically be laced on the left, such that there are five contacts on the same side and the other one at the right. This arrangement would then allow us to collect  $R_{xy}$  needed for the Hall effect.

Because carriers (electrons or holes) have a charge, when they flow, they will generate a magnetic field. This, in turn, makes them react to an externally applied magnetic field. This reacting force, known as the Lorentz force, is expressed as  $F = q(E + v \times H)$ , where  $q$  is the electron charge,  $E$  the electric field, and  $v$  the velocity. The magnetic component will deflect the carriers to one side, and the oppositely charged ones to the other until a saturation is reached. The transverse resistivity ( $\rho_{xy}$ ) as a function of field will give a slope, and the

carrier density can be calculated as:

$$n = \frac{IH}{hqV_H} \quad (2.35)$$

where  $V_H$  is the Hall voltage, and if it is negative, the carriers are electrons, where if the opposite is true, they are holes.

The electronic transport measurements presented in this work were performed with the help of Gicela Saucedo from Dr. Butch's group.

## 2.5 Density functional theory calculations

Density functional theory (DFT) is a computational chemistry tool based on quantum mechanics. In this work, we make use of DFT to help explain the observed properties to the theoretical electronic band structures modeled from the ideal crystallographic structure. The general steps performed in our DFT calculations were first to obtain the self-consistent field (SCF) to find the ground state energy and iteratively establish electron densities until convergence. The structure is then relaxed to find the lowest energy state and then the SCF calculation is performed again with this relaxed structure. To obtain the density of states (DOS) and electronic band structures, the non-self-consistent field (NSCF) calculation is then performed.

Most DFT calculations in this work, using Vienna Ab initio Simulation Package (VASP), were done by Dr. Sajjan Sheoran from Professor Dev's group at Howard University. Calculations done with QuantumESPRESSO were done by the author of this thesis.

## Chapter 3: Itinerant A-type Antiferromagnetic Order in $\text{Co}_{1/4}\text{TaSe}_2$

The work described in this chapter was published in *Physical Review B*. Hector Cein Mandujano, Gicela Saucedo Salas, Tianyu Li, Peter Y. Zavalij, Alicia Manjon-Sanz, Nicholas P. Butch, and Efrain E. Rodriguez were contributing authors. H.C.M. prepared the samples, H.C.M., G.S.S., T.L., and N.P.B. performed MPMS and PPMS measurements, and H.C.M. along with A.M.S. collected neutron powder diffraction data. H.C.M. performed the density functional theory calculations.

### 3.1 Introduction

The discovery of ferromagnetism in two-dimensional (2D) materials has sparked growing interest in the subject of itinerant 2D magnetism.[113] The nature of such lower-dimensional magnetism can arise from spin polarization of the delocalized electrons in these strongly anisotropic systems.[114] Transition metal dichalcogenides (TMDs) constitute an important and broad category of van der Waals (vdW) materials making them a rich platform to explore such 2D magnetism.[2] Particularly, niobium- and tantalum-based TMDs are known metallic systems that can host other physical phenomena such as charge density wave (CDW) instabilities.[115, 116] Notably, commensurate and incommensurate CDWs as well as superconductivity can manifest in the metallic 2H-TaSe<sub>2</sub> polytype.[117] Using these inherently metallic TMD hosts, one can then design ferro- or antiferromagnetic vdW systems

through insertion of magnetic guest species and explore how such magnetism interacts with CDWs or even superconductivity. In this article, we explore 2H-TaSe<sub>2</sub> as a host for exploring itinerant magnetism via magnetic cation intercalation.

The ease with which magnetically active metal ions can be inserted into TMD hosts has initiated a renewed surge in studying such intercalated systems[118]. Typically, the magnetic ion is a member of the first-row transition metal series such as V, Cr, Mn, Fe, Co, and Ni. The guest ion stabilizes a 3*d*-electronic band that interacts with the itinerant electronic bands of the TMD host.[25, 119, 120] Depending on the combination of the guest magnetic ion and TMD host, the symmetry of the overall system can also be altered, *e.g.*, from centrosymmetric to noncentrosymmetric. The alteration of symmetry, both chemical and magnetic, could lead to emergent properties such as the anomalous Hall effect[121] or anisotropic magnetoresistance.[122] For example, a proposed type of magnetic order known as altermagnetism has been postulated in a vanadium-intercalated TMD.[123] Unlike traditional antiferromagnets, altermagnets break time-reversal symmetry in their spin-resolved electronic band structure despite also having anti-aligned magnetic moments in real space. Since TMDs could offer a platform for exploring altermagnetism, it is imperative that metallic TMDS with long-range magnetic order be explored.

The first criterion in these studies of itinerant magnetism is to choose a TMD host that is already metallic in its pristine state. Typically, the platforms for these studies consist of metals from groups 5 (*e.g.*, Nb and Ta) and 7 (*e.g.*, Tc, Re) of the periodic table.[2] The nature of the resulting magnetic order, whether ferro- or antiferromagnetic, must therefore arise from the behavior of the electrons near the Fermi level. For example, itinerant ferromagnetism is understood to arise from conduction band-splitting that leads to spin imbalance,[124] and the emerging moments can be explained by the Stoner model[125]. In the case of itinerant antiferromagnetism (AFM), a variety of structures of structures have been observed including spin density waves, exotic spin textures, spin spirals, skyrmions,

and helimagnets.[43, 47, 51, 126–128]

In this work, we grow single crystals of  $\text{Co}_{0.25}\text{TaSe}_2$  (Figure 3.1(a) and (b)) and characterize their bulk physical properties including any anisotropy in their magnetic behavior. To the best of our knowledge, only Fe and Ni have been reported as magnetic ion intercalants into  $\text{TaSe}_2$ . [61, 68] Both  $\text{Fe}_{0.25}\text{TaSe}_2$  and  $\text{Ni}_{0.25}\text{TaSe}_2$  are known ferromagnets, albeit with different characteristics in their magnetic hysteresis. Much more explored are the sulfide-based TMDs for magnetic ion intercalation. For example, the sulfide host  $M_x\text{TaS}_2$  can take up high ratios of metal intercalation, up to  $x = \frac{1}{3}$ , and a variety of phenomena are associated with the amount of  $x$  and the  $d$ -electron count of  $M$  in  $M_x\text{TaS}_2$  ( $M = \text{V, Cr, Mn, Fe, Co, and Ni}$ ). Whereas the  $M_x\text{TaS}_2$  exhibits helimagnetism for  $M = \text{Cr}$ , [129] it adopts several collinear AFM structures for  $M = \text{V, Co, and, Ni}$ . [44, 67, 130] Meanwhile, for the case of  $M = \text{Mn and Fe}$ , they are all ferromagnets. [57, 130] Given the richness of the magnetic phase diagrams found in the sulfide TMDs, it is worth exploring the selenide counterparts. The present work would constitute the first report into the effects of Co-intercalation into  $\text{TaSe}_2$ .

## 3.2 Experimental Methods

### 3.2.1 Sample preparation and crystal growth

Polycrystalline powder samples were made by vacuum sealing Co, Ta, and Se in 1:4:8 molar ratio in a fused silica ampule at  $< 10$  mTorr. Each preparation ranged from 1 g to 4 g of sample per ampule. The ampule with the premixed reagents was heated up to  $700^\circ\text{C}$  for 1 hour before increasing the temperature further to  $900^\circ\text{C}$  where it dwelled for 5 days. After that, the samples were furnace-cooled to room temperature. The resulting powders were recovered in air, reground in an agate mortar and pestle, and reheated to  $900^\circ\text{C}$  for 5 days to improve homogeneity.

Single crystal samples of  $\text{Co}_{1/4}\text{TaSe}_2$  were obtained by chemical vapor transport (CVT) using pre-reacted powder samples and 4 mg of iodine per mL of the volume of the reaction ampule. However, due to iodine's affinity for cobalt, excess cobalt was added in the solid-state synthesis before CVT. The charge powder was thus prepared with a 1:1:2 molar ratio of Co:Ta:Se. Iodine and charge powder were loaded into a 12.5 cm-long fused silica tube with an inner diameter of 14 mm and outer diameter of 16 mm. The ampule was torch-sealed under partial vacuum and placed in a horizontal tube furnace to ensure that both precursors were at the center of a single-zone tube furnace. The hot end (furnace center) of the ampule was set to 940 °C and the cool end was measured to be 880 °C. The temperature profile of the single-zone furnace was given by the natural gradient of the furnace.

Single crystals of  $\text{Co}_{1/4}\text{TaSe}_2$  grew at the hot end of the ampule. Once recovered, they were washed with ethanol to remove residual iodine and any surface impurities. We had initially assumed the cool end of the ampule to be the growth zone, but for this system, the hot end is the actual growth zone. This observation would entail that the reaction of the transport agent with the precursor powder is exothermic.

### 3.2.2 Sample characterization and electronic structure calculations

For structure determination, a suitable single crystal of  $\text{Co}_{1/4}\text{TaSe}_2$  was selected and measured on a Bruker D8Venture with PhotonIII diffractometer. The crystal was kept at 250(2) K during data collection. The integral intensity was correct for absorption using SADABS software[131] using the integration method. The structure was solved with the ShelXT program and refined with the ShelXL[132] program using least-square minimization. No restraints were used in the structural refinement. More details on the structure determination by single crystal methods can be found in Table 3.1.

Neutron powder diffraction data were collected at the POWGEN instrument[133] located

at the Spallation Neutron Source in Oak Ridge National Laboratory. Experiments at 200 K, 120 K, and 10 K were performed on approximately 8 g of powder sample loaded into standard vanadium cans. Two different time-of-flight frames were chosen to cover 0.5-12.5 Å and 1-20.5 Å in  $d$ -spacing, respectively. Both powder X-ray and neutron diffraction data were analyzed using the Rietveld method with GSAS-II[134] software.

Powder X-ray diffraction was measured in reflection geometry on a Bruker D8 instrument with Cu K $\alpha$  wavelength and a LynxEye detector.

The elemental composition of the single crystal samples was determined using energy dispersive X-ray spectroscopy (EDS). The EDS measurements were carried out on multiple areas of several crystals from the same batch in a Hitachi SU-70 Schottky field emission gun scanning electron microscope (FEG SEM). Further composition analysis was corroborated via X-ray photoelectron spectroscopy (XPS) in a Kratos Axis Supra X-ray Photoelectron Spectrometer with an Al anode source. XPS analysis was performed using the CASAXPS[135], and the binding energies obtained are relative to the Fermi level.

Magnetization isotherms, as well as temperature-dependent zero-field, cooled (ZFC) and field-cooled (FC) DC magnetic susceptibility measurements were performed using a Quantum Design Magnetic Property Measurement System (MPMS). Resistivity and magnetoresistance measurements were done in a 14 T Quantum Design Physical Property Measurement System (PPMS-14). Specific heat was measured in a Quantum Design Dynacool PPMS upon cooling using the two-tau method.

Self-consistent field and density of states calculations were performed using the Quantum ESPRESSO software package[136] in an  $8 \times 8 \times 2$  K-point mesh and cutoff energy of 680 eV. Projector-augmented wave (PAW)-type pseudopotentials were used with the generalized gradient approximation (GGA)+U.

### 3.3 Results and Discussion

#### 3.3.1 Structure solution and refinement

First, the composition and structure of CVT-grown single crystals were solved by single crystal XRD analysis. Although the host TaSe<sub>2</sub> is known to crystallize in a variety of polytypes,[137] we have determined that Co<sub>1/4</sub>TaSe<sub>2</sub> only crystallized in the 2H-type structure, adopting the hexagonal centrosymmetric space group *P6<sub>3</sub>/mmc* (SG No. 194). The details of the structure solution are given in Table 3.1, and the refined structural parameters are summarized in Table 3.2. The occupancy parameter for all the elements were found to be unity, which results in stoichiometric Co<sub>1/4</sub>TaSe<sub>2</sub>.

To check the consistency between different single crystals and their orientations, we

Table 3.1: Single-crystal XRD structural solution results for Co<sub>1/4</sub>TaSe<sub>2</sub>.

|                         |                                  |
|-------------------------|----------------------------------|
| Cryst system            | Hexagonal                        |
| Space group             | <i>P6<sub>3</sub>/mmc</i>        |
| <i>a</i>                | 6.8828(1) Å                      |
| <i>c</i>                | 12.4535(3) Å                     |
| Volume                  | 510.92(2) Å <sup>3</sup>         |
| <i>Z</i>                | 8                                |
| Calculated density      | 9.194 g/cm <sup>3</sup>          |
| F(000)                  | 1182.0                           |
| Crystal size (mm)       | 0.24 × 0.15 × 0.015              |
| Radiation               | MoK <sub>α</sub> (λ = 0.71073 Å) |
| 2Θ range                | 6.544° to 70.034°                |
| Refl collected          | 20723                            |
| Independent refl        | 470                              |
| G.O.F.on F <sup>2</sup> | 1.349                            |
| Final R indexes         | R <sub>1</sub> 0.0164            |
| [I ≥ 2σ (I)]            | wR <sub>2</sub> 0.0359           |
| Final R indexes         | R <sub>1</sub> 0.0169            |
| [all data]              | wR <sub>2</sub> 0.0360           |
| Temperature             | 250(2) K                         |



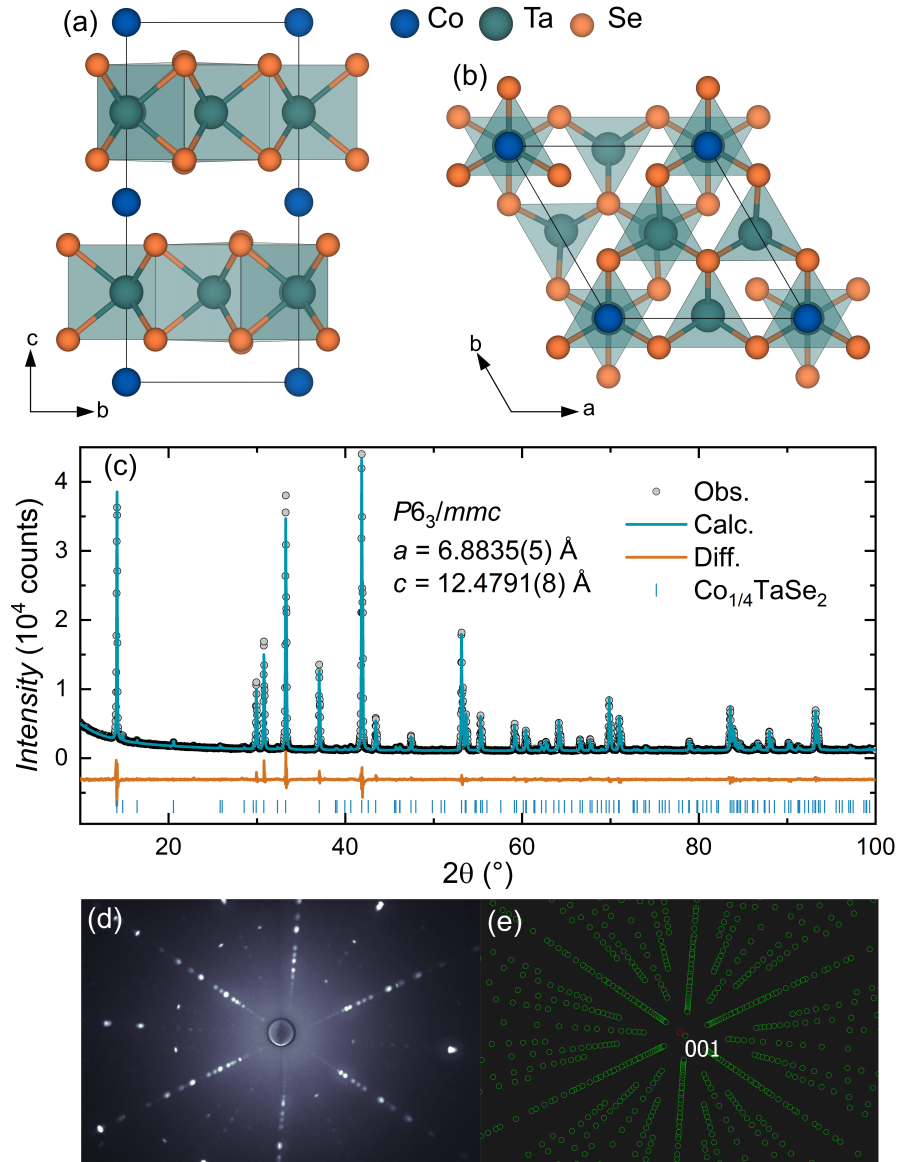


Figure 3.1: Crystal structure of  $\text{Co}_{1/4}\text{TaSe}_2$  and representative diffraction patterns. The layered 2H-polytype of  $\text{Co}_{1/4}\text{TaSe}_2$  viewed along the  $a$ -axis (a) and  $c$ -axis (b). (c) Rietveld refinement of the crystal structure with pXRD using Cu K- $\alpha$  radiation. The residual was 4.86 %, and the vertical tickmarks index the hexagonal cell. Cobalt sits in the vdW gap in the  $2a$  Wyckoff site to form a triangular sublattice. (d) Experimental Laue diffraction image and (e) simulated Laue diffraction showing the six-fold symmetry viewed along the  $c$ -direction.

Table 3.2: Structural parameters for  $\text{Co}_{1/4}\text{TaSe}_2$  obtained from single-crystal XRD results at 250 K.

| Atom | Wyc. Pos. | $x/a$      | $y/b$      | $z/c$      | Occ.       | $U_{11}$   |
|------|-----------|------------|------------|------------|------------|------------|
| Co   | $2a$      | 0          | 0          | 1/2        | 1          | 0.0073(2)  |
| Ta   | $2b$      | 0          | 0          | 1/4        | 1          | 0.0039(1)  |
| Ta   | $6h$      | 0.49148(2) | 0.98296(3) | 1/4        | 1          | 0.0056(1)  |
| Se   | $12k$     | 0.33781(3) | 0.16890(2) | 0.38160(2) | 1          | 0.0045(1)  |
| Se   | $4f$      | 1/3        | 2/3        | 0.11041(3) | 1          | 0.0051(1)  |
|      |           | $U_{22}$   | $U_{33}$   | $U_{23}$   | $U_{13}$   | $U_{12}$   |
| Co   | $2a$      | 0.0073(2)  | 0.0059(3)  | 0          | 0          | 0.00365(9) |
| Ta   | $2b$      | 0.0039(1)  | 0.0046(1)  | 0          | 0          | 0.00195(4) |
| Ta   | $6h$      | 0.0039(1)  | 0.0041(1)  | 0          | 0          | 0.00193(4) |
| Se   | $12k$     | 0.0045(1)  | 0.0046(1)  | 0.00022(3) | 0.00043(6) | 0.00226(5) |
| Se   | $4f$      | 0.0051(1)  | 0.0044(2)  | 0          | 0          | 0.00253(6) |

examined the Laue diffraction patterns of several samples. The experimental Laue XRD image in Figure 3.1(d) highlights the sixfold symmetry along the  $[001]$  direction which can be accurately simulated (Figure 3.1(e)). The thin plate morphology therefore allows us to orient the crystal samples either in the  $ab$ -plane or along the  $c$ -axis for transport and magnetization studies.

The single crystal results also afforded satellite reflections that imply superlattice formation. TMDs of the 2H-type can adopt a  $2a_0 \times 2a_0$  superlattice structure[25] where  $a_0$  is the unit cell parameter of the pristine 2H-TaSe<sub>2</sub> parent compound. Generally, this superlattice develops when  $x = 1/4$  in Nb and Ta-based TMDs. We find that  $\text{Co}_{1/4}\text{TaSe}_2$  is isostructural to  $\text{Ni}_{1/4}\text{TaSe}_2$  as well as several  $M_{1/4}\text{TaS}_2$  TMDs.[48, 68, 138] Within the  $2a_0 \times 2a_0$  superlattice, the intercalated cobalt occupies the  $2a$  Wyckoff position, leading to a 2D triangular sublattice of the  $\text{Co}^{2+}$  cations. This triangular metal sublattice with Co–Co distances equal to the unit cell parameter  $a$  is interesting in the context of magnetically frustrated systems.[139] It has also been implicated in forming toroidal structures[30] in an ordered antiferromagnetic state. We discuss the potential implications of such a triangular sublattice later in this article.

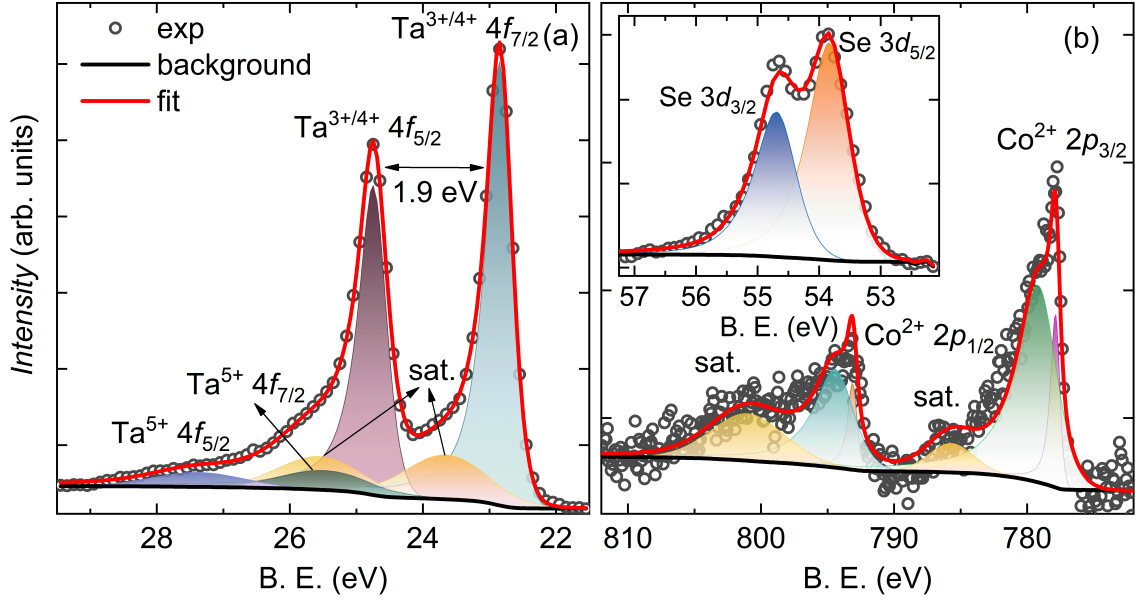


Figure 3.2: X-ray photoelectron spectroscopy analysis of  $\text{Co}_{1/4}\text{TaSe}_2$  showing the spin-orbit energy splitting of (a) Ta  $f$ , (b) Co  $p$ , and (inset) Se  $d$  doublets.

For the polycrystalline samples, we confirmed their chemical stoichiometry via Rietveld analysis. A representative fit with a pXRD pattern is shown in Figure 3.1(c). The lattice parameters from pXRD ( $a = 6.8835(5)$  Å and  $c = 12.4791(8)$  Å) at room temperature are very similar to those we found from the single crystal XRD at 250 K ( $a = 6.88280(10)$  Å and  $c = 12.4535(3)$  Å). The similarity of the unit cell dimensions indicates the closeness in composition and structure of our samples in both its polycrystalline and single crystal form.

### 3.3.2 Metal oxidation states and composition

To better understand the implications of metal oxidation states on the magnetic and electronic properties, we analyzed some of the key x-ray photoelectron spectra (XPS) of the final product. First, we discuss tantalum. The asymmetric XPS peak shapes were fit using the Gelius profile convoluted with a Gaussian. Such asymmetry is characteristic of conducting samples. Figure 3.2(a) shows the Ta  $4f$  spin-orbit split peaks at 24.7 eV ( $4f_{7/2}$ )

and 25.5 eV ( $4f_{5/2}$ ) consistent with those previously observed in  $\text{Fe}_{0.28}\text{TaSe}_2$ . [140] Satellite peaks have been observed in  $\text{TaSe}_2$  [140, 141] and are equally spaced by 1.9 eV as the main  $4f$  features. The additional peaks are inherent to samples with mixed oxidation states. From our fit, we find two distinguishable oxidation states,  $\text{Ta}^{3+}$  and  $\text{Ta}^{4+}$ . We attribute the observation of  $\text{Ta}^{5+}$  state to surface  $\text{Ta}_2\text{O}_5$ .

For the intercalated Co cations in the host, we find results largely consistent with a divalent metal. The binding energies at 777.9 and 793.1 eV in Figure 3.2(b) are close to those belonging to  $\text{CoSe}_2$ , [142], while the broader features at 779.2 and 794.4 eV correspond to Co  $2p_{3/2}$  and  $2p_{1/2}$  observed in CoO, respectively. The observation of satellite peaks separated by 6.5 eV to the main Co  $2p_{3/2}$  confirms the  $\text{Co}^{2+}$  oxidation state. [143] The presence of satellite peaks is characteristic of the high-spin state. [144, 145] However, due to the high content of surface oxidation, we cannot discard the possibility of these features being inherent to surface CoO itself. The binding energies for Se  $3d_{5/2}$  (53.8 eV) and  $3d_{3/2}$  (54.7 eV) are shown in the inset and are comparable to those observed in other similar transition metal diselenides. [141, 146] Overall, the XPS results are consistent with  $\text{Co}^{2+}$  coordinated to  $\text{Se}^{2-}$  anions in the TMD.

### 3.3.3 Magnetic Susceptibility and magnetization

The temperature-dependent magnetic susceptibilities ( $\chi$ ) collected with fields applied along the  $c$ -axis and  $ab$ -plane are shown in Figure 3.3(a). An antiferromagnetic transition is observed at  $T_N = 173$  K, and the clear difference between the susceptibilities  $\chi_{||ab}$  and  $\chi_{||c}$  indicates strong anisotropy below  $T_N$ . Such behavior suggests that the easy in  $\text{Co}_{1/4}\text{TaSe}_2$  is along the  $c$ -axis. At room temperature  $\chi_{||c}$  is greater than  $\chi_{||ab}$ , and this anisotropy resembles that of pristine 2H-TaSe<sub>2</sub> [22]. Below  $T_N$  the susceptibility  $\chi_{||ab}$  bifurcates between the ZFC and FC curves. Interestingly, the FC curve shows some degree of spin polarization

along the  $ab$ -plane. The ZFC and FC splitting in  $\chi_{||c}$  is also apparent, but the splitting is field-dependent and suppressed at higher applied fields (see Figure 3.4).

We apply as a first approximation a Curie-Weiss fit to the linear portion of the inverse magnetic susceptibility (Figure 3.3(b)). The inset in Figure 3.3(b) shows the inverse susceptibility with the field applied out of plane. The curvature in the paramagnetic region suggests some local spin order above the  $T_N$ . Due to this high-temperature anomaly, we applied the Curie-Weiss law only to the inverse of  $\chi_{||ab}$ . The negative Weiss temperature of  $\Theta_{CW} = -3914(17)$  K indicates that the paramagnetic regime does not follow the Curie-Weiss law. Likely temperature-independent Pauli paramagnetism must also be added to correct for the abnormally large  $\Theta_{CW}$ . Still, we extract a Curie constant of  $C = 2.05(1)$  K emu/Oe-mol and an effective magnetic moment of  $\mu_{\text{eff}} = 4.05(1) \mu_B$ . This value is slightly greater than the calculated value for  $\text{Co}^{2+}$  ( $d^7$ ) in the high-spin state ( $S = \frac{3}{2}$ ,  $\mu_{\text{eff}} = 3.88 \mu_B$ ). A high spin state for  $\text{Co}^{2+}$  would be consistent with previously observed cobalt intercalated  $\text{NbS}_2$  and  $\text{TaS}_2$ . [23, 65] A caveat here is that the heavier selenide may alter the ligand field strength compared to sulfide and therefore the spin-state of cobalt.

In order to reveal any subtle uncompensated magnetization within the  $ab$ -plane, we subtracted an antiferromagnetic component from the  $M - H$  curves at 2 K and 200 K. As shown in c, blocking of the  $M - H$  curve is apparent at 2 K, and the remnant magnetization at 2 K significantly increases compared to the 200 K. Switching the field direction reveals a soft hysteresis curve that saturates at  $\Delta M = 0.000183 \mu_B$  per formula unit (Figure 3.3(e)). Due to the anisotropic character of this phenomenon, we attribute this observation to be intrinsic to the title compound. Such noncollinear antiferromagnetism has been observed before in related TMDs and implicated in the anomalous Hall effect. [63, 147–150] We explore such phenomena in  $\text{Co}_{1/4}\text{TaSe}_2$  in the next section.

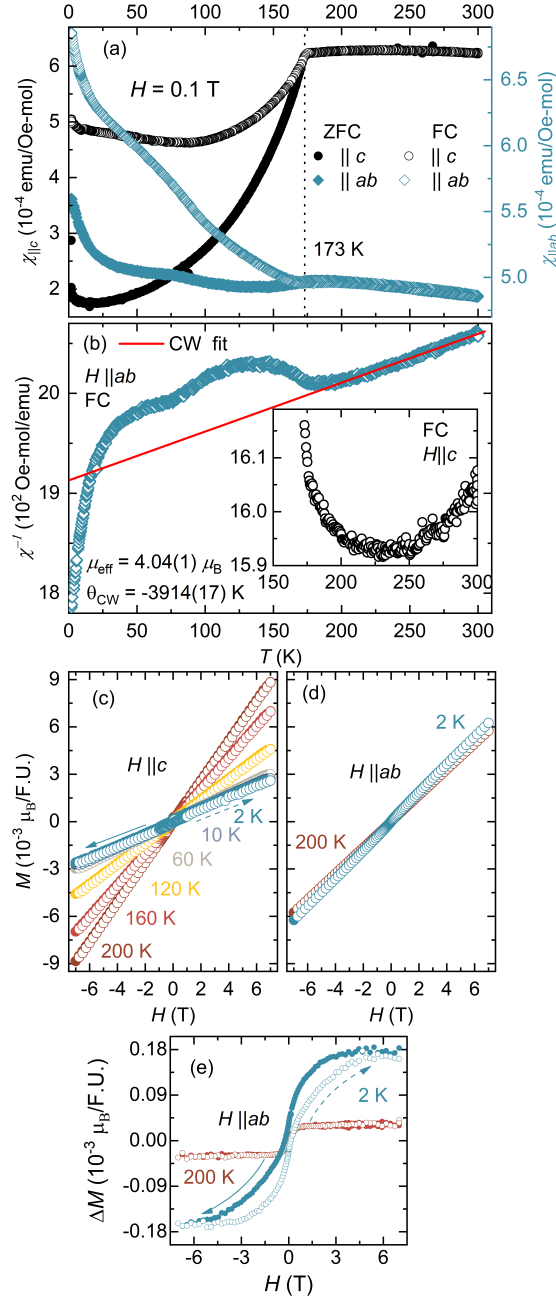


Figure 3.3: (a) Temperature-dependent ZFC and FC molar magnetic susceptibility with an applied field of  $H = 1$  kOe parallel to the  $c$ -axis and  $ab$ -plane. (b) Inverse magnetic susceptibility with field applied in the  $ab$ -plane fitted to the Curie-Weiss law. The inset shows the non-linearity of the inverse susceptibility with the field applied along the  $c$ -axis. (c) Magnetization isotherms with field along the  $c$ -axis and (d) the  $ab$ -plane. (e) FM component of (d) obtained by subtracting an AFM background slope.

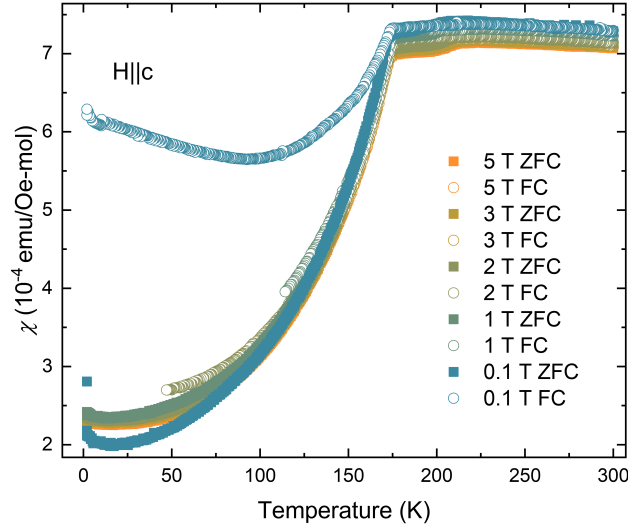


Figure 3.4: Magnetic susceptibility in various fields from 0.1 T to 5 T. No significant differences among the temperature sweeps at higher fields are observed above 1 T.

### 3.3.4 Transport and magnetotransport properties

With the magnetic properties determined, we proceed to characterize the electrical transport properties of  $\text{Co}_{1/4}\text{TaSe}_2$ . The low-temperature resistivity collected from 2 K to 300 K is shown in Figure 3.5(a) at 0 T and 14 T applied field strengths. The resistance was measured in-plane with the magnetic field applied out of the plane. There are no noticeable differences upon measuring under ZFC or FC conditions. In the paramagnetic state at higher temperatures ( $> 173$  K),  $\rho(T)$  has a linear trend and its slope is not altered immediately below  $T_N$ . Upon further cooling, however, the slope becomes noticeably steeper below 150 K, which is more noticeable in the derivative  $d\rho/dT$  (Figure 3.5(a)). Such a decrease in the resistivity is expected due to the reduction of electron scattering granted by long-range magnetic order.[31, 119] The resistivity does not change much with an increase in the applied field to 14 T below  $T_N$  (inset of Figure 3.5(a)). These magnetotransport results entail that long-range antiferromagnetism arises from electrons near the Fermi surface in  $\text{Co}_{1/4}\text{TaSe}_2$ .

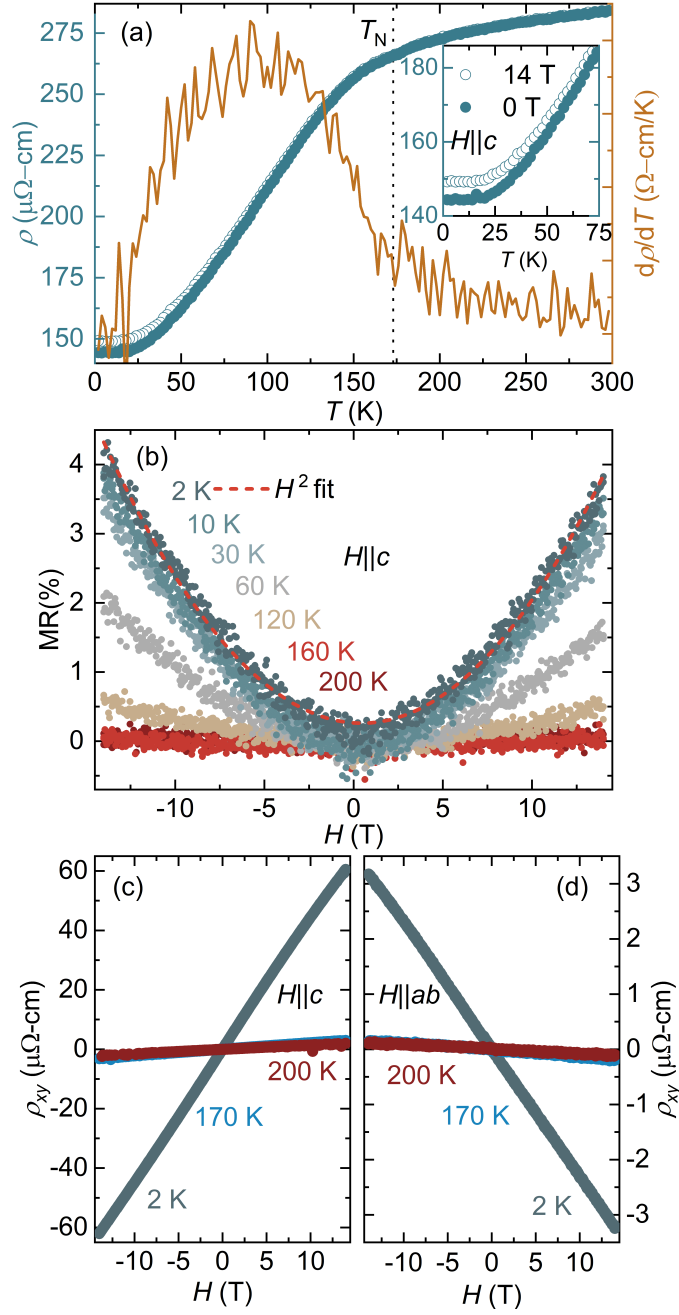


Figure 3.5: Magnetotransport measurements of  $\text{Co}_{1/4}\text{TaSe}_2$ . (a) Temperature dependence of the resistivity at 0 T and 14 T with current applied in the  $ab$ -plane. The inset highlights the low-temperature region of the resistivity. (b) Field-dependant magnetoresistance at various temperatures. (c) Transverse resistivity showing Hall effect with field applied along the  $c$ -axis (d) and the  $ab$ -plane providing the planar Hall effect.



Past studies have demonstrated that the metallic character of Ta-based TMDs decreases when cations are intercalated into their vdW gaps.[65, 151] In the present case, the metallic character follows this same trend since  $\text{Co}_{1/4}\text{TaSe}_2$  is less conductive than the pristine host[151, 152]. The residual resistivity ratio ( $\text{RRR} = \rho_{300\text{K}}/\rho_{2\text{K}}$ ) of our single crystal sample is 1.97 and its residual resistivity ( $\rho_0$ ) is  $144.3 \mu\Omega\text{-cm}$ .

Iwaya *et al.*, have noted that the magnitude of the RRR in  $2\text{H-NbSe}_2$  correlates to the prominence of the CDW ordering transition.[153] Samples with  $\text{RRR} > 10$  exhibit a stronger CDW appearance during resistivity measurements. This value can be used as an indirect way to estimate the completeness of the CDW order. At  $T < T_N$ , the resistivity contributions should be minimized providing a higher RRR in  $\text{Co}_{1/4}\text{TaSe}_2$ . However, if spin fluctuations persist down to low temperatures in  $\text{Co}_{1/4}\text{TaSe}_2$  such contributions to the resistivity remain present. Overall, the low RRR in  $\text{Co}_{1/4}\text{TaSe}_2$  below the AFM transition likely makes the emergence of CDW unlikely.

Further exploring the field dependence of the resistivity, we measured magnetoresistance (MR) from 2 K to 200 K and up to an external field strength of 14 T (Figure 3.5(b)). The MR curves obtained as  $\text{MR} = [\rho(H) - \rho(0)]/\rho(0) \times 100$  show an appreciable change only below 120 K instead of 160 K and below. This surprising result in the MR change stands in distinction to the  $M$  vs.  $H$  curves (Figure 3.3(c)) where a response or change in slope was more perceptible closer to the  $T_N$  of 173 K.

According to Kohler's rule, the MR should vary proportionally to the square of the applied magnetic field multiplied by the scattering time for a conventional metal. By plotting the MR vs.  $H/\rho_0$ , we did not observe this field dependency in the present sample (see Figure 3.6). Hence, we attribute the increase in MR effect to long-range magnetic order, where the MR reaches 4% at 2 K with no significant changes up to 30 K.

The MR response in  $\text{Co}_{1/4}\text{TaSe}_2$  is notably different from that of the isostructural  $\text{Fe}_{1/4}\text{TaSe}_2$  and  $\text{Ni}_{1/4}\text{TaSe}_2$ , which are both ferromagnets.[61, 68] Unlike  $\text{Fe}_{1/4}\text{TaSe}_2$ [138]

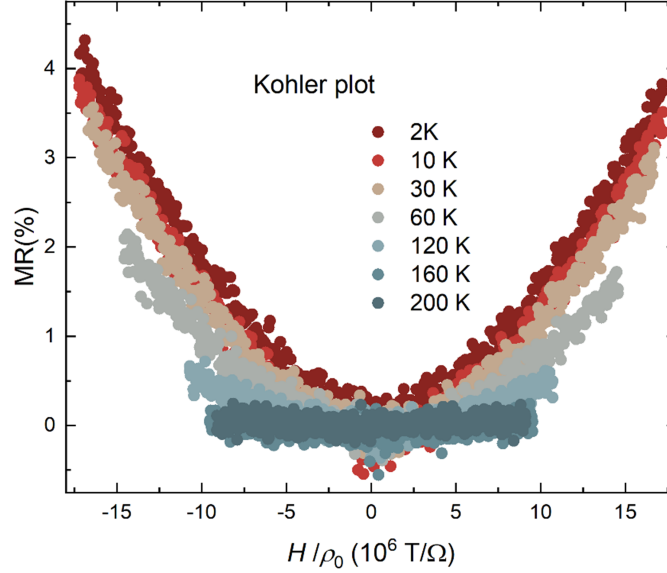


Figure 3.6: Magnetoresistance showcased in a Kohler plot where MR is plotted against the field over the resistance at zero field in the respective temperature.

and  $\text{Fe}_{1/4}\text{TaSe}_2$ [61], the MR in  $\text{Co}_{1/4}\text{TaSe}_2$  never exhibits any switching in sign of the MR upon reaching a critical field strength. Instead, it displays a quadratic response despite the field being aligned along the easy axis up to 14 T. The contrasting behavior between the Fe, Co, and Ni analogs is direct evidence of the influence of the intercalated magnetic ion over the exchange interactions affecting long-range magnetic order and consequently the electronic behavior.

We now present our exploration of whether  $\text{Co}_{1/4}\text{TaSe}_2$  expresses the anomalous Hall effect as found in other TMD systems. The transverse resistance in Figure 3.5(c) shows the Hall effect measurements with the field parallel to the  $c$ -axis. The anomalous Hall effect can be expressed as  $\rho_{xy} = R_H(B) + R_A(M)$  in ferromagnetic materials, where the first term denotes the ordinary Hall effect caused by the Lorentz force acting on the charge carriers; the second term expresses the anomalous contributions that generally originate from the internal magnetic order. Although there is a minimal linear deviation that may be caused by the interaction of the carriers and the magnetic order, we do not find a significant anomalous

contribution.

The Hall effect measurements do yield other important aspects of  $\text{Co}_{1/4}\text{TaSe}_2$ . The positive slope of  $\rho_{xy}$  signifies hole-type carriers. We obtain the charge carrier density with  $n = 1/R_H$ , resulting in  $n_{2K} \approx 1.4 \times 10^{22}/\text{cm}^3$ ,  $n_{170K} \approx 2.8 \times 10^{23}/\text{cm}^3$ , and  $n_{200K} \approx 4.0 \times 10^{23}/\text{cm}^3$ . The decrease in carrier density upon cooling suggests a reduction in the Fermi surface induced by the development of antiferromagnetic order.

Although we did not find an anomalous contribution to the Hall effect, we must issue a caveat on the limitations of our measurement. The easy axis is along  $c$ , and we encountered sample geometry limitations to measure the conventional Hall effect along this easy axis. We thus measured the planar Hall effect with current perpendicular to the field as shown in Figure 3.5(d). Overall, the present sample does not display any additional contributions from the ordinary Hall effect in this configuration. Other intercalated TMDs such as  $\text{Mn}_{1/4}\text{NbS}_2$ , however, afford complex anomalous Hall effect contributions below the transition temperature with in-plane ferromagnetic moments[52].

### 3.3.5 Specific heat and magnetic entropy analysis

To better characterize the contributions of the AFM order on the specific heat of  $\text{Co}_{1/4}\text{TaSe}_2$ , we analyze the electronic and phonon contributions as well. The temperature dependence of the specific heat  $C_p(T)$  is shown in Figure 3.7(a). The high-temperature region of the  $C_p(T)$  approaches the classical Dulong-Petite value  $3NR = 81 \text{ J mol}^{-1} \text{ K}^{-1}$ , where  $R$  is the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $N$  is the number of atoms. A characteristic second-order transition peak is observed at  $T_N \approx 173 \text{ K}$  belonging to the emergence of the AFM order.

The inset in Figure 3.7(a) shows the low-temperature region of the specific heat and a fit to a general polynomial function to obtain the electronic and vibration contributions. The

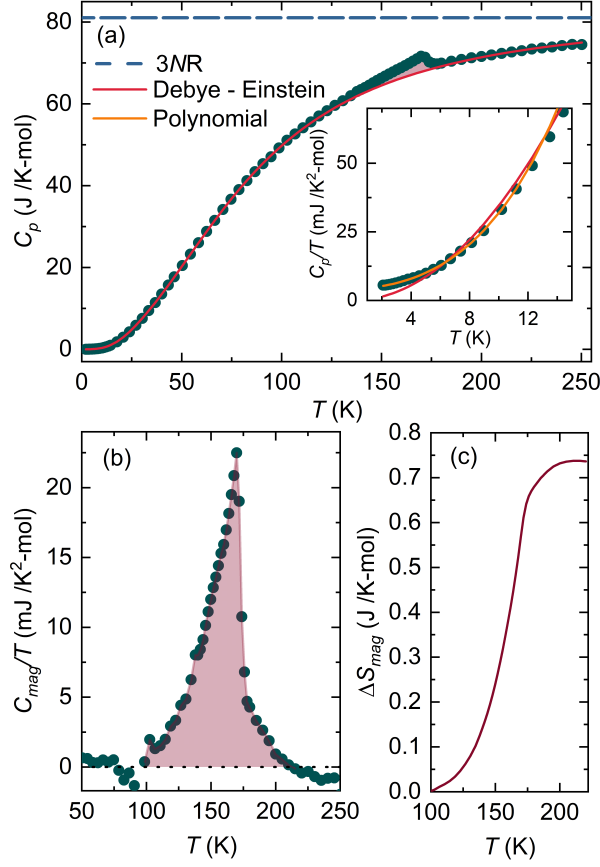


Figure 3.7: Specific heat measurement of  $\text{Co}_{1/4}\text{TaSe}_2$ . (a) Specific heat fitted to the Debye-Einstein model and a general polynomial in the low-temperature region (inset). The inset is plotted in  $C_p/T$  showing the deviation from both models. (b) Magnetic specific heat. The shaded area indicates the integrated region used to obtain (c) the magnetic entropy from 100 K to 220 K.

crossover temperature where the electronic specific heat becomes greater than that of the lattice is seen at 5 K. Therefore, the low-temperature region from 2 K to 12 K was fit with  $C_p/T = \gamma + \beta T^2 + \delta T^4$ , where the electronic contributions are given by the Sommerfeld coefficient  $\gamma = 4.38(8) \text{ mJ mol}^{-1} \text{K}^{-2}$ . The resultant  $\gamma$  is comparable to that of the host  $2\text{H-TaSe}_2$  and that of other intercalated TMDs.[16, 151, 154] The Debye temperature ( $\Theta_D$ ) in this region can be obtained from  $\beta = 0.21(3) \text{ mJ mol}^{-1} \text{K}^{-4}$  by using  $\Theta_D^{low-T} = (12\pi^4 NR/5\beta)^{1/3}$ . The resulting  $\Theta_D^{low-T} = 310(1) \text{ K}$ , although larger than in the parent compound, is similar to the sulfide counterpart.[65] Such contrast may be a consequence

of the symmetry changes caused by the increasing amount of intercalated cation amount,  $x$ . [120, 151, 155] The  $\delta$  term is added to account for the fact that the  $T^3$ -law is only valid through  $\Theta_D/50 = 6.2$  K [156] resulting in  $\delta = 6.2(2) \times 10^{-4} \text{ mJ mol}^{-1} \text{ K}^{-6}$ .

To inspect the magnetic specific heat  $C_{\text{mag}}$ , the high-temperature lattice contributions were subtracted from the total  $C_p(T)$ . We consider  $C_{\text{lattice}} = C_{\text{Debye}} + C_{\text{Einstein}}$ , where:

$$C_{\text{Debye}} = 9nR \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (3.1)$$

and

$$C_{\text{Einstein}} = 3aR \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}, \quad (3.2)$$

The best fit for the full temperature range was obtained with one Debye term giving  $\Theta_D = 190(5)$  K,  $n = 1.22(15)$ , and an Einstein term  $\Theta_E = 313(4)$  K,  $a = 2.07(6)$ , where  $N = n + a$  accounts for the total number of atoms per formula unit. The magnetic contribution to the specific heat isolated by subtracting the Einstein-Debye model is shown in Figure 3.7(b). The magnetic entropy in Figure 3.7(c) was then approximated by integrating  $\Delta S_{\text{mag}} = \int C_p(T)/T dT$  yielding  $\sim 26\%$  of the expected value for  $S = 3/2$ . This lower than expected value may indicate that the  $\text{Co}^{2+}$  cation may either not be in a high-spin configuration, or that significant magnetic fluctuations persist below the ordering temperature due to the triangular lattice. If the former, then the  $d^7$  cation in a low-spin state would yield a magnetic entropy term better described by  $S = 1/2$ . However, as we describe below in our neutron results, this low-spin argument may not be the most probable given that this diminished moment size has been observed in other related TMDs.

### 3.3.6 Neutron powder diffraction: Collinear antiferromagnetism

To elucidate the long-range magnetic structure, we conducted neutron powder diffraction analysis above and below  $T_N$ , specifically at 200 K, 120 K, and 10 K (Figure 5.9(a-c)). Based on the results from magnetic susceptibility and specific heat measurements, we observed a magnetic order transition at  $T_N = 173$  K. The emergence of magnetic Bragg reflections in the NPD patterns is discernible at 120 K and 10 K as highlighted by the dashed line in Figure 5.9(d). Two configurations of the time-of-flight diffractometer were used to cover the  $d$ -range from 0.485 Å to 13 Å and 1.07 Å to 21 Å (Figure 5.9(e)). This wide  $d$ -range was to ensure the observation of all possible magnetic reflections. In both configurations, we observed only two magnetic reflections corresponding to the (101) and (111) planes. Only the former coincides with a nuclear Bragg index as the (111) is disallowed by the systematic absences of the parent space group. Nevertheless, the magnetic unit cell coincides with that of the nuclear unit cell, and thus the magnetic propagation vector  $k = (0, 0, 0)$ .

We solved the magnetic structure in our Rietveld refinements with the NPD data by analyzing the possible magnetic symmetries provided by k-SUBGROUPMAG[102] tool from the Bilbao Crystallographic Server within GSAS-II. Of the 8 possible magnetic subgroups, the best refinement was obtained with  $P6_3'/m'm'c$  magnetic space group (No. 194.268). This magnetic order is isostructural to the sulfide-based antiferromagnets  $\text{Cr}_{1/4}\text{NbS}_2$  and  $\text{Fe}_{1/4}\text{NbS}_2$ [48, 58]. Such magnetic symmetry allows for ferromagnetic moments aligned in the  $ab$ -plane while antiferromagnetically along the  $c$ -axis (Figure 5.9(f)). The moment direction is collinear and fully along the  $c$ -direction, consistent with the magnetic susceptibility and magnetization results in Figure 3.3. This configuration is an A-type antiferromagnet with all moments collinear to the [001] direction.

The total magnetic moment obtained from neutron diffraction at 120 K is  $1.08(11) \mu_B$  and increases to  $1.35(11) \mu_B$  at 10 K per Co site. These results indicate that there is missing

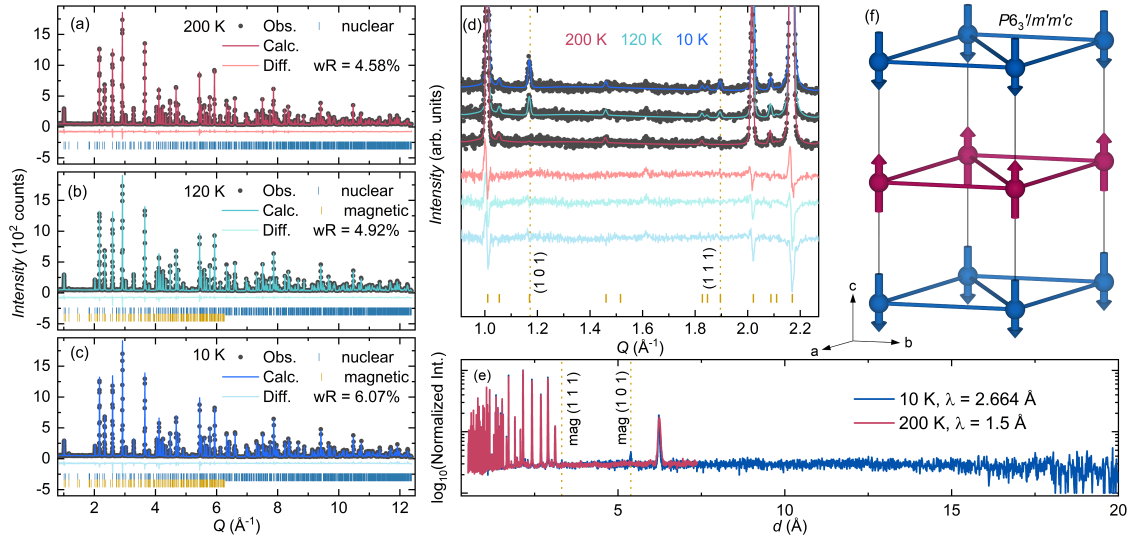


Figure 3.8: Neutron powder diffraction of  $\text{Co}_{1/4}\text{TaSe}_2$ . The data is fit using the Rietveld method at (a) 200 K, (b) 120 K, and (c) 10 K. Only a magnetic phase is added for the 120 K and 10 K datasets. (d) Low- $Q$  region of (a-c) highlighting the emerging magnetic reflections corresponding to (101) and (111). (e) absence of magnetic reflections at higher  $d$ -spacing. (f) A-type antiferromagnetic structure of  $\text{Co}_{1/4}\text{TaSe}_2$  with propagation vector  $k = (0\ 0\ 0)$ .

moment if  $\text{Co}^{2+}$  is in the high-spin state assuming that  $g = 2$  for  $\mu = g \cdot S$ . Consequently, the observed total moment is about a third of the expected  $3\ \mu_B$  for the high-spin state. Refinement of the magnetic moment in the Ta site was attempted, but the resulting moment was negligibly small and thus fixed to zero. Such phenomena where the magnetic moment is smaller than expected for the intercalated magnetic ion has been observed in other intercalated tantalum-based TMDs,[64, 67, 157] but not to the extent seen in our results. Our results in moment size match that of the sulfide analogue  $\text{Co}_{1/3}\text{TaS}_2$ , [64] where the authors also recover about a third of the expected moment. This reduction in the ordered moment for Co-intercalated Ta-based TMDS could be attributed to the metallic nature of these compounds. The interaction between a localized band due to Co and an itinerant  $5d$ -band due to Ta could lead to partial screening of the local moments. As mentioned earlier in the discussion of the specific heat measurements, another possible explanation could include quantum spin fluctuations due to the frustrated triangular sublattice of the

Co cations. Both explanations are worth pursuing with more studies that include inelastic neutron scattering.

Finally, the temperature-dependent NPD patterns allowed us to search for possible CDW formation in  $\text{Co}_{1/4}\text{TaSe}_2$ . At all temperatures, no indication of CDW ordering was found as known to occur in the parent 2H-TaSe<sub>2</sub>[17, 158]. The nuclear structure could be fully fit with the centrosymmetric hexagonal structure ( $P6_3/mmc$ ), consistent with the single crystal XRD results. The refined lattice parameters from neutron diffraction are  $a = 6.88155(7)$  Å and  $c = 12.45907(8)$  Å at 200 K decreasing to  $a = 6.87637(8)$  Å and  $c = 12.43289(9)$  Å at 10 K. Notably, the Co-Co distance is shorter along the  $c$  direction than along the interplanar direction. This interplanar distance is further shortened at lower temperatures. The contraction reduces the Co-Ta distance by  $0.0065(4)$  Å from 200 K to 10 K. This reduction in proximity could have implications on the orbital overlap between metal centers. We now discuss the electronic structure and how it could be responsible for an itinerant AFM ground state in  $\text{Co}_{1/4}\text{TaSe}_2$ .

### 3.4 Itinerant A-type AFM origins

Based on the smaller than expected value of the ordered magnetic moment from NPD and specific heat measurements, we can surmise that the emergent magnetic order is tied to the itinerant nature of  $\text{Co}_{1/4}\text{TaSe}_2$ . The absence of a substantial amount of magnetic entropy from Figure 3.7(c) contributes to the idea that the  $3d$  electrons of cobalt should not be considered entirely localized[159]. It is understood that the intercalated ions strongly donate electrons into the Ta  $5d_{z^2}$  conduction band[32, 91, 160]. Furthermore, when the intercalated ion is a first-row transition metal, its own  $d$ -orbitals hybridize substantially with the Ta  $d_{z^2}$  band. In the case of  $\text{Co}^{2+}$ , we find an expected  $\mu_{\text{eff}}$  close to that of  $S = 3/2$ , but the abnormally large  $|\Theta_{\text{CW}}|$  points to the  $\chi$  having a large Pauli paramagnetic contribution,



which further supports the notion of delocalized magnetism.

Since  $\text{Co}_{1/4}\text{TaSe}_2$  and its sulfide analog are structurally similar, the main exchange pathways are expected to be similar. Their energies, however, are obviously different enough to lend to two distinct ground states. While the sulfur counterpart has been reported to present ferromagnetic interactions[65, 130], we have observed the present composition to have an AFM order with an easy axis along the [001] direction. A key reason for this distinction may be the non-centrosymmetric spacegroup in which  $\text{Co}_{0.22}\text{TaS}_2$  crystallizes, leading to various types of coupling, most importantly the Dzyaloshinskii–Moriya interaction[25]. Provided that the  $5d_{z^2}$  orbital is effectively hybridized with the Co  $3d$  in  $\text{Co}_{1/4}\text{TaSe}_2$ , it would imply a stronger one-dimensional character propagating in the vertical direction, reducing the dimensionality of the strong interactions.

The partial density of states calculation in Figure 3.9 corroborates these arguments and is comparable with the experimental XPS near the Fermi edge. The valence bands close to the Fermi level (-0.44 eV) are predominantly those belonging to the  $d$  orbitals of Co and  $d_{z^2}$  of Ta. The Co and Ta vertical arrangement supports the argument that the exchange interaction between the Co magnetic ions is mediated along the vertically orientated  $d_{z^2}$  orbital[161]. This band overlap is likely strengthened as a function of lattice contraction observed in comparing the  $c$  lattice parameter from neutron diffraction at high (200 K) vs low temperatures (10 K).

In the case of the sulfur analog, the ferromagnetic exchange mechanism is of the RKKY interaction type[130]. Such interaction is mediated by the conduction electrons[64] and it is therefore equally likely to fit the present case. Here we find a ferromagnetic coupling in plane and antiferromagnetic interaction out of plane. Selenium thus plays an important role in the exchange mechanism.

What is interesting to consider is why  $\text{Co}_{1/4}\text{TaSe}_2$  is an A-type itinerant antiferromagnet while  $\text{Fe}_{0.25}\text{TaSe}_2$  and  $\text{Ni}_{0.25}\text{TaSe}_2$  are ferromagnets. In the RKKY mechanism, the distance

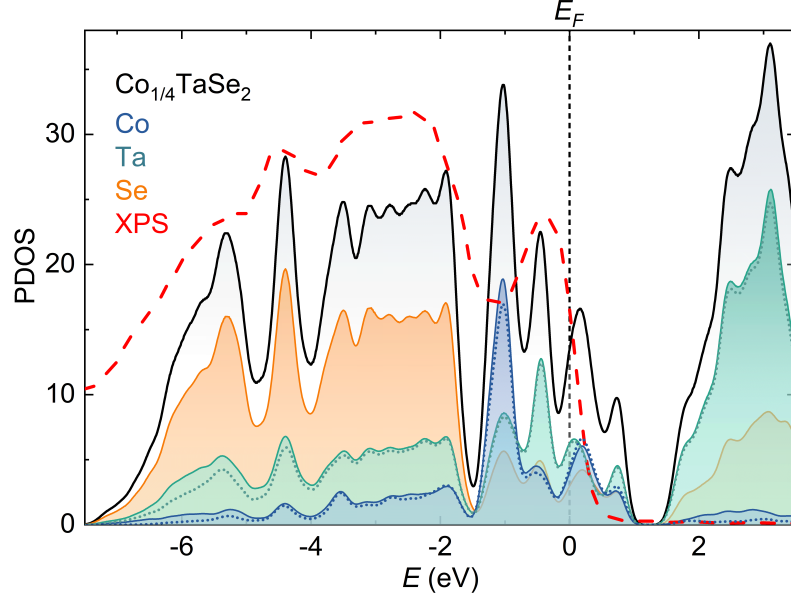


Figure 3.9: Non-magnetic partial density of states. The black curve shows the total density of states of  $\text{Co}_{1/4}\text{TaSe}_2$  which resembles that of the experimentally observed states through XPS (red dashed curve). The dotted lines indicate the contributions from the Co  $3d$  (blue) and Ta  $5d$  orbitals (green). The overestimated bands at  $-1.0$  eV belong primarily to all the Co  $3d$  orbitals except  $d_{z^2}$ .

variable in energy expression determines the nature of the magnetic ground state[25, 33, 34]. Within the intercalated  $\text{TaSe}_2$  layers, the  $a$ -axis remains largely unaffected ( $\sim 6.88$  Å). Therefore, the fixed intraplanar distance leads to ferromagnetic coupling within the triangular sublattice regardless of whether the intercalated ion is Fe, Co, or Ni. However, comparing the  $c$ -axis of  $\text{Co}_{0.25}\text{TaSe}_2$  ( $c = 12.4791(8)$  Å) to that of the ferromagnets  $\text{Fe}_{0.25}\text{TaSe}_2$  ( $c = 12.7394(2)$  Å) and  $\text{Ni}_{0.25}\text{TaSe}_2$  ( $c = 12.506(5)$  Å), we find that the *interplanar* metal-metal distance is the shortest for the present compound. The out of plane Co–Co distances is below a critical distance to flip the exchange coupling from ferromagnetic to antiferromagnetic along the  $c$ -direction. Despite its different ground state compared to closely related compounds,  $\text{Co}_{1/4}\text{TaSe}_2$  exhibits magnetic behavior consistent with other metallic TMDs whereby the conduction electrons interact strongly with the isolated spins and mediate exchange mechanisms.[26, 64, 65, 67, 76]

Finally, the long-range magnetic order does not seem to be related to the CDW that the vacant host lattice presents. Intercalating metal cations into the vdW gap of the host TMD disrupts the charge ordering likely formed from lattice distortions rather than Fermi surface nesting[116, 152, 162]. We do not, however, discard the possibility of such phenomena being found in an interplay with the magnetic ions. We speculate this is unlikely as the long-range magnetic order emerges at a higher temperature than the CDW suppressing its emergence.

### 3.5 Conclusion

In summary, we have grown single crystals of  $2\text{H-Co}_{1/4}\text{TaSe}_2$  and characterized the physical and magnetic properties of this novel intercalated transition metal dichalcogenide. Our measurements and analysis reveal the antiferromagnetic nature of  $\text{Co}_{1/4}\text{TaSe}_2$  with collinear *A*-type antiferromagnetic order along the *c*-axis. We observe that there is a significant deficit of magnetic moment and entropy of the localized Co *3d* orbitals. This is best explained via an interplay between cobalt's *3d* orbitals and the itinerant electrons of Ta ions, which dominates the interaction with neighboring Co captured by our electronic density of states calculations. Deeper theoretical work is needed to provide insight into the origin of the itinerant antiferromagnetism. Our study on the Hall effect measurements reveals an ordinary behavior inherent to a classical metal expected from a traditional collinear AFM.

Since  $\text{Co}_{1/4}\text{TaSe}_2$  is a new itinerant antiferromagnetic, we checked its spin order to see if it qualifies as a potential altermagnet. The nuclear symmetry in conjunction with the magnetic structure obtained from NPD was used in the program Amcheck[163], which is a symmetry analysis program to search for potential altermagnets. The Amcheck program indicates that  $\text{Co}_{1/4}\text{TaSe}_2$  is an altermagnet candidate. The nuclear and magnetic symmetry, as well as the observation of an in-plane ferromagnetic component, suggest that the title

compound be further investigated as an altermagnet.

## Chapter 4: Coexistence of Commensurate and Incommensurate Antiferromagnetic Groundstates in $\text{Co}_x\text{NbSe}_2$ Single Crystal

The work described in this chapter was published in *Physical Review Materials*. Hector Cein Mandujano, Peter Y. Zavalij, Alicia Manjon-Sanz, Huibo Cao, and Efrain E. Rodriguez were contributing authors. H.C.M. prepared the samples, performed MPMS and PPMS measurements, H.C.M. and P.Y.Z. solved the single crystal structure, H.C.M. and A.M.S. collected neutron powder diffraction data and H.C.M with H.C. collected single crystal neutron diffraction data.

### 4.1 Introduction

In transition metal dichalcogenides (TMDs) of the 2H-type, the electronic properties are intrinsically linked to the symmetry of the system. For the TMDs intercalated by magnetic 3d-metals, the concentration determines the structure and magnetic order. Depending on the intercalation level, these systems can adopt one of two distinct space groups, each associated with a specific phenomenon. When the intercalant concentration is  $x \sim 1/4$ , the system exhibits a centrosymmetric space group  $P6_3/mmc$ . In this configuration, the intercalated  $M$  ions form a  $2a_h \times 2a_h$  sublattice, where  $a_h$  is the unit cell length of the host  $\text{TMQ}_2$  along the  $a$ -axis. This symmetry strongly influences the magnetic structure, leading to one set of magnetic correlations and higher transition temperatures ( $T_N$ ) [25, 26, 49, 118, 120, 164–

166]. For ratios closer to  $x \sim 1/3$ , the structure is non-centrosymmetric and chiral ( $P6_322$ ), with intercalated ions arranged in a  $\sqrt{3}a_h \times \sqrt{3}a_h$  sublattice. This distinct symmetry leads to a different set of magnetic and structural properties, often associated with lower  $T_N$  values and different magnetic ordering [25, 57, 138]. Furthermore, at the higher intercalation ratio limit, the magnetic interactions are extremely sensitive to the intercalant occupancy displaying an array of complex magnetic structures[47, 55, 76, 167]. These well-defined symmetries play a critical role in determining the phase transitions and coexistence of multiple orders.

The chemical composition or the ratio of intercalated magnetic ions to TMD host can be crucial in determining the structure and magnetic phase[118]. In layered materials, phase separation due to stacking sequence, faults, or layer disorder is common, with layers accommodating various structural configurations[127, 168]. For instance, in  $\text{CrI}_3$ , three magnetic transitions coexist, defined by structural changes and phase separation [169, 170]. In such cases, each layer and its interaction with neighboring layers can be considered a single domain, creating a localized environment that affects the overall physical properties [171, 172]. However, unexpected phenomena can emerge when structural discrepancies propagate between layers, as in interplanar domain ordering, further complicating the magnetic and structural behavior.

Coexisting order parameters, such as charge density waves (CDWs) and magnetic transitions, attract interest due to their potential applications in spintronics, particularly properties of exchange bias [173, 174]. In TMDs intercalated with magnetic ions, the interaction between these coexisting phases and the material's ground state, defined by site occupation and antiferromagnetic spin configuration, can lead to exchange bias and other novel properties [83, 175].

A canonical example of a TMD hosting both superconductivity and a CDW is pristine  $2\text{H-NbSe}_2$ , which undergoes a superconducting transition at 7 K and a CDW transition at 31

K [5, 176, 177]. Intercalating 3d metal ions into the van der Waals (vdW) gaps of NbSe<sub>2</sub> has further expanded the plethora of magnetic phenomena, offering new platforms for studying phase competition and coexistence [120, 177, 178].

In this work, we revisit Co<sub>x</sub>NbSe<sub>2</sub>, previously studied by Voorhoeve et al. [49], and is recently being proposed as an A-type altermagnet for  $x = 1/4$  by Regmi et al.[74, 179]. Our single-crystal studies focus on Co<sub>0.28</sub>NbSe<sub>2</sub> containing both sublattices, from which we exclusively observe the magnetic phase associated with the  $x \sim 1/4$  ratio through single-crystal neutron diffraction. We provide novel insights into the magnetic structure of Co<sub>1/3</sub>NbSe<sub>2</sub> for the first time using neutron powder diffraction. Through these structural measurements, we explore these magnetic transitions and their coexistence, deriving the magnetic structures using irreducible representation analysis.

## 4.2 Experimental Methods

### 4.2.1 Synthesis

We synthesized powder samples of Co<sub>x</sub>NbSe<sub>2</sub> with nominal compositions of  $x = 1/3$  and  $x = 1/4$  by mixing elemental powders in molar ratios of 1.15:3:6 and 1:4:8, respectively. The mixed powders were vacuum-sealed in fused silica tubes and annealed at 900 °C for 5 days. Phase formation and purity were verified via the Rietveld method on the powder X-ray diffraction using GSAS-II[134]. For crystal growth, we aimed to obtain Co<sub>1/3</sub>NbSe<sub>2</sub> via chemical vapor transport (CVT), using 3.5 mg/mL of I<sub>2</sub> as the transport agent and the corresponding powder as the charge source. The CVT was carried out in a 12.5 cm long ampule with an inner diameter of 14 mm. The vacuum-sealed ampule was placed in a single-zone furnace with a natural temperature gradient of 80 °C; the heating profile was a one-step heating ramp to 875 °C at the hot zone and 815 °C at the cold growth end. This temperature was maintained for 10 days before allowing the furnace to

naturally cool. Despite compensating for cobalt loss due to the formation of  $\text{CoI}_2$  by adding excess cobalt powder during vapor transport, the resulting composition consistently yielded  $\text{Co}_{0.28\pm\delta}\text{NbSe}_2$ .

Single crystals of isolated  $\sqrt{3}a_h \times \sqrt{3}a_h$  domain phase were grown under the same CVT conditions. However, instead of using  $\text{I}_2$  as the transport agent, we used  $\text{NbCl}_4$  at a 1:1 mol conversion ratio based on I:Cl. Furthermore, the charge powder was prepared in a 1.2:3:6 ratio. This is 5% more than the previous sample. As a control, we replicated this growth with  $\text{I}_2$  as well.

#### 4.2.2 Elemental Analysis and Phase Identification

We verified the composition of the crystals using single-crystal X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDS). We used several crystals of the same batch in the EDS analysis compiled in Table 4.1 using a Hitachi SU-70 FEG scanning electron microscope.

Table 4.1: EDS composition results of  $\text{Co}_x\text{NbSe}_2$  crystals and powders

| Atom (%)    | $\text{Co}_{0.28}\text{NbSe}_2$ single crystal |                |                |                | Powder                         |                                |
|-------------|------------------------------------------------|----------------|----------------|----------------|--------------------------------|--------------------------------|
|             | 1                                              | 2              | 3              | 4              | $\text{Co}_{1/3}\text{NbSe}_2$ | $\text{Co}_{1/4}\text{NbSe}_2$ |
| Co          | $8.25\pm0.18$                                  | $8.78\pm0.18$  | $8.87\pm0.18$  | $8.81\pm0.18$  | $9.89\pm0.28$                  | $7.90\pm0.23$                  |
| Nb          | $30.29\pm1.34$                                 | $31.69\pm1.28$ | $31.45\pm1.27$ | $31.47\pm1.28$ | $29.57\pm1.32$                 | $30.68\pm1.33$                 |
| Se          | $61.46\pm3.21$                                 | $59.53\pm1.42$ | $59.67\pm1.42$ | $59.71\pm1.42$ | $60.53\pm3.06$                 | $61.42\pm3.02$                 |
| Co/Nb ratio | 0.272                                          | 0.277          | 0.282          | 0.280          | 0.334                          | 0.258                          |

Magnetic susceptibility and bulk property measurements were performed using a Quantum Design magnetic properties measuring system and a Dynacool physical property measuring system, respectively. Electrical transport was done using 4-probes.

The nuclear structure was determined through single-crystal X-ray diffraction with SHELXT program and refined in the SHELXL[131, 132]. Single-crystal neutron diffraction experiments on  $\text{Co}_{0.28}\text{NbSe}_2$  were conducted at the DEMAND (HB-3A) beamline with



$\lambda = 1.546 \text{ \AA}$  at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL)[180]. Neutron powder diffraction experiments for  $\text{Co}_x\text{NbSe}_2$  with  $x = 1/3$  and  $x = 1/4$  were performed at the POWGEN (BL-11A) beamline with  $\lambda = 1.5 \text{ \AA}$  at the Spallation Neutron Source (SNS) at ORNL [133].

### 4.3 Results and Discussion

The physical properties of  $\text{Co}_{0.28}\text{NbSe}_2$ , as shown in Figure 4.1(b-d), reveal two distinct magnetic phase transitions coexisting within a single crystal sample. Powder samples, however, indicate that each transition corresponds to a defined symmetry inherent to the intercalated cobalt ratio (refer to Figure 4.2 and 4.3). As illustrated by Figure 4.1(a), the low transition temperature ( $T_N^S$ ) is associated with the non-centrosymmetric  $P6_322$  (No. 182) symmetry while the high transition temperature ( $T_N^A$ ) pertains to the higher symmetry and centrosymmetric  $P6_3/mmc$  (No. 194). The  $T_N^A$  transition is observable only in the  $\chi||c$  configuration (Figure 4.1(b)), indicating a strong anisotropy and defining the antiferromagnetic easy axis for this phase. In the case of  $T_N^S$ , the transition is visible in both applied field directions, indicating distinct magnetic interactions.

We only show the ZFC data of the magnetic susceptibility for  $\text{Co}_x\text{NbSe}_2$  for  $x = 1/6$ ,  $1/4$ , and  $1/3$  powders in Figure 4.3 as we observed minimal bifurcation below  $T_N$  between ZFC and FC measurements. We fit the susceptibility above the transition temperature to the Curie-Weiss law with the addition of a temperature-independent term  $\chi_0$ :

$$\chi = \chi_0 + \frac{C}{T + \theta_{CW}} \quad (4.1)$$

where  $C$  is the Curie constant,  $\theta_{CW}$  is the Weiss temperature, and the temperature-independent term incorporates the diamagnetic and Pauli susceptibility ( $\chi_0 = \chi_d + \chi_P$ ). Notably,  $\chi_0$  increases as more intercalant is added. Considering that the diamagnetic term

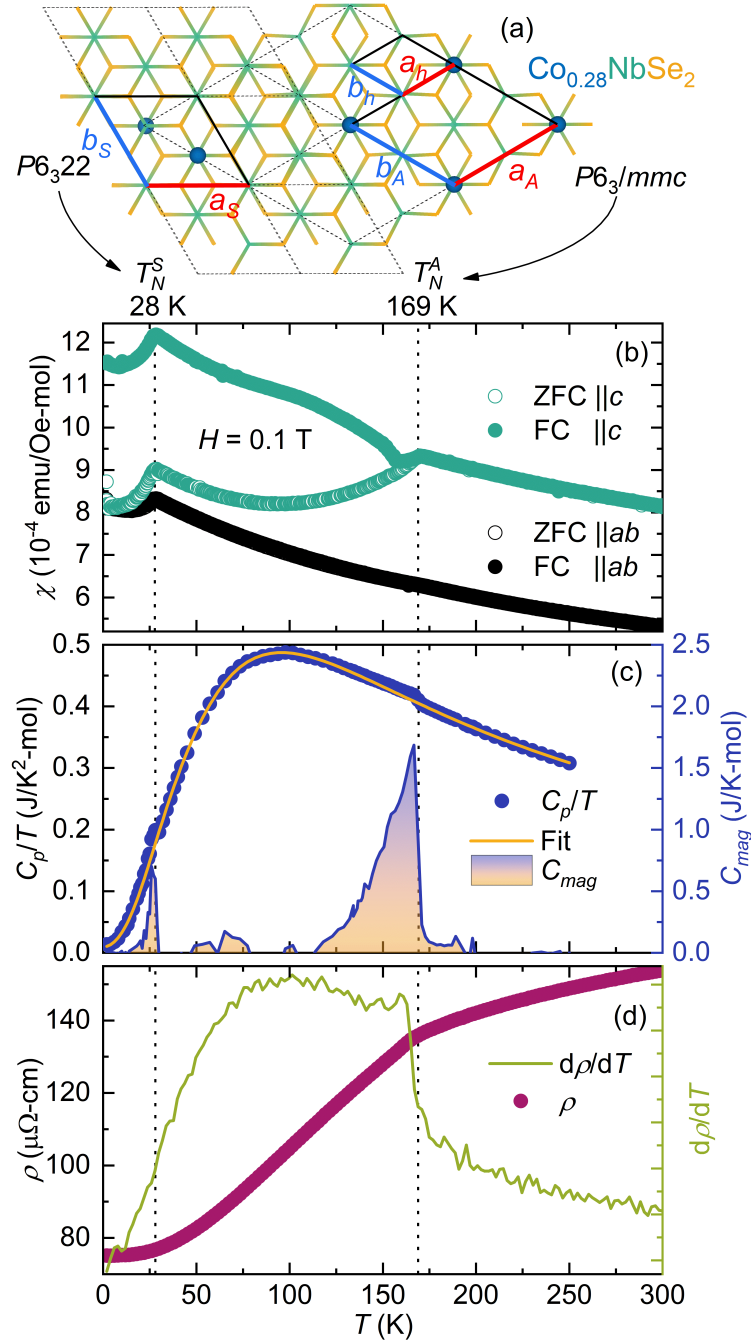


Figure 4.1: Structure association to bulk properties of  $\text{Co}_{0.28}\text{NbSe}_2$ . (a) Layered 2H-polytype of  $\text{NbSe}_2$  host lattice viewed along the  $c$ -axis with  $a_h \approx 3.44 \text{ \AA}$ . On the left is the noncentrosymmetric  $P6_322$  where  $a_s = \sqrt{3}a_h \times \sqrt{3}a_h$ . To the right is the centrosymmetric  $P6_3/mmc$  where  $a_A = 2a_h \times 2a_h$ . These cobalt arrangements originate the distinct magnetic phases observed in the directional zero field-cooled and field-cooled magnetic susceptibility (b) with field applied out of plane (green) and in-plane (black). (c) Specific heat over temperature (blue) and Debye-Einstein fit (yellow); the subtraction provides the net magnetic specific heat. (d) Resistivity (red) and its derivative (light green).

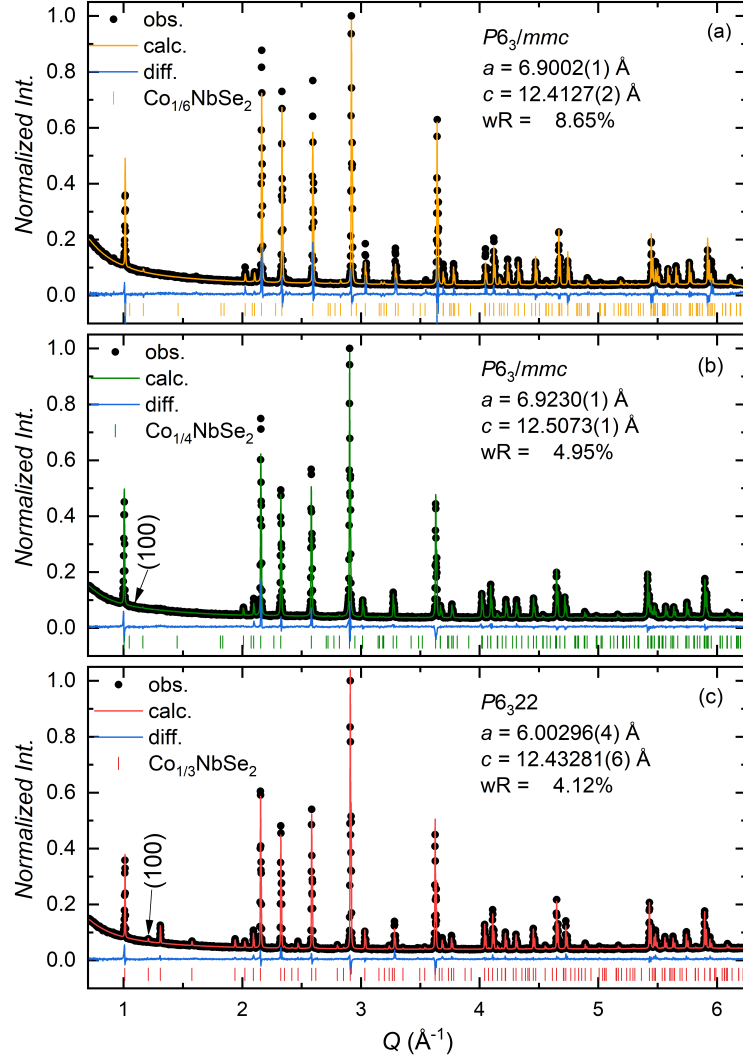


Figure 4.2: Laboratory powder X-ray diffraction of (a)  $\text{Co}_{1/6}\text{NbSe}_2$ , (b)  $\text{Co}_{1/4}\text{NbSe}_2$ , and (c)  $\text{Co}_{1/3}\text{NbSe}_2$ . The data was collected using a  $\text{CuK}\alpha$  source. Both intercalated ratios where  $x < 1/3$  refine in the centrosymmetric  $P6_3/mmc$  spacegroup. The absence of the (100) reflection indicates cobalt site disorder, therefore disrupting the full occupancy of the  $2a \times 2a$  superlattice.

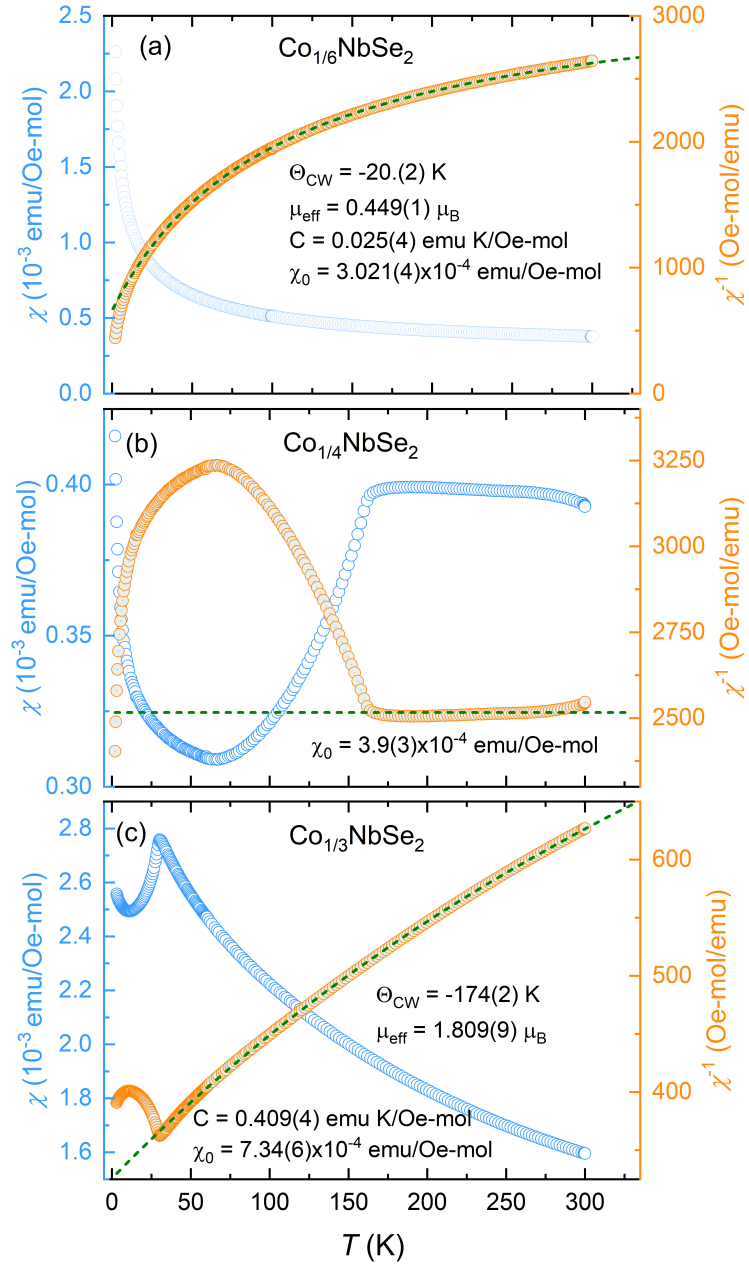


Figure 4.3: Magnetic susceptibility and inverse magnetic susceptibility of powder (a)  $\text{Co}_{1/6}\text{NbSe}_2$ , (b)  $\text{Co}_{1/4}\text{NbSe}_2$ , and (c)  $\text{Co}_{1/3}\text{NbSe}_2$ .

should be relatively constant and small, this term should shift greatly due to the insertion of electrons in the Fermi level, reflected in the Pauli paramagnetic term.

We estimate the magnetic entropy associated with each phase by subtracting the Debye-Einstein fit from the experimental specific heat data (Figure 4.1(c) and 4.4). The larger area under the  $T_N^A$  peak indicates stronger magnetic correlations in this phase. Furthermore, only  $T_N^A$  appears to influence the Fermi surface, as demonstrated by the temperature-dependent resistivity measurements. The impact is made clear through the first derivative of the resistivity (Figure 4.1(d)). The lack of a discernible response from  $T_N^S$  in resistivity does not necessarily imply that the Fermi surface remains unchanged. The sulfur analog,  $\text{Co}_{1/3}\text{NbS}_2$ , for example, has been shown to host nontrivial 2D bands in the antiferromagnetic state, observed via anomalous Hall measurements[147, 148]. We speculate that the absence of a response at  $T_N^S$  could be attributed to the dilute magnetic scattering of the  $P6_322$  domains. This aligns with observations in other intercalated systems, such as  $\text{Li}_x\text{Fe}_{1/4}\text{NbS}_2$ , where the  $\sqrt{3}a \times \sqrt{3}a$  motif domain phases are suppressed with increasing lithiation[58]. To the best of our knowledge, while structural phase coexistence in 3d-metal intercalated TMDs has also been reported recently by Xie et al.[? ], our work demonstrates well-defined magnetic transitions that can be distinctly associated with each structural phase, providing new insights into their interplay.

From Figure 4.1(a), it is clear how the rigid 2H-NbSe<sub>2</sub> framework can accommodate intercalated cobalt sites generating two distinct symmetries. Having identified both high- and low-temperature magnetic transitions, we examined the structural coexistence of these phases using single-crystal XRD. As a first approach, we solve the structure of  $\text{Co}_{0.28}\text{NbSe}_2$  in the  $P6_3/mmc$  spacegroup, with the characteristic  $2a_h \times 2a_h$  ( $a_A$ ) sublattice and unit cell dimensions of  $a_A = 6.90580(10)$  Å and  $c = 12.3630(4)$  Å. However, upon a closer inspection of the precession images (Figure 4.5(a-d)), we observe satellite reflections. These satellite reflections are indexed by the nuclear propagating vector  $q_{2S} = (1/3, 1/3, 0)$  with respect

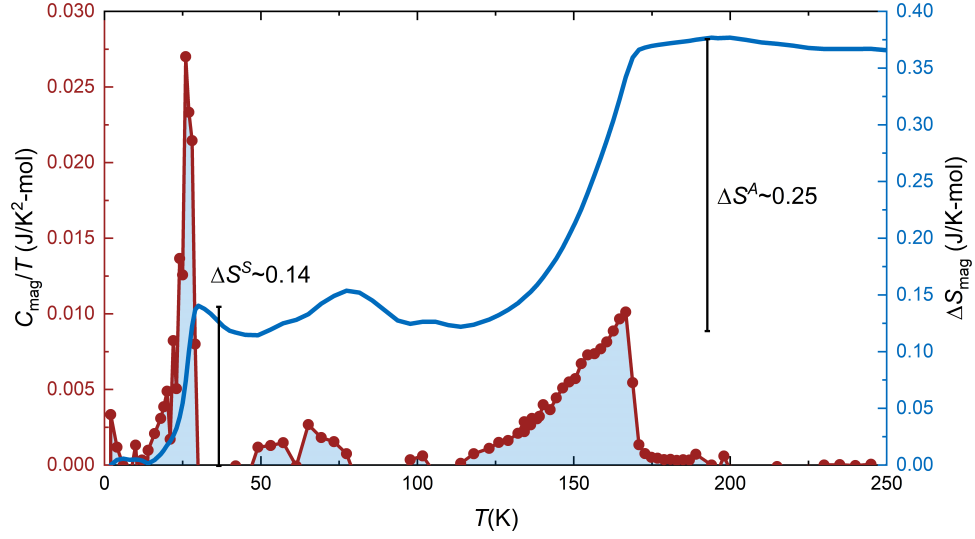


Figure 4.4: Magnetic specific heat and integrated entropy of  $\text{Co}_{0.28}\text{NbSe}_2$  single crystal. The entropy was estimated by integrating  $\Delta S = \int C_{\text{mag}}/T dT$ .

to the host unit cell. These satellite reflections can equivalently be indexed by  $q_{2S} = (2/3, 2/3, 0)$  on the basis of the  $2a_h \times 2a_h$  lattice. This larger supercell rendered in Figure 4.5(e) is solved in the  $P6_322$  space group, with twice the lattice dimensions of the  $\sqrt{3}a_h \times \sqrt{3}a_h$  cell ( $a_{2S} = 11.9622(3) \text{ \AA}$ ). This supercell allocates cobalt sites such that both the  $a_A$  ( $2a_h \times 2a_h$ ) and the  $a_S$  ( $\sqrt{3}a_h \times \sqrt{3}a_h$ ) sublattices coexist (Figure 4.5(e and f)). The Miller indices of the  $a_{2S}$  supercell and the host lattice are related by:

$$\begin{bmatrix} h \\ k \\ l \end{bmatrix}^{a_h} = \begin{bmatrix} 1/6 & 1/6 & 0 \\ -1/6 & 1/3 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} h \\ k \\ l \end{bmatrix}^{a_{2S}}$$

Where the superscripts refer to the corresponding lattice. The site occupancy and their intralayer distances significantly influence their magnetic interactions. The higher cobalt intercalation ratio disrupts spatial inversion symmetry, leading to two distinct magnetic ground states [25, 26, 121]. Despite our results, domains may not necessarily coexist in the same

layer but stacked; some layers containing  $2a_h \times 2a_h$  domains and others with  $\sqrt{3}a_h \times \sqrt{3}a_h$  appearing as both phases being superimposed. Table 4.2 contained the structural details of single-crystal X-ray diffraction solved in the  $2a_h \times 2a_h$  and  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  supercell settings.

Table 4.2: Single-crystal XRD structural solution results for  $\text{Co}_{0.28}\text{NbSe}_2$  in the  $2a_h \times 2a_h$  and  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  supercell settings.

|                                                  | $\text{Co}_{0.28}\text{NbSe}_2$                          | $\text{Co}_{0.29}\text{NbSe}_2$                              |
|--------------------------------------------------|----------------------------------------------------------|--------------------------------------------------------------|
| Empirical formula                                | $\text{Co}_{0.28}\text{NbSe}_2$                          | $\text{Co}_{0.29}\text{NbSe}_2$                              |
| Formula weight                                   | 267.08                                                   | 267.64                                                       |
| Crystal system                                   | Hexagonal                                                | Hexagonal                                                    |
| Space group                                      | $P6_3/mmc$                                               | $P6_322$                                                     |
| $a$ (Å)                                          | 6.90580(10)                                              | 11.9622(3)                                                   |
| $b$ (Å)                                          | 6.90580(10)                                              | 11.9622(3)                                                   |
| $c$ (Å)                                          | 12.3630(4)                                               | 12.3636(5)                                                   |
| $\alpha$ (°)                                     | 90                                                       | 90                                                           |
| $\beta$ (°)                                      | 90                                                       | 90                                                           |
| $\gamma$ (°)                                     | 120                                                      | 120                                                          |
| Volume (Å <sup>3</sup> )                         | 510.60(2)                                                | 1532.14(10)                                                  |
| Z                                                | 8                                                        | 24                                                           |
| Calculated density (g/cm <sup>3</sup> )          | 6.949                                                    | 6.962                                                        |
| Absorption coefficient $\mu$ (mm <sup>-1</sup> ) | 34.557                                                   | 34.609                                                       |
| F(000)                                           | 932.0                                                    | 2801.0                                                       |
| Crystal size (mm)                                | $0.226 \times 0.199 \times 0.015$                        | $0.226 \times 0.199 \times 0.015$                            |
| Radiation                                        | $\text{MoK}_\alpha$ ( $\lambda = 0.71073$ Å)             | $\text{MoK}_\alpha$ ( $\lambda = 0.71073$ Å)                 |
| 2 $\Theta$ range for data collection (°)         | 6.592 to 59.97                                           | 5.13 to 59.966                                               |
| Index ranges                                     | $-9 \leq h \leq 9, -9 \leq k \leq 9, -17 \leq l \leq 17$ | $-16 \leq h \leq 16, -16 \leq k \leq 16, -17 \leq l \leq 17$ |
| Reflections collected                            | 12699                                                    | 41980                                                        |
| Independent reflections                          | 319 [ $R_{\text{int}} = 0.032, R_\sigma = 0.0217$ ]      | 1503 [ $R_{\text{int}} = 0.033, R_\sigma = 0.0313$ ]         |
| Data/restraints/parameters                       | 319/0/21                                                 | 1503/0/64                                                    |
| Goodness-of-fit on $F^2$                         | 1.172                                                    | 1.132                                                        |
| Final R indexes ( $I \geq 2\sigma$ (I))          | R <sub>1</sub> 0.0166<br>wR <sub>2</sub> 0.0396          | R <sub>1</sub> 0.0312<br>wR <sub>2</sub> 0.0762              |
| Final R indexes (all data)                       | R <sub>1</sub> 0.0195<br>wR <sub>2</sub> 0.0408          | R <sub>1</sub> 0.0761<br>wR <sub>2</sub> 0.0884              |
| Temperature (K)                                  | 250(2)                                                   | 250(2)                                                       |
| Largest diff. peak/hole (e Å <sup>-3</sup> )     | 0.74 / -0.71                                             | 2.27 / -1.23                                                 |

Provided with a crystal containing both magnetic phases, we first studied  $\text{Co}_{0.28}\text{NbSe}_2$  single crystal sample with neutron diffraction to obtain the magnetic structure. However, no satellite reflections were observed. Upon closer examination of the nuclear reflections, we noted that certain Bragg intensities increased below  $T_N^A$ , as demonstrated by the (-2 -1 2) reflection (Figure 4.6(a)). This intensity growth observed between 200 K and 50 K, is consistent with the  $T_N^A$  transition, but no further changes were detected down to

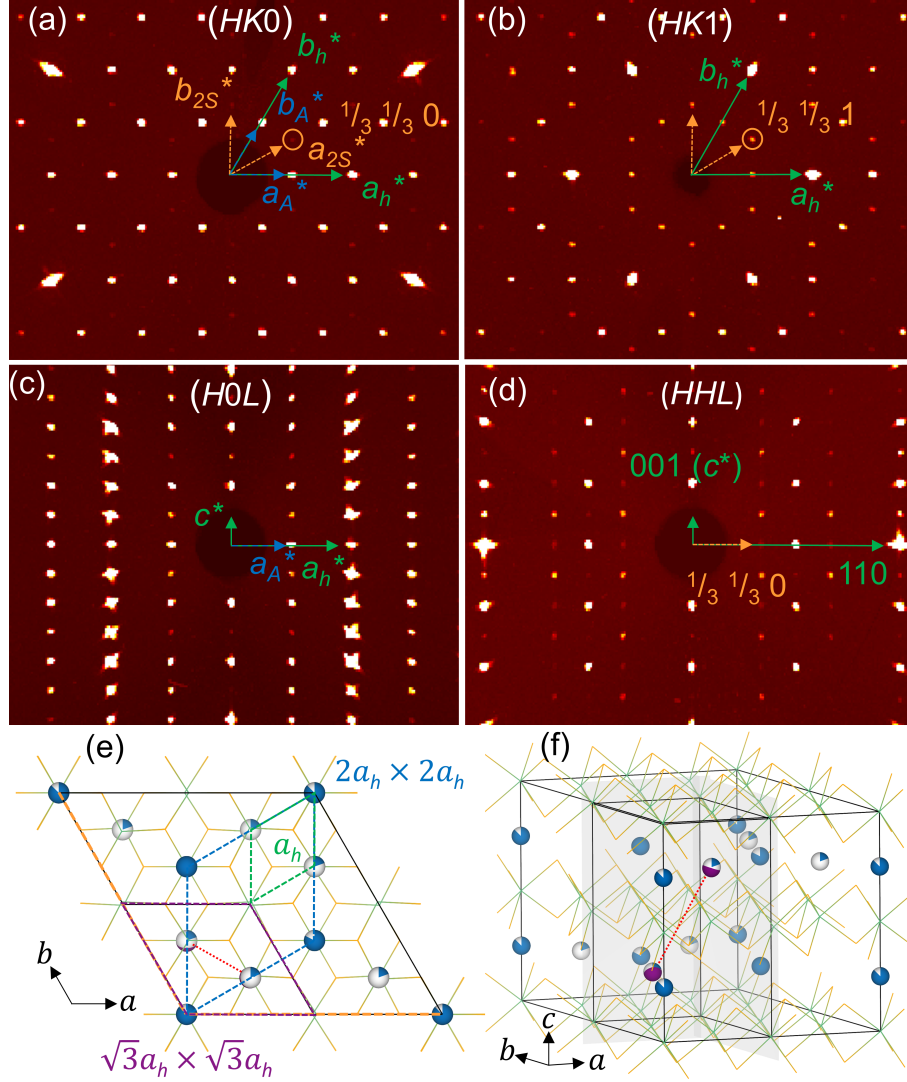


Figure 4.5: Single crystal X-ray diffraction results showing lattice coexistence. Precession images along the  $(HK0)$  (a),  $(HK1^*)$  (b),  $(H0L)$  (c), and  $(HHL)$  (d) planes. Green arrows indicate the host unit cell of  $2\text{H-NbSe}_2$  and the yellow vector points toward the observed satellite reflections indexed by the nuclear propagation vector  $q_{2S} = (1/3, 1/3, 0)$ . The blue arrows correspond to the  $2a_h \times 2a_h$  cell ( $a_A$ ). The resulting structure solution with  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  ( $a_{2S}$ ) dimensions viewed along the  $c$ -direction (e) and  $ab$ -plane (f). The red dotted line marks the trajectory to the next-nearest neighboring cobalt atom in the adjacent layer, defining the  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains (labeled as  $a_S$ ).



5 K. Therefore, all magnetic reflections correspond exclusively to  $T_N^A$ . The magnetic reflections overlapping with the nuclear ones indicate a propagating vector  $q_m = (0\ 0\ 0)$ . Through irreducible representation analysis, we identified twelve possible magnetic structures. Based on susceptibility data, we inferred that the magnetic moment aligns along the  $c$ -axis. From Table 4.3, only two representations,  $\Gamma_3$  (ferromagnetic) and  $\Gamma_7$  (antiferromagnetic), meet this requirement. Ultimately, we deduced the correct magnetic structure, corresponding to the antiferromagnetic  $\Gamma_7$  representation (Figure 4.6(b) and (d)). The resulting structure is equivalent to the  $P6_3'/m'm'c$  magnetic space group that describes other  $M_{1/4}TQ_2$  A-type structures[48, 58, 66] and recently reported in  $\text{Co}_{1/4}\text{NbSe}_2$ [179]. This structure and composition have attracted attention for its spin and spatial symmetry elements, identifying it as a potential altermagnet[70, 123]. We find a total magnetic moment of  $1.5(4)\ \mu_B/\text{Co}^{2+}$ , which is lower than expected for  $S = 3/2$ . The depleted moment likely arises from the interaction between the intercalant's  $3d$  orbitals and the host material's  $d_{z^2}$  itinerant electrons from vertically neighboring Nb [32, 66, 68, 120].

We follow the temperature evolution of  $T_N^A$  ordering by measuring the intensity of the (101) nuclear Bragg reflection as a function of temperature (Figure 4.6(c)). We find that the integrated peak intensity of the nuclear reflection increases near the high-temperature magnetic anomaly. To obtain the critical exponent  $\beta$ , we fit the order parameter data to the power law expressed by  $I = I_0 + A(1 - T/T_N)^{2\beta}$ . The obtained critical value  $\beta = 0.38(3)$  best approximates the Heisenberg class ( $\beta = 0.366$ )[181]. Given the dimensionality of the structure and A-type magnetic ordering, it would be intuitive to assume the exponent to behave as Ising class[182, 183].

Given the absence of magnetic reflections from the  $T_N^S$  phase in the single-crystal neutron diffraction, we turned to neutron powder diffraction to investigate  $\text{Co}_{1/3}\text{NbSe}_2$ . Powder diffraction data, as shown in Figure 5.9(a), refined to the non-centrosymmetric  $P6_322$  space group at 40 K, revealing purely nuclear reflections. When comparing data

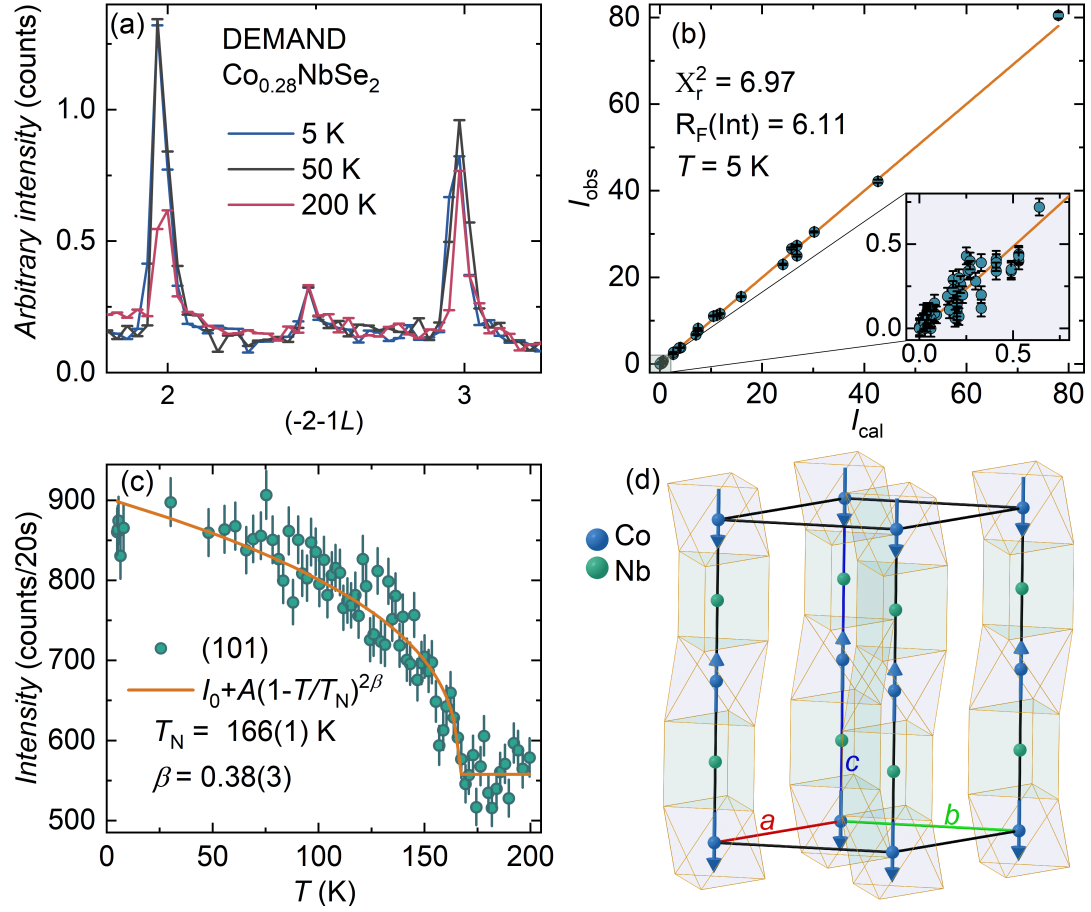


Figure 4.6: Single crystal neutron diffraction results. (a) Intensity of  $\text{Co}_{0.28}\text{NbSe}_2$  along  $(-2 -1 L)$ . The peak at  $(-2 -1 2.5)$  corresponds to  $\lambda/2$ . (b) Observed versus calculated neutron diffraction intensities. (c) The magnetic order parameter collected upon the (101) reflection and is fitted to the power law function. (d) Magnetic structure solution. The nuclear structure was solved via single crystal XRD and was used to obtain the magnetic structure using representation analysis in Mag2Pol[184].

Table 4.3: Allowed basis vectors ( $\psi_i$ ) for each irreducible representation ( $\Gamma_n$ )  $\text{Co}_{1/4}\text{NbSe}_2$  with  $q = (0, 0, 0)$ .

| $\Gamma_n$    | $\psi_i$ | Co1 (0, 0, 1/2)              | Co2 (0, 0, 0)                |
|---------------|----------|------------------------------|------------------------------|
| $\Gamma_1$    | $\psi_1$ | -                            | -                            |
| $\Gamma_2$    | $\psi_1$ | -                            | -                            |
| $\Gamma_3$    | $\psi_1$ | (0, 0, 1)                    | (0, 0, 1)                    |
| $\Gamma_4$    | $\psi_1$ | -                            | -                            |
| $\Gamma_5$    | $\psi_1$ | -                            | -                            |
| $\Gamma_6$    | $\psi_1$ | -                            | -                            |
| $\Gamma_7$    | $\psi_1$ | (0, 0, 1)                    | (0, 0, -1)                   |
| $\Gamma_8$    | $\psi_1$ | -                            | -                            |
| $\Gamma_9$    | $\psi_1$ | (0.612 - 0.354i, -0.707i, 0) | (-0.612 + 0.354i, 0.707i, 0) |
|               | $\psi_2$ | (-0.707i, 0.612 - 0.354i, 0) | (0.707i, -0.612 + 0.354i, 0) |
| $\Gamma_{10}$ | $\psi_1$ | -                            | -                            |
| $\Gamma_{11}$ | $\psi_1$ | (0.612 - 0.354i, -0.707i, 0) | (0.612 - 0.354i, -0.707i, 0) |
|               | $\psi_2$ | (-0.707i, 0.612 - 0.354i, 0) | (-0.707i, 0.612 - 0.354i, 0) |
| $\Gamma_{12}$ | $\psi_1$ | -                            | -                            |

collected at 40 K and 10 K, we observed the appearance of magnetic peaks associated with the  $T_N^S$  transition. The powder sample exhibited a single magnetic phase, corresponding to the low-temperature  $T_N^S$  state. At low- $Q$  values (Figure 5.9(d)), we identified a distinct triplet-like feature, suggesting the coexistence of two magnetic propagating vectors: a commensurate vector,  $q_1 = (0, 1/3, 0)$ , and an incommensurate vector,  $q_2 = (0, 1/3, 0.048(4))$ . The middle peak in the triplet corresponds to the (001) reflection, indexed by  $q_1$ , while the side peaks arise from incommensurate modulations of  $q_2$ . Refining the magnetic structure, we find  $q_1$  has a small in-plane component (refer to Table 4.4 for basis vectors). Still, most of its magnetic moment is along the  $c$ -direction with a total magnetic moment of  $1.2(2)\mu_B/\text{Co}^{2+}$  refined using  $\Gamma_2$  with equal opposing magnitude constraints (Figure 5.9(b) and Table 4.5). The magnetic order from  $q_2$  fits to a sine wave shape oscillating along the  $c$ -axis with  $2.9(2)\mu_B/\text{Co}^{2+}$  total moment, which is close to the expected value. The length of this propagating wave is approximately 255 Å spanning 20 unit cells (Figure 5.9(c) and Table 4.6). The individual moments composing this sine wave are parallel to the

Table 4.4: Allowed basis vectors ( $\psi_i$ ) for each irreducible representation ( $\Gamma_n$ ) of  $\text{Co}_{1/3}\text{NbSe}_2$  with  $q_1$  and  $q_2$ .

| $q_n$                     | $\Gamma_n$ | $\psi_i$ | Co1 (2/3, 1/3, 1/4) | Co2 (1/3, 2/3, 1/4) |
|---------------------------|------------|----------|---------------------|---------------------|
| $q_1 = (0, 0.334, 0)$     | $\Gamma_1$ | $\psi_1$ | (0.447, 0.894, 0)   | (0.447, 0.894, 0)   |
|                           | $\Gamma_2$ | $\psi_1$ | (1, 0, 0)           | (1, 0, 0)           |
|                           |            | $\psi_2$ | (0, 0, 1)           | (0, 0, 1)           |
| $q_2 = (0, 0.334, 0.048)$ | $\Gamma_1$ | $\psi_1$ | (1, 0, 0)           | (1, 0, 0)           |
|                           |            | $\psi_2$ | (0, 1, 0)           | (0, 1, 0)           |
|                           |            | $\psi_3$ | (0, 0, 1)           | (0, 0, 1)           |

*ab*-plane. The fixture of the incommensurate component of  $q_2$  remains an open question as it may undergo a commensurate locking at a lower temperature[17]. The oscillating spin moments observed here corroborate the presence of Dzyaloshinskii-Moriya (DM) interaction when  $x \geq 1/3$  where spatial inversion symmetry is broken[25, 67, 183]. Additionally, the RKKY mechanism is inversely dependent on  $R_{ij}^3$  (where  $R$  is the distance between metallic centers), may be used to understand the preferred moment orientation of both AFM orders encountered[33–35].

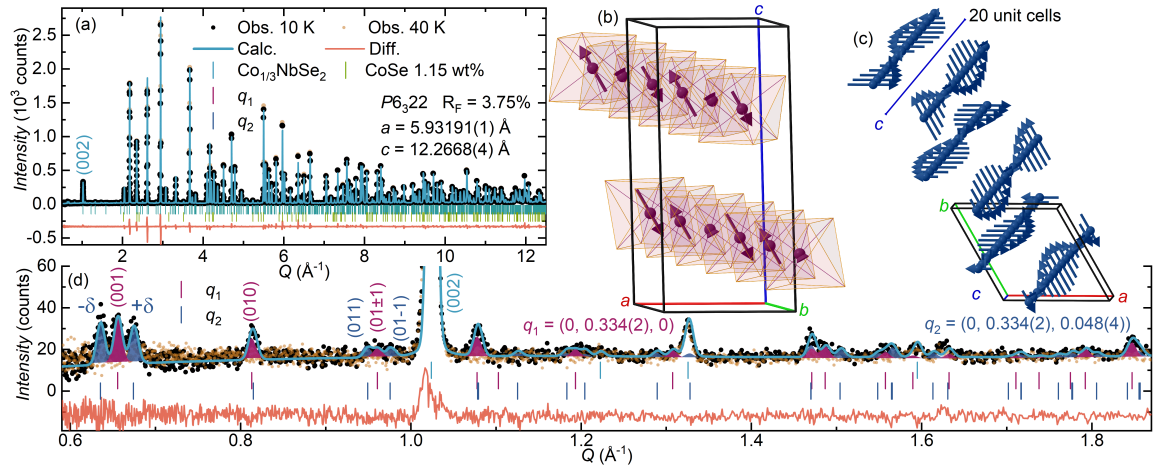


Figure 4.7: Neutron powder diffraction of  $\text{Co}_{1/3}\text{NbSe}_2$ . Rietveld refinement results at (a) 10 K overlayed on 40 K. Resulting magnetic structure obtained from commensurate  $q_1$  (b) and incommensurate  $q_2$  (c). (d) Low- $Q$  region of (a) showing the two magnetic propagating vectors;  $q_1$  (red) and  $q_2$  (blue).

Table 4.5: Magnetic structure parameters of  $\text{Co}_{1/3}\text{NbSe}_2$  refined with  $q_1 = (0, 0.334, 0)$ . All values are given in Bohr Magnetons ( $\mu_B$ ). In order to obtain reasonable values  $C_n^{\text{Co1}} = -C_n^{\text{Co2}}$  and  $\phi^{\text{Co1}} = -\phi^{\text{Co2}}$  parameter constraints were used.

| Atoms | $C_1$  | $C_2$  | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $\phi$ |
|-------|--------|--------|-------|-------|-------|-------|--------|
| Co1   | -0.604 | -1.055 | 0     | 0     | 0     | 0     | 0.047  |
| Co2   | 0.6(2) | 1.1(2) | 0     | 0     | 0     | 0     | -0.047 |

Table 4.6: Magnetic structure parameters of  $\text{Co}_{1/3}\text{NbSe}_2$  refined with  $q_2 = (0, 0.334, 0.048)$ . All values are given in Bohr Magnetons ( $\mu_B$ ). Parameter constraint  $C_1^{\text{Co1}} = C_1^{\text{Co2}}$  was used to obtain reasonable values.

| Atoms | $C_1$ | $C_2$  | $C_3$ | $C_4$ | $C_5$ | $C_6$ |
|-------|-------|--------|-------|-------|-------|-------|
| Co1   | 2.870 | 0      | 0     | 0     | 0     | 0     |
| Co2   | 0     | 2.9(2) | 0     | 0     | 0     | 0     |

Our study indicates that the intercalation of Co ions into pristine 2H-NbSe<sub>2</sub> suppresses both the CDW and superconductivity. However, CDW has been observed to coexist with magnetic ordering in  $\text{Fe}_x\text{NbS}_2$  [183]. In the novel  $\text{Co}_x\text{NbSe}_2$  phases investigated here, similar charge instabilities may enhance exchange interactions between the intercalated localized magnetic moments.

#### 4.4 Isolating $\text{Co}_{1/3}\text{NbSe}_2$ phase in single crystal

So far, isolating the  $\sqrt{3}a_h \times \sqrt{3}a_h$  intercalant domains of cobalt within NbSe<sub>2</sub> layers had posed a challenge. However, a continuation of the work above led to further considerations on the chemistry involved during the attempts to grow  $\text{Co}_{1/3}\text{NbSe}_2$  via CVT. From powder synthesis, we know making this phase is possible,  $\text{CoI}_2$  has been a competing factor. To decrease its formation, there are several options. One way is to increase the Co:TMD ratio in the starting charge powder. Hence, the 1.2:3:6 increment ratio in the solid state synthesis. An alternative is to decrease the  $\text{I}_2$  used and increase the charge powder to

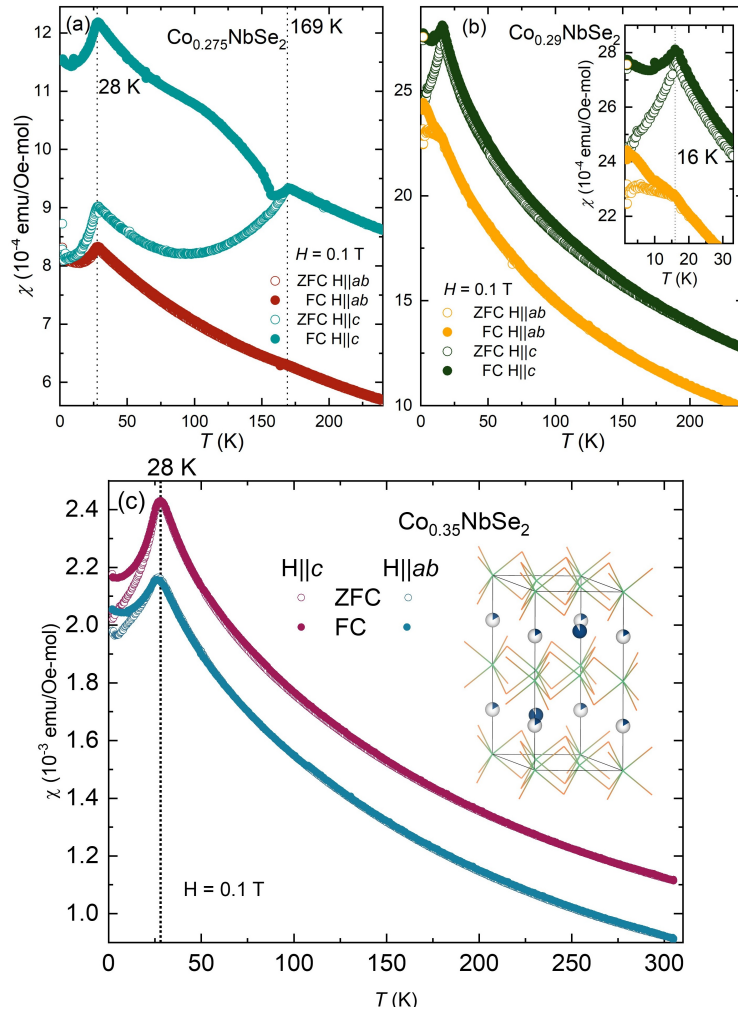


Figure 4.8: Temperature-dependent magnetic susceptibility of  $\text{Co}_{1/3}\text{NbSe}_2$  grown via CVT using  $\text{I}_2$  (a and b) and  $\text{NbCl}_5$  (c).

tilt the balance in Co:I ratio. This, however, dramatically increases the time required to transport the charge, elongating the growth time. A better option is to consider the formation enthalpies of transition metal halides involved in the reaction to select a transport agent that will discourage competing byproducts. Here, we opted to use  $\text{NbCl}_5$  as it has a low boiling point ( $\sim 482^\circ\text{C}$ ), and successfully transports the charge powder to form the desired  $\text{Co}_{1/3}\text{NbSe}_2$  phase. We compare the intercalation success rate in  $\text{Co}_x\text{NbSe}_2$  by tracking the magnetic phase transitions through temperature-dependent susceptibility in Figure 4.8.

Using  $I_2$  as transport will always decrease the cobalt intercalation. Figure 4.8 (a) shows the coexisting transitions from using  $Co_{1.15}Nb_3Se_6$  charge powder. Increasing the cobalt content of the charge powder to  $Co_{1.2}Nb_3Se_6$  will isolate the low temperature transition; however, we later find out that this is a disordered state producing a spin-glass phase. We discuss this in Chapter 5. This disorder state is noticeable from the lowering of  $T_N = 16$  K, rather than the expected  $T_N = 28$  K. Furthermore, there is a strong bifurcation of the ZFC and FC curve, along with anisotropic character. The in-plane susceptibility seems to have weaker AFM interactions as it polarizes with the applied field.

Using  $NbCl_5$  with the excessive cobalt-containing charge powder ( $Co_{1.2}Nb_3Se_6$ ) produces good quality single crystals with the desired phase transition (Figure 4.8 (c)). The magnetic susceptibility shows a true AFM transition at  $T_N = 28$  K in both in-plane and out-of-plane field measurements. Our single-crystal X-ray diffraction results confirm the  $\sqrt{3}a_h \times \sqrt{3}a_h$  domain formation and refine the cobalt content to  $Co_{0.35}NbSe_2$  shown in the inset of 4.8 (c).

This crystal composition had hitherto never been grown successfully. We argue that this is driven by the stability of the transition metal halides that are involved during the transport growth. The formation enthalpy is the energy released when a solid is formed. If it is negative, the reaction is exothermic, and the more negative it is, the more stable the compound is. Table 2.1 has a compilation of formation enthalpies of potential by product of the growth reaction. If we consider the formation enthalpies of  $CoI_2$  (-89.5 kJ/mol) against  $CoCl_2$  (-312.5 kJ/mol) tell us that using chlorine is not favorable as cobalt will prefer binding to the more electronegative chlorine anion. The key here is the presence of  $Nb^{5+}$  cations already incorporated.  $NbCl_5$  has a formation enthalpy of -797.5 kJ/mol, outcompeting the formation of  $CoCl_2$ . We verify this indirectly by attempting a CVT using  $NH_4Cl$ , which will produce small, thick single crystals. However, there is poor intercalation ratio. The formation enthalpy of  $NH_4Cl$  (-314.6 kJ/mol) is almost the same as that of  $CoCl_2$ , justifying

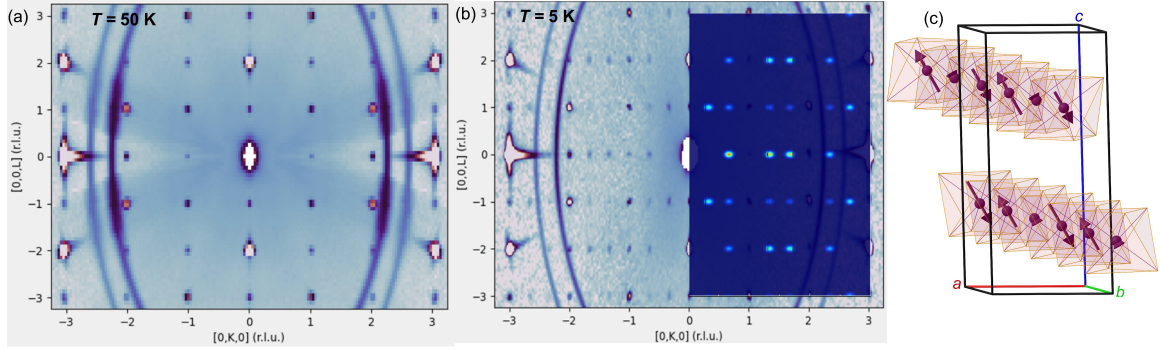


Figure 4.9: Single crystal neutron diffraction collected at CORELLI viewed along  $(0KL)$ . (a) Paramagnetic diffraction at 50 K, (b) magnetically ordered at 5 K. Inset of (b) is a simulated magnetic-only pattern using previously obtained (c) SDW model of  $q_1$ .

the need for the  $\text{Nb}^{5+}$  cations for a successful reversible CVT reaction.

Having isolated the desired domains, we took a large single crystal of  $\sim 33$  mg to CORELLI at the SNS. Figure 4.9 (a) shows the diffraction pattern at the paramagnetic phase collected at 50 K. This diffraction pattern accurately indexes to the noncentrosymmetric  $P6_322$  space group. Cooling the crystal down to 5 K, below  $T_N^S$ , we observe the appearance of magnetic satellite reflections (Figure 4.9 (b)). These reflections are modulated by magnetic propagation vector  $q_1 = (0, 1/3, 0)$  but has domain equivalence with  $q_1 = (1/3, 0, 0)$  and  $q_1 = (1/3, -1/3, 0)$ . This has momentarily generated difficulties in refining the magnetic moments and structure. The inset in Figure 4.9 (b) shows a simulation of  $q_1$  using the refined model from the powder results in Table 4.5 and Figure 4.9 (c). Despite this complication, the simulation shows good qualitative agreement, with the commensurate part of the SDW.

Searching for the incommensurate portion of the SDW in the single crystal sample is still an open task. We speculate that it may not be as prominent in a highly ordered single-crystal sample, or the wave has a much longer pitch requiring a higher resolution neutron diffractometer.



## 4.5 Conclusions

We successfully isolated  $\text{Co}_x\text{NbSe}_2$  polycrystalline phases for  $x = 1/4$  and  $1/3$  while assigning their magnetic structures. We propose that the simplicity of the collinearly compensated  $A$ -type order in the  $x = 1/4$  phase arises from the vertically ordered Co sites and their alignment with the Nb  $4dz^2$  orbital. In contrast, the more complex double- $q$  magnetic structure observed in the  $x = 1/3$  phase likely contributes to enhanced metallic interactions, including DM interactions. Both structural and magnetic phases coexist within a  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  superlattice, accommodating these distinct magnetic orders. To fully address the implications between neighboring magnetic centers, future inelastic neutron scattering experiments are essential for exploring this rich compound series.

We continue this project by successfully crystallizing  $\text{Co}_{1/3}\text{NbSe}_2$  with isolated  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains. We use thermodynamic principles and enthalpy constants to direct the crystal growth in our favor and produce quality samples for future experiments.

## Chapter 5: Evolution of Altermagnetism to Spin Density Waves in $\text{Co}_x\text{NbSe}_2$

The work in this chapter was published in the *Journal of American Chemical Society*. Hector Cein Mandujano, Sajjan Sheoran, Yuanpeng Zhang, Tianyu Li, Stephanie J. Hong, Pratibha Dev, and Efrain E. Rodriguez were contributing authors. H.C.M. prepared samples and performed MPMS and specific heat measurements, S.S. and P.D. made the density functional theory calculations, and chemical composition was determined by T.L. and S.J.H., H.C.M and Y.Z. made the reverse Monte Carlo modeling.

### 5.1 Introduction

The van der Waals gap in layered transition metal dichalcogenides (TMDs) offers many opportunities to explore and tune magnetic properties through intercalation in these two-dimensional systems. Group-V TMDs with partially filled states at the Fermi level form intermediate itinerant magnetic systems[2], producing a wide range of phases depending on the host and the intercalated species. Intercalating  $3d$  transition metals typically yields ordered magnetic ground states with diverse electronic and magnetic properties[25, 185]. While the exact properties depend on the chemical identity of both the intercalant and the host, one can often associate structural and physical characteristics with the intercalant-to-host ratio[55, 118, 120, 165, 186–188]. Near ratios of  $1/3$  and  $1/4$ , the structure is described by a  $\sqrt{3}a_h \times \sqrt{3}a_h$  or  $2a_h \times 2a_h$  unit cell, respectively, where  $a_h$  denotes the  $a$ -axis lattice

parameter of the host TMD[164]; each ratio produces distinct interactions that lead to different properties.

Understanding guest-host interactions within group-V TMDs as a function of the intercalant (guest) concentration is of broad interest to the 2D magnetism community. Several of these intercalated TMDs are known to display a variety of coexisting phases between magnetism and charge order[55, 183, 189]. Within this family of TMDs,  $\text{Co}_x\text{NbSe}_2$  stands out by presenting non-relativistic spin splitting, also known as altermagnetism, at  $x = 1/4$  and a spin density wave (SDW) at  $x = 1/3$ [1, 190]. In general, the search for altermagnetism (AM) in cobalt-intercalated TMDs began with the observation of the anomalous Hall effect in the sulfide  $\text{Co}_{0.33}\text{NbS}_2$  along with observation of unconventional band splitting along high-symmetry points[147, 191]. Despite its classification at the time as a collinear antiferromagnet[157], it displayed properties more consistent with a ferromagnet, which breaks time-reversal symmetry. When the magnetic structure was revisited, it became clear that these physical properties arose from a non-collinear antiferromagnetic order[63, 192, 193]. Although  $\text{Co}_{0.33}\text{NbS}_2$  is not an altermagnet, several group-V TMDs intercalated by 3d metals have now been proposed as candidates[66, 69, 71, 73, 194]. In the case of  $\text{Co}_{0.25}\text{NbSe}_2$ , strong evidence exists for altermagnetic behavior[74, 190, 195]. Furthermore, we recently found that this composition can host coexisting magnetic and structural phases[66].

Careful crystallographic studies of these magnetic TMDs are needed to understand how the crystal structure pre-establishes the conditions necessary for distinct magnetic phases. We list some of the key known structure-property relationships in these systems: (1) When the intercalant forms continuous chains along the  $c$ -axis, the structure adopts the centrosymmetric space group  $P6_3/mmc$  with  $2a_h \times 2a_h$  dimensions (Figure 5.1(a), (b)). This arrangement strengthens vertical orbital interactions between the non-magnetic TMD host and magnetic guest species, enhancing exchange interactions mediated primarily by the

host's  $d_{z^2}$  and guest's  $3d$  orbitals. (2) When the intercalant is off-centered from one layer to the next, the structure becomes non-centrosymmetric, adopting the chiral space group  $P6_322$  (Figure 5.1(c),(d)), which allows for Dzyaloshinskii-Moriya (DM) interactions[196? , 197]. These interactions within the  $\sqrt{3}a_h \times \sqrt{3}a_h$  lattice commonly give rise to complex magnetic configurations such as helical and SDW structures[45–47, 55, 63, 67, 77], a promising venue for pursuing current-controlled antiferromagnetic states[198–200]. Additionally, the off-centering along the vertical axis is expected to weaken the interaction with the host, as the continuous coupling involving the host's  $d_{z^2}$  orbital is disrupted[120, 201]. (3) Off stoichiometric ratios, meaning when  $x \neq 1/4$  or  $1/3$ , will lead to disordered phases[84, 202, 203]. In this context, we view these systems as an opportunity to study a range of localized-to-itinerant limits in the antiferromagnetic behavior of the intercalant[64, 66, 68, 130, 204–206].

Little is known about the local structure and interstitial disorder of these systems. The arrangement and structural accommodation of the intercalants are expected to play a crucial role in determining the magnetic interactions, mediated by various exchange pathways and mechanisms[25, 29, 60, 64]. The thermal history of synthesis can be used to tune structural order. Quenching can kinetically trap metastable disordered states, while slow cooling allows atomic rearrangement toward thermodynamic equilibrium. These contrasting pathways can yield either phase or domain segregation via heterogeneous nucleation, or high-entropy site disorder within a uniform lattice, affecting the observed bulk electronic and magnetic properties[207–211] Because these systems are itinerant, their magnetic interactions are generally described by the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange mechanism.[25, 26, 64, 182]. This mechanism is particularly sensitive to the local distribution of magnetically active intercalants due to its radially oscillatory character[33–35].

The thermodynamic stability of the intercalated TMD likely determines the extent of

order and disorder[49, 187]. Intercalation becomes feasible when the work function of the intercalant is lower than the electron affinity of the host[50]. Although cobalt's work function (5.0 eV[212]) is smaller than that of NbSe<sub>2</sub> (5.9 eV[213]), suggesting favorable intercalation, previous studies have reported difficulties in achieving precise intercalant-to-host ratios above 1:4[1, 49]. In this work, we study the structural and magnetic properties of Co<sub>x</sub>NbSe<sub>2</sub> powders prepared under two different cooling profiles to induce varying degrees of order and disorder. A greater control of the arrangement and structural accommodation of the intercalants is crucial for designing the resulting magnetic interactions through various exchange pathways and mechanisms. We examine the conditions under which a wide range of physical properties emerge, from AM to SDW, which we find either coexist or are bridged by a spin-glass-like phase. We demonstrate that these phases are strongly dependent on the order and site preference of the Co intercalants in the host structure.

## 5.2 Methods

### 5.2.1 Air-quenched and Furnace-cooled Synthesis

We synthesized two sets of polycrystalline Co<sub>x</sub>NbSe<sub>2</sub> powder samples, an air-quenched series and a furnace-cooled series, using the conventional solid-state method. We prepared both series by mixing Co, Nb, and Se powders in a  $x$ :1:2 stoichiometric ratio, with  $x$  ranging from 0.29 to 0.36 in 0.01 increments. We then vacuum-sealed 2-3 g of each mixture in a fused silica ampule. For the initial heating, we warmed both series from room temperature to 725 °C at 420 °C/hour, holding this temperature for 30-60 minutes to prevent ampule bursting. We then increased the temperature to 900 °C at a rate of 10 °C/hour. We held the air-quenched set at 900 °C for 4 days and the furnace-cooled set for 7 days. For cooling, we turned off the furnace for the air-quenched series, allowing it to cool naturally to 600 °C before removing the ampules and air-quenching them on a room-temperature surface.

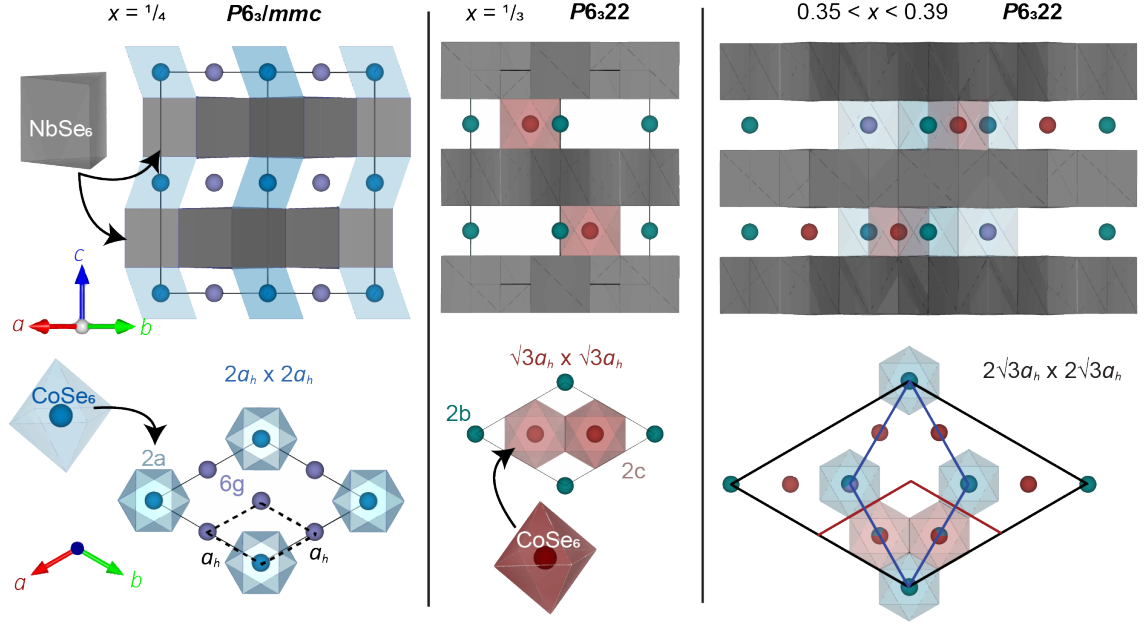


Figure 5.1: Crystal structures of  $\text{Co}_x\text{NbSe}_2$  where  $x$  is the amount of intercalated Co atoms into the host, which consists of all edge-sharing  $\text{NbSe}_6$  trigonal prisms (grey). In (a), the  $[110]$  perspective shows how the Co atoms mostly occupy the octahedral  $2a$  Wyckoff site (blue) with partial occupation of the  $6g$  (purple) site. In (b), the  $\mathbf{c}^*$  perspective shows how the host structure consists of a  $2a_h \times 2a_h$  superlattice with respect to the unit cell parameter  $a_h$  of the pristine  $\text{NbSe}_2$  host. In (c), the structure is shown for the compositions with  $x$  greater than  $\frac{1}{4}$  as viewed down the  $\mathbf{a}^*$  axis. In (d), the structure is represented down the  $\mathbf{c}^*$  axis adopts a  $\sqrt{3}a_h \times \sqrt{3}a_h$  unit cell. In (e), the proposed structural model crystallizes in the chiral space group  $P6_322$  and allows for a convenient manner to follow the distribution of the Co atoms that encompasses both the  $2a_h \times 2a_h$  and  $\sqrt{3}a_h \times \sqrt{3}a_h$  sublattice. This superlattice is shown in (f) to be  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  in size. The Wyckoff sites for all Co occupation are also displayed in order to relate to the previous sublattice structures.

We cooled the furnace-cooled samples at  $15^\circ\text{C}/\text{hour}$  to  $600^\circ\text{C}$ , then allowed the furnace to cool naturally to room temperature before extraction.

For neutron powder diffraction experiments, we combined ampules of the same composition and set them for a second heating step. We rapidly heated the air-quenched set to  $800^\circ\text{C}$  and held it for 24 hours. We held the furnace-cooled set at  $900^\circ\text{C}$  for 36 hours before repeating the same cool-down profile used in the first heating.

### 5.2.2 Composition

The compositions of the polycrystalline powder samples were determined by energy-dispersive X-ray spectroscopy in a Hitachi SU-70 Schottky field emission gun scanning electron microscope (FEG SEM). We found a slight cobalt deficiency in all samples as depicted in Figure 5.2. To simplify the nomenclature, we refer to the samples by their nominal compositions.

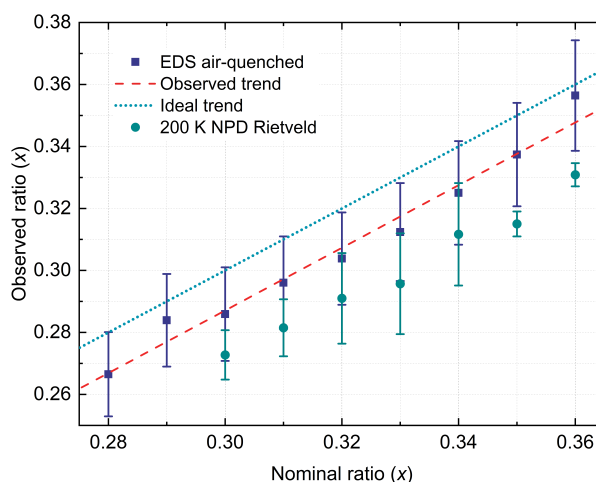


Figure 5.2: Observed vs nominal cobalt to NbSe<sub>2</sub> ratio obtained from energy dispersive spectroscopy and resulting refined occupancies from Rietveld analysis of neutron powder diffraction.

### 5.2.3 X-ray and neutron powder diffraction

Powder X-ray diffraction was performed using a Bruker D8 Advance X-ray diffractometer with a CuK $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) source from  $10^\circ$  to  $130^\circ$  and a nominal step of  $0.02^\circ$ . Neutron powder diffraction experiments were carried out at HB-2A (POWDER) located at the High Flux Isotope Reactor (HFIR), and BL-11A (POWGEN) located at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL)[214]. For the HB-2A

data collection, approximately 6 grams of powder of the air-quenched samples were loaded into aluminum cans. The germanium wafer-stack monochromator was positioned in the Ge(113) orientation to obtain the selected wavelength of 2.41 Å. The diffraction was then collected at 4 K and 175 K to locate the magnetic Bragg reflections.

The same samples and the furnace-cooled  $\text{Co}_{0.32}\text{NbSe}_2$  powder sample were transferred into standard 6 mm vanadium cans and taken to BL-11A. The center wavelengths used were 2.665 Å for higher resolution at low- $Q$  ( $0.30\text{--}5.87 \text{ Å}^{-1}$ ), while a centered wavelength of 0.8 Å was used to obtain diffuse scattering at high- $Q$  ( $0.76\text{--}46.88 \text{ Å}^{-1}$ ). Diffraction data were collected in the paramagnetic phase at 200 K during this experiment. The Orange cryostat was used to collect diffraction at 1.8 K for samples with  $T_N < 16$  K, while the POWGEN automatic changer was used to collect data at 7 K. Rietveld analysis was performed on all diffraction data using GSAS-II[134] and Mag2Pol[184].

Pair distribution function analysis was obtained by taking the Fourier transform of the high- $Q$  region ( $Q_{\text{max}} = 30.0 \text{ Å}^{-1}$ ) of the total scattering data collected with a centered wavelength of 0.8 Å. Small-box modeling was performed using the PDFgui suite[105, 106], while large-box modeling was performed using reverse Monte Carlo (RMC) built within the RMCProfile package[107]. In this method, we used an automatic weight optimization[108] of the diffraction and total scattering data in reciprocal  $Q$ -space and real  $r$ -space (Figure 5.3).

#### 5.2.4 Property measurements

Magnetic susceptibility and magnetization were measured using a Quantum Design 7 T Magnetic Property Measurement System. Specific heat measurements were taken in a 14 T Quantum Design Dynacool Physical Property Measurement System. Samples for specific heat were prepared by pressing powder samples into pellets and annealing at 600



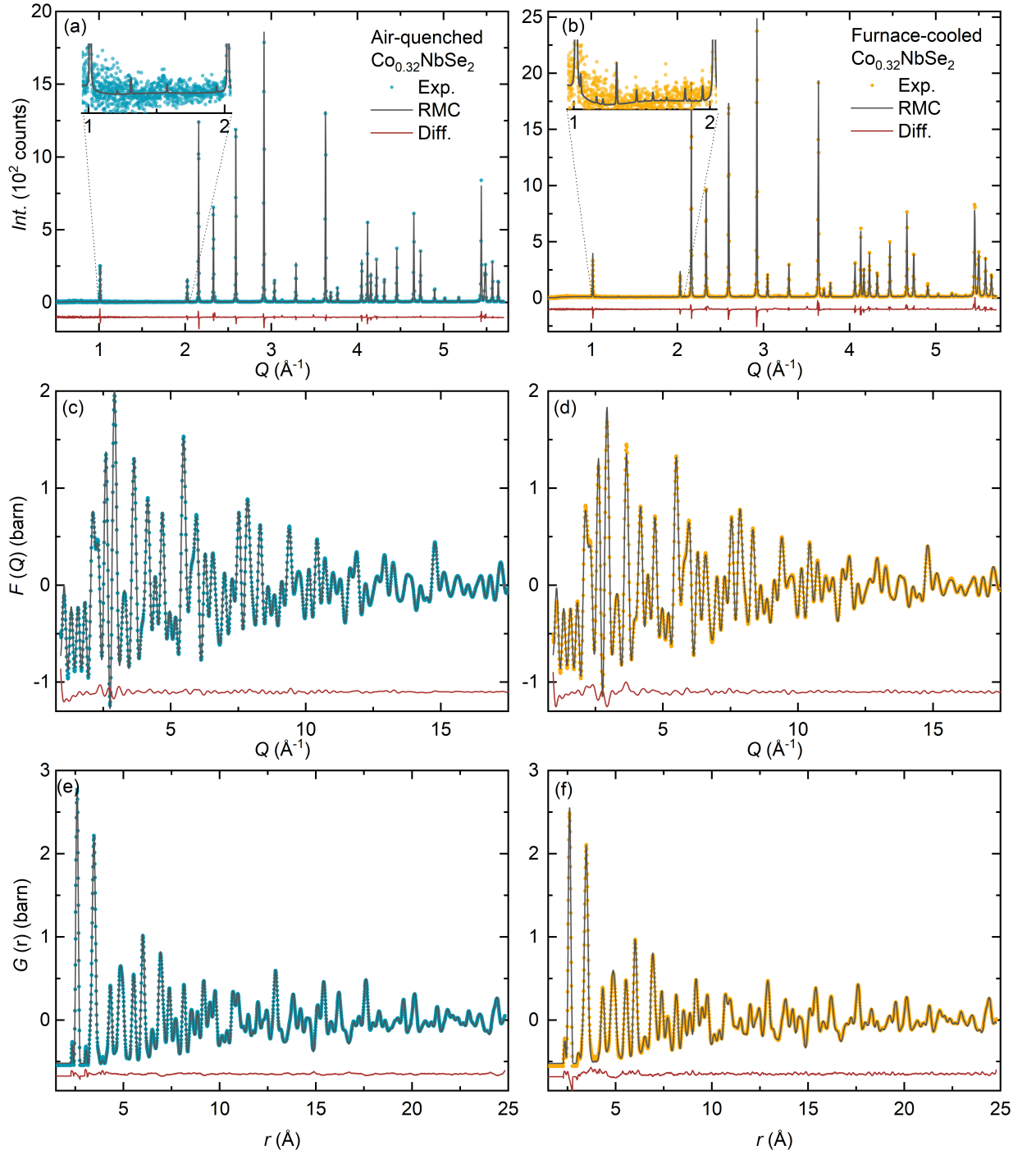


Figure 5.3: Combined big-box neutron powder pair distribution function analysis of air-quenched (left) and furnace-cooled (right)  $\text{Co}_{0.32}\text{NbSe}_2$  collected at 200 K. (a-b) Diffraction data, (c-d) total scattering in  $Q$ -spacing, and (e-f) total scattering in  $r$ -space.

°C overnight. A fragment of approximately 4 mg of the pellet was then used.

## Computational Methods

Density functional theory (DFT) simulations were performed using the projector-augmented wave method[215] as implemented in the Vienna ab initio simulation package (VASP)[216]. We used the Perdew-Burke-Ernzerhof (PBE)[217] formulation of the generalized-gradient approximation to the exchange-correlation functional. Earlier works[118, 190, 195] showed that the energy difference between FM and AFM states of  $\text{Co}_x\text{NbSe}_2$  does not depend on the Hubbard  $U$  correction. Therefore, this correction is not considered in the simulations. The crystal structures are fully relaxed using the conjugate gradient algorithm until the force on each atom is smaller than 1 meV/Å with experimental ones as a starting point. The Brillouin zone was sampled using the Monkhorst-Pack grid with  $k$ -spacing of  $0.02 \text{ Å}^{-1}$ . The Wannier representation of the tight-binding Hamiltonian for  $\text{Co}_x\text{NbSe}_2$  ( $x = 1/4, 1/3$ ) was obtained by projecting Bloch states from the DFT simulations on Co- $d$ , Nb- $d$ , and Se- $p$  orbitals[218]. The exchange interactions are obtained using the Green's function method, treating local rigid spin rotations as a perturbation, as implemented in TB2J[219]. The Bilbao Crystallographic Server [220], Findsymb[221], Findspingroup[222], PyProcar[223], and Vaspkit[224] were used for pre and post processing of results.

## 5.3 Results

### 5.3.1 Site Disorder, Domain Coexistence, and Magnetic Transitions

#### Cobalt site disorder in air-quenched samples

We compare the structural and magnetic transitions of the air-quenched and furnace-cooled solid-solution series in Figure 5.4. A lattice expansion predominantly along the  $c$ -axis

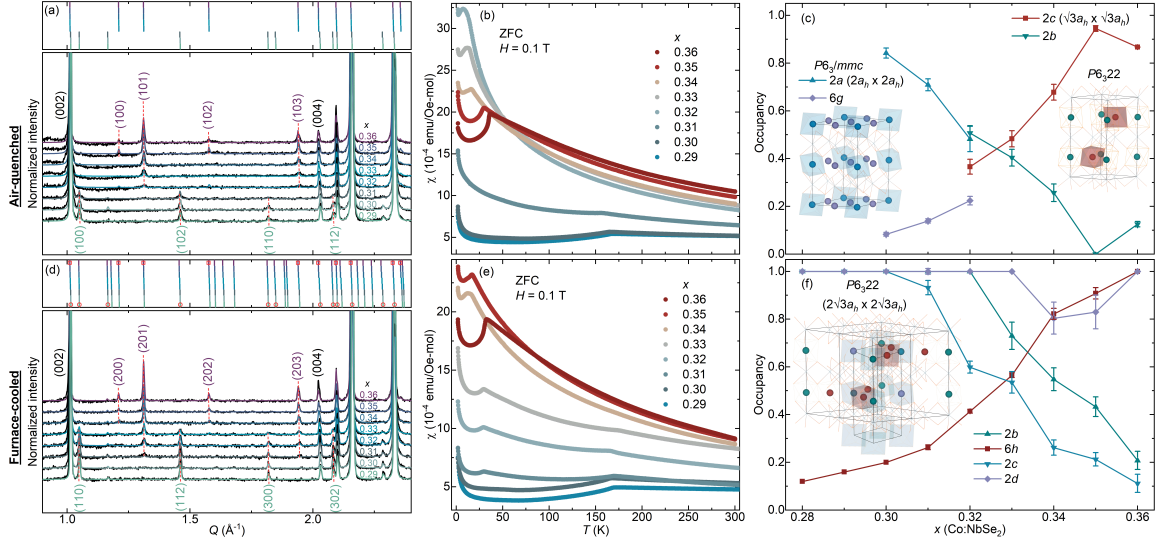


Figure 5.4: Structure and magnetic phase comparison of air-quenched (top row) and furnace-cooled (bottom row)  $\text{Co}_x\text{NbSe}_2$ . (a and d) show the pXRD patterns ( $\text{Cu}_{k\alpha}$ ) of both solid solution series; the top panel of each plot indicates the Bragg index of each Rietveld refinement. For the furnace-cooled XRD patterns (d), the red squares mark the  $P6_322$  Bragg reflections. Red circles indicate the centrosymmetric Bragg reflections of the  $P6_3/mmc$ . (b and e) Zero-field cooled magnetic susceptibility of powder samples. (c and f) Refined occupancies of cobalt sites. Insets in c illustrate the  $2a_h \times 2a_h$  centrosymmetric (left) and non-centrosymmetric  $\sqrt{3}a_h \times \sqrt{3}a_h$  (right) unit cells. Both cells can be arranged within a larger  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  supercell (inset in f). Occupancies for the air-quenched samples were obtained from Rietveld analysis on the NPD (Figure 5.5) and held constant in the pXRD analysis. For the pXRD Rietveld of furnace-cooled, the constraint equation  $(\text{Occ.}^{\text{Co}2b} + \text{Occ.}^{\text{Co}2c} + \text{Occ.}^{\text{Co}2d})/12 + (\text{Occ.}^{\text{Co}6h})/4 = x$  was applied. The  $2a$  site in the  $2a_h \times 2a_h$  is equivalent to the  $2b$  site in the  $\sqrt{3}a_h \times \sqrt{3}a_h$ ; similarly, the  $6g$  corresponds to the  $2c$ .

is observed, induced by cobalt intercalation (Figure 5.6). Characteristic Bragg reflections, located between the (002) and (004) peaks, distinguish between centrosymmetric and non-centrosymmetric intercalant arrangements. The (100) reflection of the  $P6_3/mmc$  ( $2a_h \times 2a_h$ ) and the (101) reflection of the  $P6_322$  ( $\sqrt{3}a_h \times \sqrt{3}a_h$ ) structures are most prominent. In the case of air-quenched series (Figure 5.4(a)), the intensity of these reflections interchange continuously from  $x = 0.29$  to 0.36. At  $x = 0.32$ , only the (101) reflection appears broadly, suggesting it's the critical ratio between the two symmetry preferences.

Each structural arrangement corresponds to a distinct magnetic ordering: the non-centrosymmetric structure with  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains exhibits an antiferromagnetic tran-

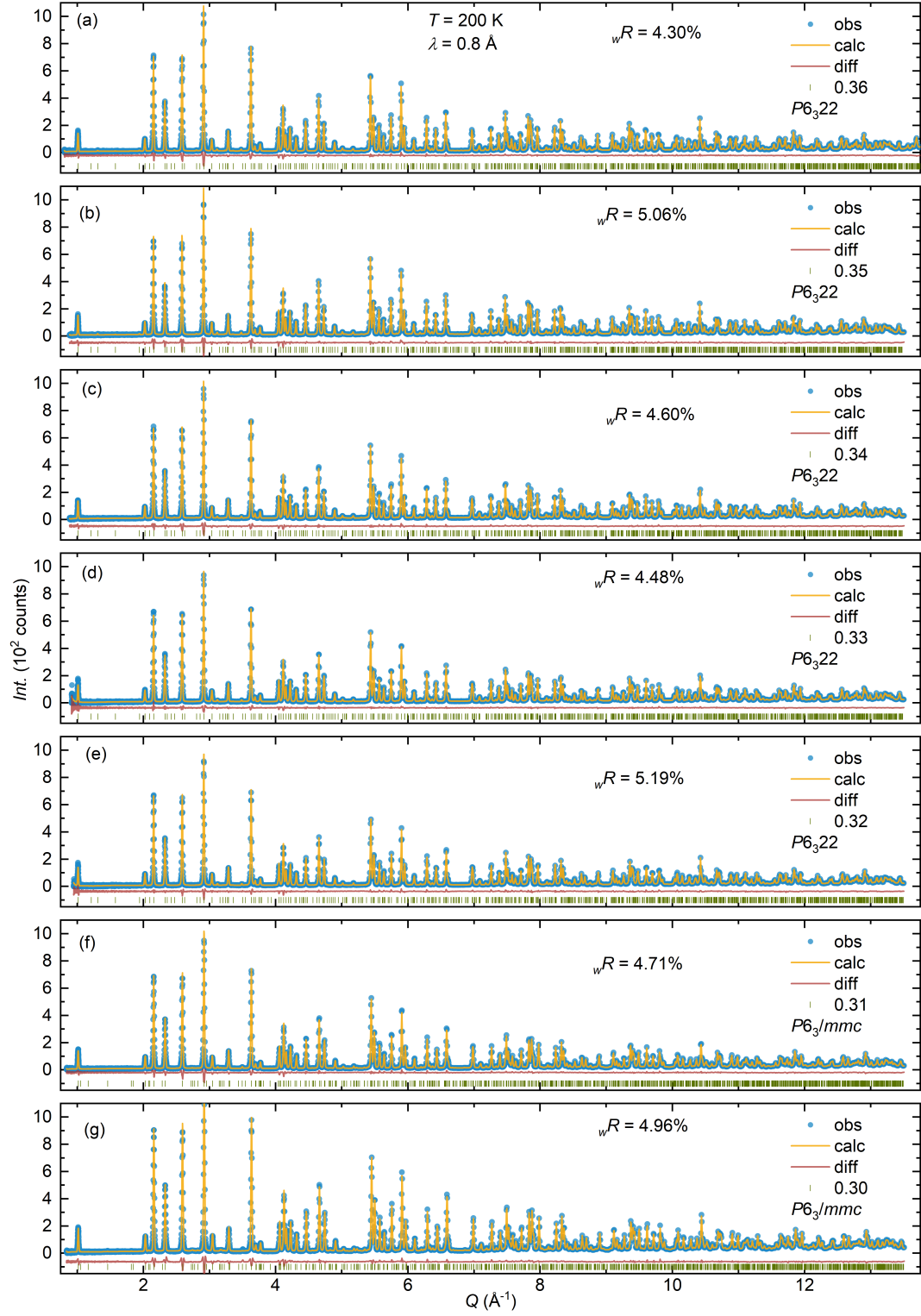


Figure 5.5: (a-h) Neutron powder diffraction of air-quenched series at 200 K using  $\lambda = 0.8 \text{ \AA}$ .

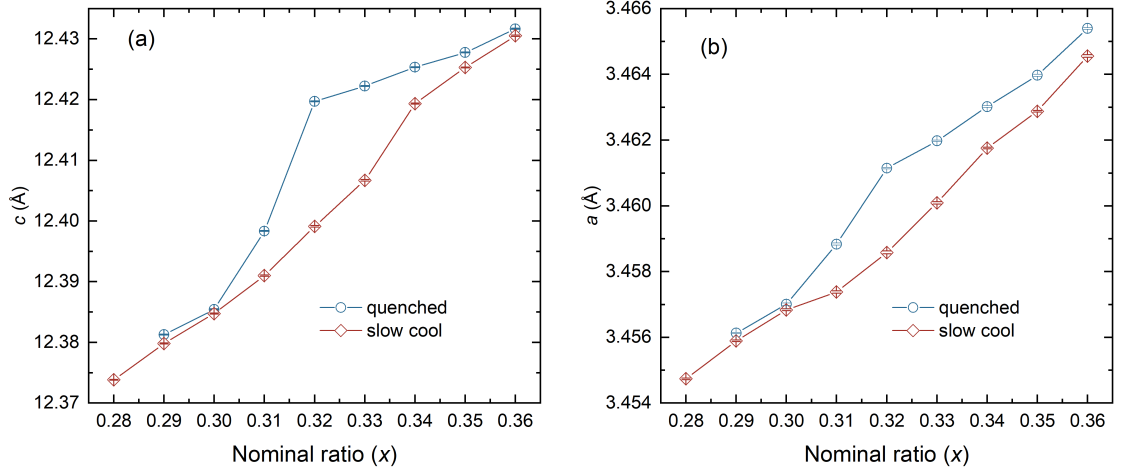


Figure 5.6: Lattice parameters (a)  $c$  and (b)  $a$  obtained from powder X-ray diffraction Rietveld refinement analysis. The  $a$ -axis lattice parameter was normalized to the host  $\text{NbSe}_2$  lattice dimensions by dividing by a factor corresponding to the respective supercell.

sition at  $T_N^S \leq 36$  K, while the centrosymmetric ordering of  $2a_h \times 2a_h$  domains hosts the altermagnetic phase with  $T_N^A \approx 170$  K[1]. These transitions are evident in the temperature-dependent magnetic susceptibility (Figure 5.4(b)). At high cobalt concentrations, the AFM transition appears near 36 K and decreases with decreasing  $x$ , reaching a minimum of  $\sim 7$  K at  $x = 0.32$ . Below this cobalt content, it vanishes, giving way to a high-temperature transition near 157 K for  $x = 0.31$ , which increases to 171 K as  $x$  approaches the ideal 1/4 stoichiometry.

These magnetic and diffraction signatures confirm the evolution of preferred cobalt site domain configurations:  $\sqrt{3}a_h \times \sqrt{3}a_h$  for  $x \geq 0.32$  and  $2a_h \times 2a_h$  for  $x \leq 0.31$ . We quantify site occupancies through Rietveld refinements (Figures 5.7 and 5.8) using the appropriate  $P6_322$  or  $P6_3/mmc$  space groups (Figure 5.4(c)). Since only the exact compositions  $x = 1/4$  and  $x = 1/3$  allow for fully occupied sublattices without disorder, deviations from these stoichiometries introduce occupancy of additional sites, which can be identified from

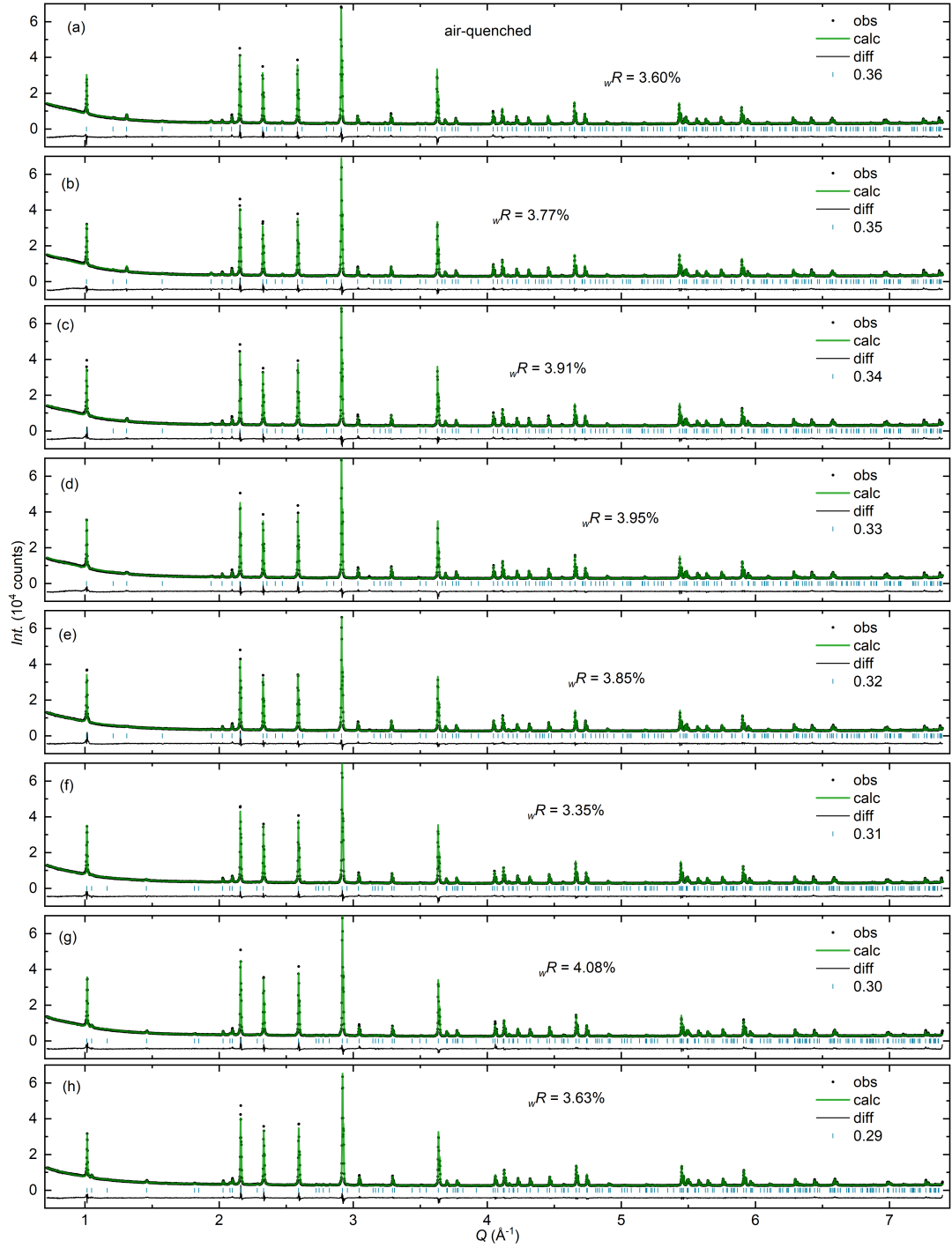


Figure 5.7: Full range Rietveld analysis of powder X-ray diffraction on the air-quenched samples. Rietveld analysis for  $x \geq 0.32$  (a-e) was done using  $P6_322$  space group while  $x \leq 0.31$  (f-h) with  $P6_3/mmc$ .

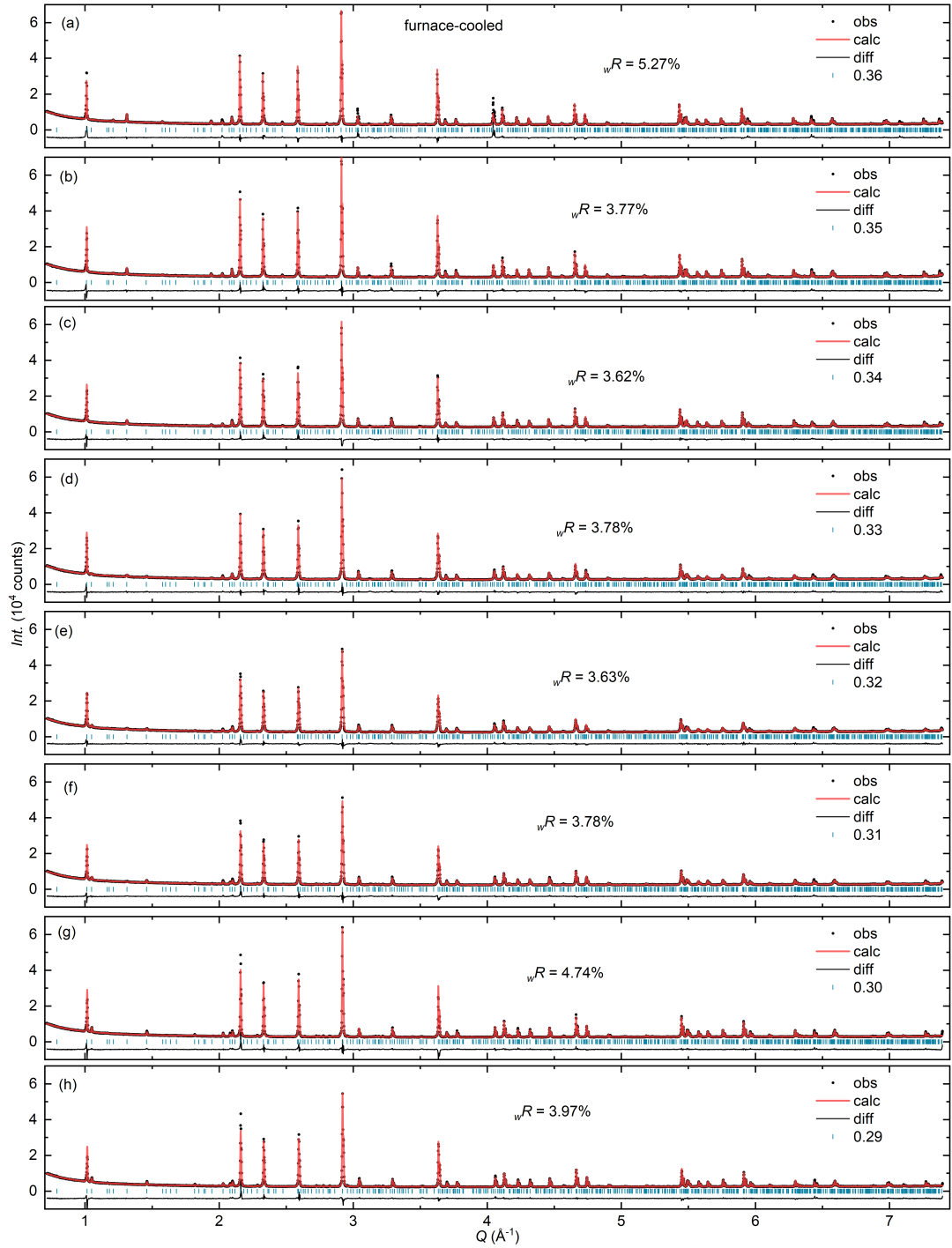


Figure 5.8: Full range Rietveld analysis of powder X-ray diffraction on the furnace-cooled samples. All data (a-h) were refined using the super lattice ( $2\sqrt{3}a \times 2\sqrt{3}a$ )  $P6_322$  space group.

difference Fourier maps[28].

The connections between the  $2a_h \times 2a_h$  and  $\sqrt{3}a_h \times \sqrt{3}a_h$  sublattices can be understood by considering how the Co intercalant occupancy of the Wyckoff positions are interrelated in their respective space groups. For  $x = 1/3$ , cobalt preferentially occupies the  $2c$  Wyckoff site to form the  $\sqrt{3}a_h \times \sqrt{3}a_h$  sublattice highlighted by red octahedra in Figure 5.1. When the intercalant content exceeds this value or becomes disordered, cobalt begins to populate the adjacent  $2b$  site (Figure 5.1d). Similarly, at  $x = 1/4$ , cobalt orders on the  $2a$  site to form the  $2a_h \times 2a_h$  sublattice, while excess cobalt occupies the  $6g$  site (Figure 5.1b). We observe that the  $2a$  site occupancy, which defines the  $2a_h \times 2a_h$  sublattice, increases with cobalt content up to  $x = 0.32$ . At this composition, the occupancy of the  $2a$  site matches that of the  $2b$  site from the  $P6_322$  structure. Beyond this point,  $2b$  site occupancy decreases with increasing  $x$ . Simultaneously, the  $6g$  site occupancy in the  $P6_3/mmc$  structure increases and drives the population of the  $2c$  sites associated with the  $\sqrt{3}a_h \times \sqrt{3}a_h$  sublattice.

## Domain coexistence in furnace-cooled samples

The second row of Figure 5.4 presents data for furnace-cooled  $\text{Co}_x\text{NbSe}_2$  samples of the same compositions. Unlike the air-quenched series, these pXRD patterns show Bragg reflections from both the  $2a_h \times 2a_h$  and  $\sqrt{3}a_h \times \sqrt{3}a_h$  sublattices (Figure 5.4(d)), indicating structural coexistence. While the diffraction profiles can be fit using a two-phase Rietveld refinement, it leads to unnecessary redundancies and poorer quality fits. For example, the intercalant distance from site  $2c$  to  $2b$  in the  $\sqrt{3}a_h \times \sqrt{3}a_h$  arrangement equals  $a_h$ , which is equivalent to the distance from the  $6g$  site to the  $2c$  within the  $2a_h \times 2a_h$  model (Figure 5.1). The two-phase fit leads to worse residuals in the refinement as well in addition to having to create many constraints to stabilize the two-phase fit. One crystallographic model, however, significantly simplifies the fitting routine. Finally, our prior work on single-crystal samples



demonstrated that the two sublattices coexist within a single structural framework.

We therefore propose that the superlattice structure given by  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  (Figure 5.1(e)(f)), is a convenient model for describing the intermediate phases with domain mixture. This is different from phase mixing in the sense that within a single crystal or crystallite, both the  $2a_h \times 2a_h$  and  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains are found. Such a model has been proposed previously by us[1] and Corbett *et al.* for the  $\text{Fe}_x\text{NbS}_2$  system[225]. As a bulk technique, the powder diffraction patterns cannot discern whether this coexistence occurs as staging of different domains in different layers or as domains coexisting at the nanoscale within lateral dimensions. Likely, a technique such as electron microscopy is needed to elucidate which of the two scenarios best describes the domain coexistence. From a diffraction perspective, we can index the superlattice reflections of  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  within the same space group  $P6_322$  of  $\sqrt{3}a_h \times \sqrt{3}a_h$  by doubling the indices in the  $hk$ -plane. To extend this model to the  $2a_h \times 2a_h$  model, we perform the following transformation of the Bragg reflection indices:

$$\begin{bmatrix} h \\ k \\ l \end{bmatrix}^{2a_h \times 2a_h} = \begin{bmatrix} 1/3 & 1/3 & 0 \\ 1/3 & -2/3 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} h \\ k \\ l \end{bmatrix}^{2\sqrt{3}a_h \times 2\sqrt{3}a_h}$$

Temperature-dependent magnetic susceptibility of the furnace-cooled series reveals two coexisting AFM transitions in the range  $0.31 \leq x \leq 0.33$  (Figure 5.4(e)). Within this window, both the low-temperature transition ( $T_N^S$ ) associated with the  $\sqrt{3}a_h \times \sqrt{3}a_h$  sublattice and the high-temperature transition ( $T_N^A$ ) characteristic of  $2a_h \times 2a_h$  are observed. Outside this composition range, only one magnetic transition appears, corresponding to the single dominant sublattice.

The presence of both magnetic transitions is linked to cobalt site occupancy. Rietveld analysis using the  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  structure provides the site distribution of the intercalant plotted in Figure 5.4(f). As cobalt content increases, the  $6h$  site is gradually populated,

analogous to how the  $6g/2c$  site is populated in the air-quenched series. The  $6h$  site is particularly significant because its occupation breaks inversion symmetry, as observed by the absence of a cobalt neighbor directly above or below in the adjacent vdW layer.

When either the  $2c$  or  $2d$  site is occupied, inversion is broken. However, they have the same site symmetry, and if they are simultaneously and equally populated, then inversion symmetry is reintroduced. If only the  $2b$  site were occupied, then inversion would also be reasserted, and the structure made centrosymmetric. Thus, increasing  $6h$  occupancy, along with decreasing occupation of the  $2b$  and  $2c/d$  sites, enhances the overall non-centrosymmetric character of the structure. The advantage of the  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  model is that it can successfully capture the smooth transition from a centrosymmetric structure to a noncentrosymmetric one and also their coexistence according to occupation of certain Wyckoff sites. Clearly, the model has its limits as it physically cannot have both types of occupancy within a single unit cell, as shown in Figure 5.1(e) and (f). However, its advantage is a crystallographic one that helps track the occupancy of the Co atom for both polycrystalline and single crystal samples and for a broad range of  $x$  in  $\text{Co}_x\text{NbSe}_2$ .

A notable comparison arises at  $x = 0.32$ : the air-quenched sample shows negligible formation of either the  $2a_h \times 2a_h$  or  $\sqrt{3}a_h \times \sqrt{3}a_h$  sublattices, while the furnace-cooled counterpart displays clear evidence of both. This contrast highlights the strong influence of synthesis conditions on stabilizing competing structural domains. We will later revisit the local structures of these two samples prepared by different thermal treatments.

### 5.3.2 Neutron Diffraction: from Altermagnetism to Spin Density Waves

Neutron diffraction of air-quenched  $\text{Co}_x\text{NbSe}_2$  (Figure 5.9(g and h)) reveals three distinct magnetic ground states. For  $x \geq 0.35$ , a two- $q$  magnetic structure is observed below  $T_N^S < 36$  K (Figure 5.10). As  $x$  decreases, the magnetic signal weakens and becomes undetectable

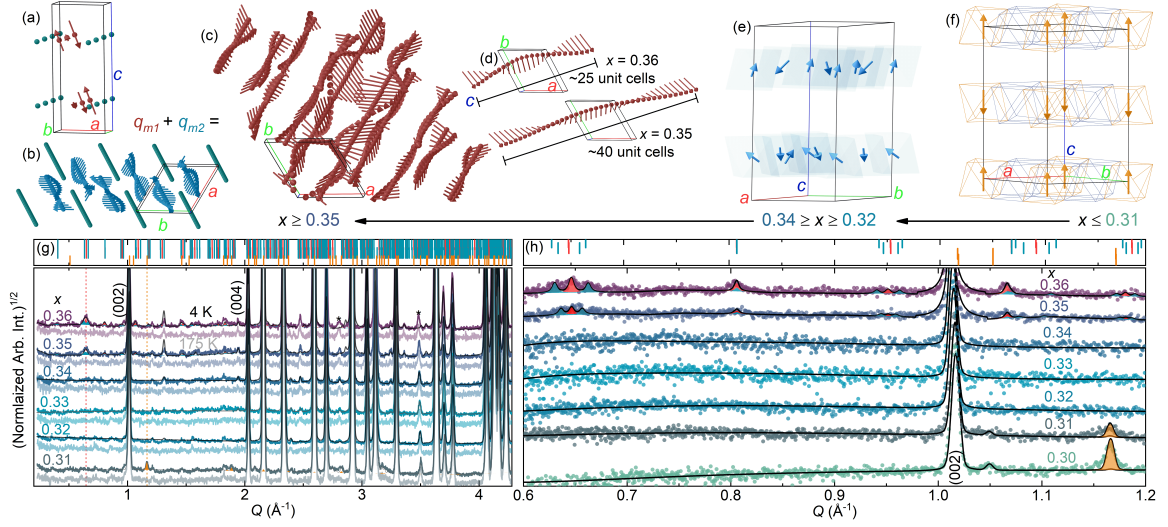


Figure 5.9: (a-f) Magnetic structures of  $\text{Co}_x\text{NbSe}_2$  obtained from Rietveld refinements of neutron powder diffraction collected at (g) POWDER and (h) POWGEN. The top panels from refinements only show magnetic Bragg indices. Red indices correspond to the commensurate  $q_{m1} = (0, 1/3, 0)$  structure (a) and blue indices to incommensurate  $q_{m2} = (0, 1/3, \delta)$  (b), both refined in the  $P6_322$  space group. Adding both magnetic propagation vectors gives the double- $q$  structure (c). (d) Approximation of the spin density wave length along the vertical  $c$ -axis for  $x = 0.36$  and  $0.35$ . (e) Fictitious representation of spin-glass-like magnetic disorder. (h) A-type altermagnetic structure indexed by the orange Bragg indices corresponds to the  $q_m = (0, 0, 0)$  in the  $P6_3/mmc$  symmetry (f). The bottom arrow guides the eye to the structure evolution as the cobalt content,  $x$ , increases.

Table 5.1: Refined magnetic structure parameters of  $\text{Co}_x\text{NbSe}_2$ . All values are given in Bohr Magnetons ( $\mu_B$ ). Representation analysis and constraints were kept the same as in Reference [1].

| $q_1 = (0, 1/3, 0)$      |                  |        |        |           |          |                |
|--------------------------|------------------|--------|--------|-----------|----------|----------------|
| $x$                      | $\text{Co}^{2c}$ | $C_1$  | $C_2$  | $C_{3-6}$ | $\phi$   | $ \mu_{tot.} $ |
| 0.36                     | 1                | -1.09  | -2.35  | 0         | -0.047   | 2.5(3)         |
|                          | 2                | 1.1(3) | 2.3(2) | 0         | 0.05(1)  |                |
| 0.35                     | 1                | -0.74  | -1.53  | 0         | -0.049   | 1.6(4)         |
|                          | 2                | 0.7(4) | 1.5(3) | 0         | 0.05(2)  |                |
| $q_2 = (0, 1/3, \delta)$ |                  |        |        |           |          |                |
| $x$                      | $\text{Co}^{2c}$ | $C_1$  | $C_2$  | $C_{3-6}$ | $\delta$ | $ \mu_{tot.} $ |
| 0.36                     | 1                | 2.48   | 0      | 0         | 0.041(8) | 2.5(2)         |
|                          | 2                | 0      | 2.5(2) | 0         |          |                |
| 0.35                     | 1                | 1.89   | 0      | 0         | 0.026(2) | 1.9(2)         |
|                          | 2                | 0      | 1.9(2) | 0         |          |                |

for  $0.34 \geq x \geq 0.32$ . Long-range magnetic order reappears below  $x \leq 0.31$  with a single commensurate vector  $q_m = (0, 0, 0)$ .

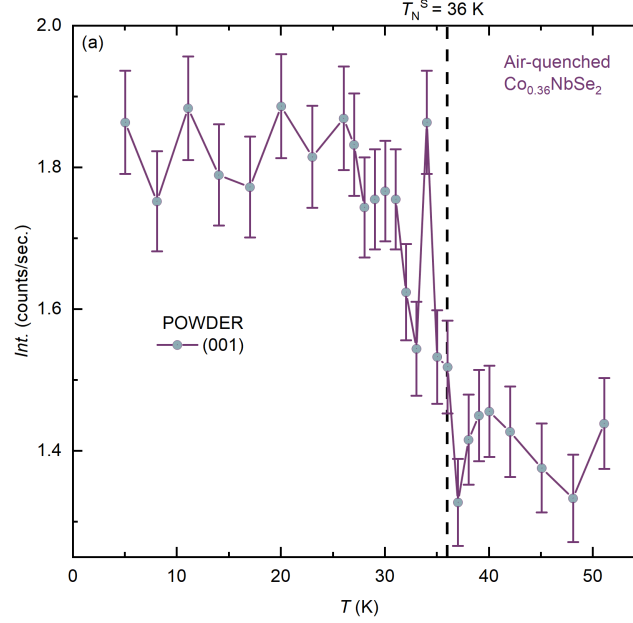


Figure 5.10: Temperature-dependent order parameter of  $\text{Co}_{0.36}\text{NbSe}_2$  following the (001) magnetic reflection indexed by  $q_{m1} = (0, 1/3, 0)$  using neutron diffraction.

At  $x = 0.35$  and  $0.36$ , the magnetic structure consists of a commensurate  $q_{m1} = (0, 1/3, 0)$  and an incommensurate SDW  $q_{m2} = (0, 1/3, \delta)$  (Figure 5.9(a and b)). Superimposing these two propagation vectors forms a double- $q$  SDW shown in Figure 5.9(c). In the SDW,  $q_{m1}$  propagates in-plane with moments out-of-plane, while  $q_{m2}$  propagates along  $c$  with in-plane moments. The periodicity of the incommensurate SDW spans  $\sim 40$  unit cells at  $x = 0.35$ , shrinking to  $\sim 25$  when  $x$  increases to  $0.36$ , alongside a larger moment amplitude as shown in Figure 5.9(d). The refined magnetic structure parameters are listed in Table 5.1. At  $x \approx 0.37$  (10% Co-excess), the incommensurate signal further intensifies with a shortened periodicity (20 cells)[1]. Similar magnetostructural deviations have been observed in  $\text{Co}_x\text{TaS}_2$  and  $\text{Cr}_x\text{MS}_2$ , where excess doping or synthesis conditions tune helical or SDW

states[24, 64, 188]. We attribute the SDW enhancement to excess Co occupying the  $2a$  site (Figure 5.4(c)), which introduces magnetic frustration through competing exchange interactions.

For  $x \leq 0.31$ ,  $\text{Co}_x\text{NbSe}_2$  exhibits a collinear  $A$ -type AM structure (Figure 5.9 (f)) consistent with the high-temperature  $T_N^A$ [190]. This structure belongs to the magnetic space group  $P6'_3/m'm'c$ [1, 48, 58, 66]. The ordered moment increases from  $1.13(7)\mu_B$  at  $x = 0.31$  to  $1.61(7)\mu_B$  at  $x = 0.30$ , trending towards the  $1/4$  stoichiometry. We find that long-range magnetic order correlates with Co occupancy on the  $2a$  site (Figure 5.4(c)), which varies between  $0.709(25) \geq \text{Occ.}^{\text{Co}2a} \geq 0.482(53)$  for intercalant ratios of  $0.31 \leq x \leq 0.32$ . In contrast, compositions with  $0.32 \leq x \leq 0.34$  show no detectable magnetic reflections up to  $d_{\text{max}} = 27.7 \text{ \AA}$ , suggesting a spin-glass state in this range (Figure 5.9(e)). This speculation is explored further through bulk magnetism and specific heat measurements.

### 5.3.3 Specific Heat and Entropy Suppression in Disordered Phases

Specific heat measurements shown in Figure 5.11 were performed to understand the nature of the magnetic anomaly, where no long-range order was observed. The broadness of the specific heat at the transition, along with the bifurcating ZFC and FC magnetic susceptibility (Figures 5.27 and 5.28), strongly suggests a spin-glass transition; a metastable state in which the spin moments freeze in a random direction under ZFC conditions. Such behavior is well-documented in intercalated TMDs, including  $\text{Fe}_x\text{NbS}_2$ , where sharp antiferromagnetic transitions at the stoichiometric  $1/3$  phase broaden at off-stoichiometric intercalation ratios[80, 83, 84, 203, 226].

We estimate the magnetic entropy (Figure 5.11(c)) by subtracting a fitted Debye-Einstein baseline from the specific heat. The phase transition order changes as the sharp transition of  $x = 0.36$  broadens in the lesser cobalt samples. Integrating the area under the magnetic

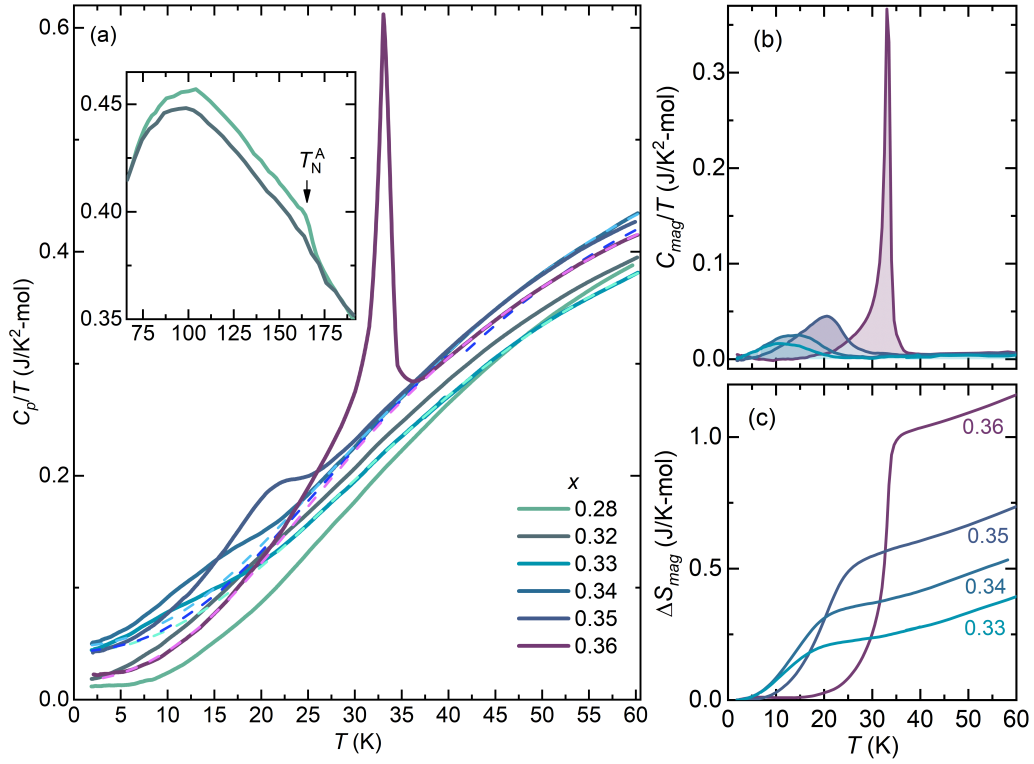


Figure 5.11: (a) Specific heat over temperature fitted to the Debye-Einstein model (dashed lines). The data between 3 K and 40 K were excluded from the fitting. The inset shows the high-temperature specific heat of  $x = 0.28$  and  $0.32$ . (b) Magnetic specific heat estimated by subtracting the Debye-Einstein fit. (c) Magnetic entropy is obtained from integrating the magnetic specific heat over temperature.

specific heat curve demonstrates that less magnetic entropy is released with decreasing cobalt content, indicating spin disorder[59, 83]. This entropy suppression is also consistent with the metallic character of the system, leading to delocalized itinerant moments[32, 66, 68].

### 5.3.4 Glassy Magnetic Hysteresis in Intermediate Compositions

Magnetization curves measured at 2 K form a dome-like trend across the series, with the highest moment observed at  $x = 0.32$  (Figure 5.13 (a)). More details and high-temperature curves are provided in Figure 5.12. While most samples follow a predominantly linear AFM response, small deviations from linearity are seen in intermediate compositions. To isolate

this deviation, we subtract a linear AFM background extrapolated from high-field data.

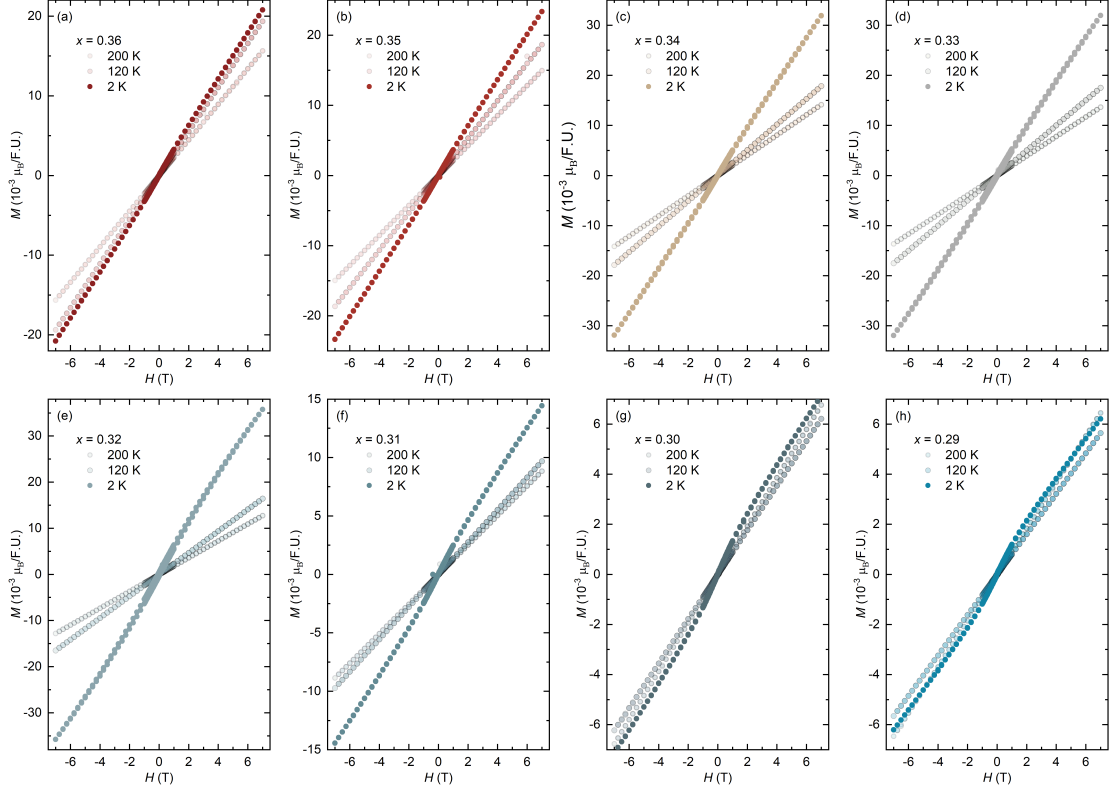


Figure 5.12: (a-h) Field-dependent magnetization curves at 200 K, 120 K, and 2 K of air-quenched  $\text{Co}_x\text{NbSe}_2$ , for  $x = 0.36$  to  $0.29$ .

The resulting magnetization difference,  $\Delta M$  (Figure 5.13(b)), reveals a hysteresis loop for  $0.34 \geq x \geq 0.32$  samples, with the largest coercive field  $H_c \approx 0.3$  T observed at  $x = 0.32$  (Figure 5.13(c)). This hysteresis appears only in samples that exhibit spin-glass behavior, suggesting that it is tied to a metastable magnetic phase stabilized from quenching. The coercivity may lead to exchange-bias[81, 82], which would be worth studying in a single-crystal sample.

We propose that this glassy phase may result from the formation of frustrated triangular clusters of intercalated Co atoms, which prevent long-range order while suppressing mag-

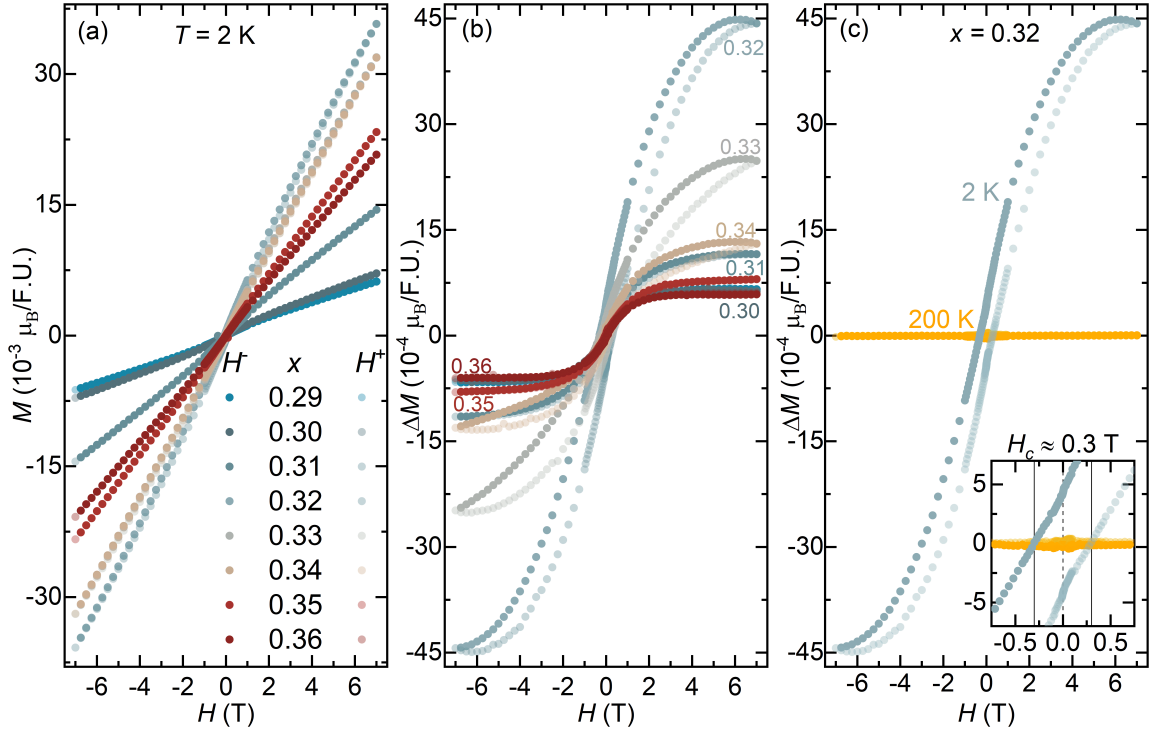


Figure 5.13: (a) Magnetization curves of air-quenched  $\text{Co}_x\text{NbSe}_2$  at 2 K. (b) Magnetization curve after subtracting a linear antiferromagnetic background slope at 2 K. (c) Subtracted magnetization of  $\text{Co}_{0.32}\text{NbSe}_2$  at 2 K and 200 K. Inset displays the coercive field.

netic entropy release[83, 227–230]. Such frustration is consistent with the small entropy changes observed in the specific heat data.

It has been well established that stoichiometric  $\text{Co}_{0.25}\text{NbSe}_2$  hosts a robust A-type AM structure under applied field[231, 232]. Thus, we argue here that the weak ferromagnetic components of the non-glassy samples are likely due to the magnetization of isolated, uncoupled  $\text{Co}^{2+}$  spins of the intercalant[177, 233, 234].

### 5.3.5 $\text{Co}_{0.32}\text{NbSe}_2$ Ground States

Intercalant site preference dictates  $\text{Co}_x\text{NbSe}_2$ 's magnetic ground state. We compare the structures of furnace-cooled and air-quenched  $\text{Co}_{0.32}\text{NbSe}_2$  samples in this section, followed by a discussion of the local structural mechanism.



## Average Nuclear and Magnetic Structure

We refine the nuclear structure from neutron powder diffraction at 200 K and determine the average site occupancy of cobalt (Figure 5.14(a)). The air-quenched sample, as previously established, was fitted in the  $P6_322$  space group (Figure 5.14(c) and Table 5.2); however, it is also possible to fit the pattern in  $P6_3/mmc$  (Table 5.3). This indicates that cobalt sites are almost evenly distributed in the layer. We further qualify this statement: if the weak sublattice reflections between (002) and (004) are neglected, the pattern can then be indexed by the  $a_h \times a_h$  host lattice parameters, implying a disordered cobalt distribution in the interstitial vdW gap with no preferred sites. Nonetheless, the presence of sublattice reflections and the low spin-glass freezing temperature ( $T_f \approx 7$  K) point to preferred occupation of the  $\sqrt{3}a_h \times \sqrt{3}a_h$  sites, albeit with sufficient disorder to suppress long-range magnetic ordering below  $T_f$ .

Table 5.2: Atomic Coordinates and Parameters of air-quenched  $\text{Co}_{0.32}\text{NbSe}_2$  in the  $P6_322$  from neutron powder diffraction collected at 200 K.

| Atom          | Wyck. Pos. | $x$                          | $y$       | $z$                           | Fracc.    | $U_{iso} (\text{\AA}^2)$ |
|---------------|------------|------------------------------|-----------|-------------------------------|-----------|--------------------------|
| Co1           | $2c$       | 1/3                          | 2/3       | 3/4                           | 0.366(31) | 0.0006(5)                |
| Co2           | $2b$       | 0                            | 0         | 3/4                           | 0.507(31) | 0.0006(5)                |
| Nb1           | $2a$       | 0                            | 0         | 1/2                           | 1         | 0.0016(1)                |
| Nb2           | $4f$       | 1/3                          | 2/3       | 0.4985(2)                     | 1         | 0.0024(4)                |
| Se1           | $12i$      | 0.3342(9)                    | 0.3354(9) | 0.6342(2)                     | 1         | 0.00291(3)               |
| $wR = 5.19\%$ |            | Unit cell parameters         |           |                               |           |                          |
| $P6_322$      |            | $a = 5.99416(5) \text{ \AA}$ |           | $c = 12.40675(2) \text{ \AA}$ |           |                          |

In contrast, the furnace-cooled sample has strong contributions from both the  $2a_h \times 2a_h$  and  $\sqrt{3}a_h \times \sqrt{3}a_h$  sublattices. Thus, the average cobalt occupancies are determined using the  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  superlattice. The  $2b$  and  $2d$  sites that define the  $2a_h \times 2a_h$  arrangement are nearly fully occupied (Figure 5.14(b)), while the  $6h$  and  $2c$  sites show partial occupation, each below 50% (Table 5.4).

Concomitant to the structural coexistence, two magnetic phase transitions are observed

Table 5.3: Atomic Coordinates and Parameters of air-quenched  $\text{Co}_{0.32}\text{NbSe}_2$  in the  $P6_3/mmc$  from neutron powder diffraction collected at 200 K.

| Atom                 | Wyck. Pos.                    | $x$        | $y$                            | $z$        | Fracc.    | $U_{iso} (\text{\AA}^2)$ |
|----------------------|-------------------------------|------------|--------------------------------|------------|-----------|--------------------------|
| Co1                  | $2a$                          | 0          | 0                              | 1/2        | 0.482(53) | 0.0013(5)                |
| Co2                  | $6g$                          | 1/2        | 0                              | 0          | 0.224(18) | 0.0013(5)                |
| Nb1                  | $2b$                          | 0          | 0                              | 1/4        | 1         | 0.0029(8)                |
| Nb2                  | $6h$                          | 0.499(2)   | 0.998(4)                       | 1/4        | 1         | 0.00234(3)               |
| Se1                  | $12k$                         | 0.33345(8) | 0.1667(4)                      | 0.38344(6) | 1         | 0.00291(3)               |
| Se2                  | $4f$                          | 1/3        | 2/3                            | 0.1135(2)  | 1         | 0.0031(6)                |
| $wR = 4.65\%$        |                               |            |                                |            |           |                          |
| Unit cell parameters |                               |            |                                |            |           |                          |
| $P6_3/mmc$           | $a = 6.919554(48) \text{\AA}$ |            | $c = 12.402160(68) \text{\AA}$ |            |           |                          |

Table 5.4: Atomic Coordinates and Parameters of furnace-cooled  $\text{Co}_{0.32}\text{NbSe}_2$  in the  $P6_322$  from neutron powder diffraction collected at 200 K.

| Atom                 | Wyck. Pos.                    | $x$        | $y$                           | $z$        | Fracc.     | $U_{iso} (\text{\AA}^2)$ |
|----------------------|-------------------------------|------------|-------------------------------|------------|------------|--------------------------|
| Co1                  | $2b$                          | 0          | 0                             | 1/4        | 0.9323(12) | 0.00064(8)               |
| Co2                  | $6h$                          | 0.1685     | 0.3370                        | 1/4        | 0.397 (12) | 0.00064(8)               |
| Co3                  | $2c$                          | 1/3        | 2/3                           | 1/4        | 0.3273(12) | 0.00064(8)               |
| Co4                  | $2d$                          | 2/3        | 1/3                           | 1/4        | 0.9622(12) | 0.00064(8)               |
| Nb1                  | $2a$                          | 0          | 0                             | 1/2        | 1          | 0.0023(2)                |
| Nb2                  | $12i$                         | 0.1618(28) | 0.3331(21)                    | 0.5044(4)  | 1          | 0.0023(2)                |
| Nb3                  | $4f$                          | 1/3        | 2/3                           | 0.5055(6)  | 1          | 0.0023(2)                |
| Nb4                  | $6g$                          | 0.5045(53) | 0.5045(53)                    | 1/2        | 1          | 0.0023(2)                |
| Se1                  | $12i$                         | 0.1677(39) | 0.1677(39)                    | 0.3672(17) | 1          | 0.0029(3)                |
| Se2                  | $12i$                         | 0.0001(10) | 0.3345(28)                    | 0.3589(1)  | 1          | 0.0029(3)                |
| Se3                  | $12i$                         | 0.3333(66) | 0.4995(34)                    | 0.3681(9)  | 1          | 0.0029(3)                |
| Se4                  | $12i$                         | 0.4984(35) | 0.3333(65)                    | 0.3675(9)  | 1          | 0.0029(3)                |
| $wR = 7.74\%$        |                               |            |                               |            |            |                          |
| Unit cell parameters |                               |            |                               |            |            |                          |
| $P6_322$             | $a = 11.97998(24) \text{\AA}$ |            | $c = 12.38341(16) \text{\AA}$ |            |            |                          |

in magnetic susceptibility (Figure 5.4(e)), each corresponding to a sublattice. Neutron diffraction at 40 K for the  $x = 0.31$  composition has magnetic reflections corresponding to the A-type AM phase responsible for  $T_N^A$  (Figure 5.15). In the superlattice setting, the magnetic space group is  $P6_3'22'$  and is structurally equivalent to the  $P6_3'/m'm'c$  symmetry of the  $2a_h \times 2a_h$  structure (Figure 5.16). At base temperature ( $T < T_N^S$ ), no new magnetic reflections appear. The lack of the expected SDW magnetic Bragg reflections supports the argument that site occupancy directly governs the emergence of long-range magnetic order.

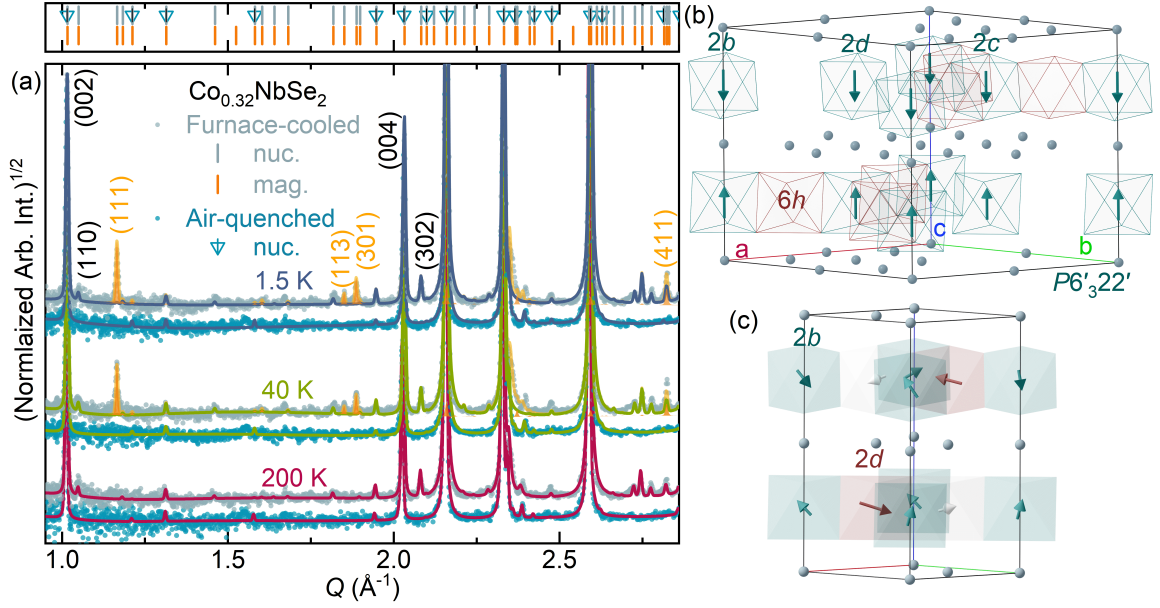


Figure 5.14: (a) Neutron powder diffraction of furnace-cooled and air-quenched  $\text{Co}_{0.32}\text{NbSe}_2$ . The top panel shows nuclear Bragg reflections with a triangle tick mark for the air-quenched data set and line tick marks for furnace-cooled. Magnetic Bragg reflections are shown below with orange line tick marks. (b) A-type altermagnetic structure obtained from Rietveld analysis of the furnace-cooled sample using the  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  model. (c) Refined nuclear structure of the air-quenched sample depicting site disorder leading to a lack of long-range order in the  $\sqrt{3}a_h \times \sqrt{3}a_h$  model.

Whether the long-range order of both the AM and SDW phases coexist at higher cobalt intercalation ratios remains unresolved. We posit that one phase will always be suppressed as the other is enhanced, as shown in Figure 5.4(f).

## Preferred Local Domain Formation

While diffraction techniques provide a reliable estimate of average intercalant occupancy, they suffer from intrinsic correlations between occupancy and atomic displacement parameters. To address this limitation and probe short-range structural correlations, we employed pair distribution function (PDF) analysis, which captures local atomic environments. We implement small-box modeling to determine the preferred sublattice domain formation and big-box modeling for the preferred site occupancy.

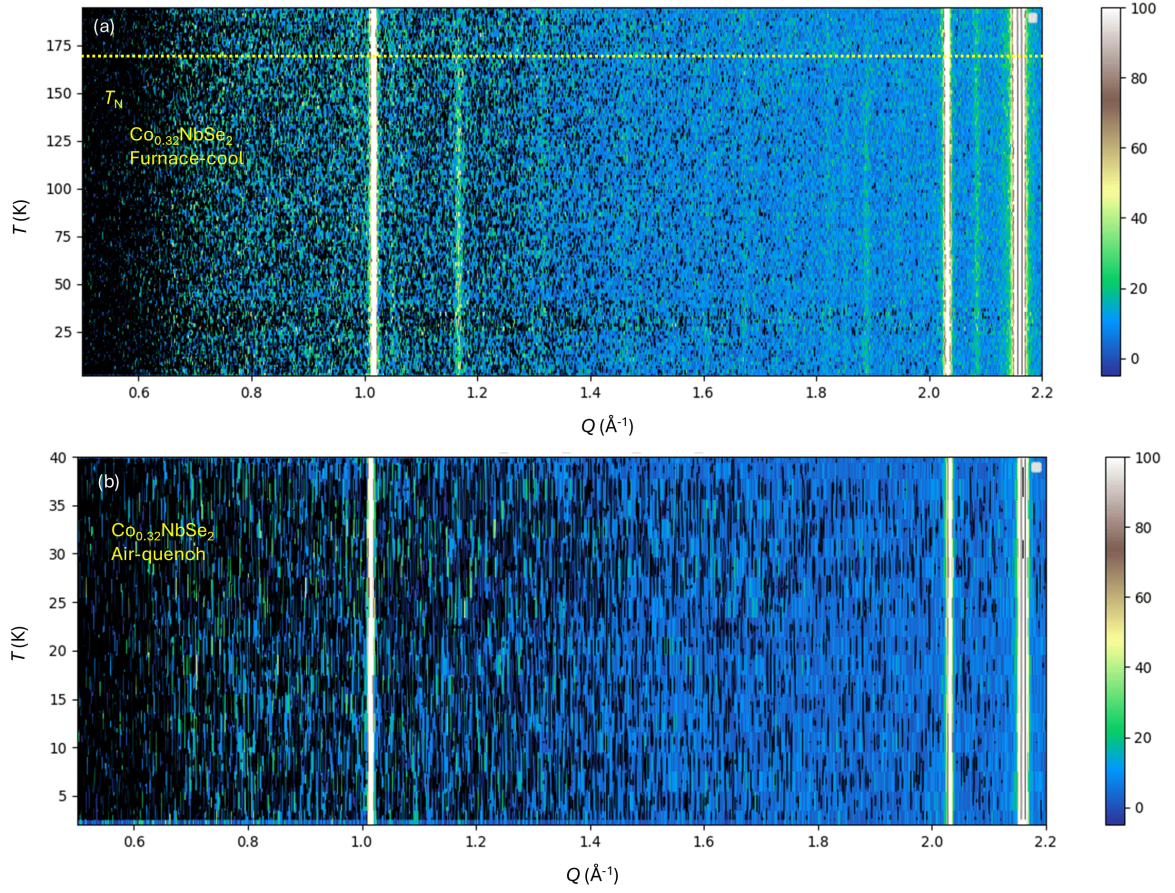


Figure 5.15: Order parameter of neutron powder diffraction as a function of temperature of (a) furnace-cooled and (b) air-quenched  $\text{Co}_{0.32}\text{NbSe}_2$ . Intensity is on a logarithmic scale.

Small-box refinements show good agreement with the average crystallographic structure for all samples with  $x \geq 0.32$  (Figure 5.17). However, for  $x \leq 0.31$ , we find local  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains are present (Figure 5.18). In the context of intercalant domain formation, we find that the Co-Co partial contribution is relatively negligible compared to the host  $\text{NbSe}_2$ , rendering any results from refining the cobalt site occupancies unreliable (Figure 5.19). We thus resort to the reverse Monte Carlo method (*i.e.*, big-box) to determine the intercalant's local ordering tendencies.

To enable a direct comparison of structural motifs in the RMC analysis, we expanded

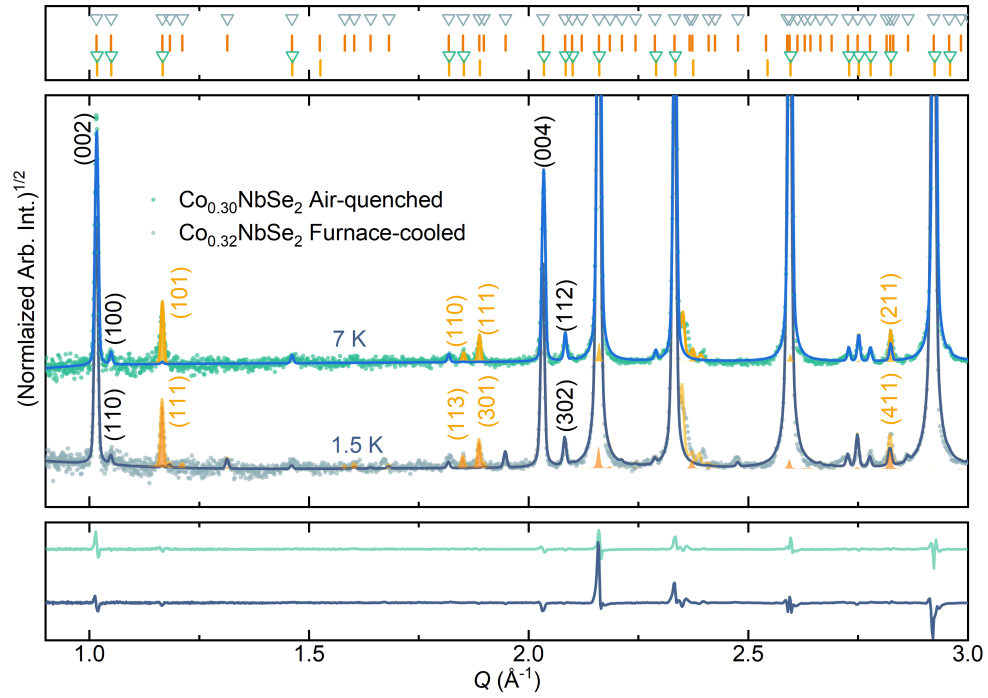


Figure 5.16: Neutron powder diffraction comparison of air-quenched  $\text{Co}_{0.30}\text{NbSe}_2$  and furnace-cooled  $\text{Co}_{0.32}\text{NbSe}_2$ .

the unit cells of each parent structure to equivalent supercell dimensions: a  $16 \times 16 \times 4$  supercell for the  $\sqrt{3}a_h \times \sqrt{3}a_h$  structure (air-quenched) and an  $8 \times 8 \times 4$  supercell for the  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  structure (furnace-cooled), both reduced to  $P1$  symmetry. The cobalt content was fixed to the Rietveld-derived occupancies, and a 0.2 site-swapping probability between cobalt and vacant octahedral sites was permitted. Figures 5.20(a) and (b) show the resulting RMC fits, with structural models recombined into the  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  setting for comparison.

We analyzed the resulting supercells by calculating the bond angle distributions for both cobalt octahedra (Figure 5.20(c)) and niobium trigonal prisms (Figure 5.20(d)). The results reveal a trade-off: increasing cobalt site uniformity induces greater distortion of the

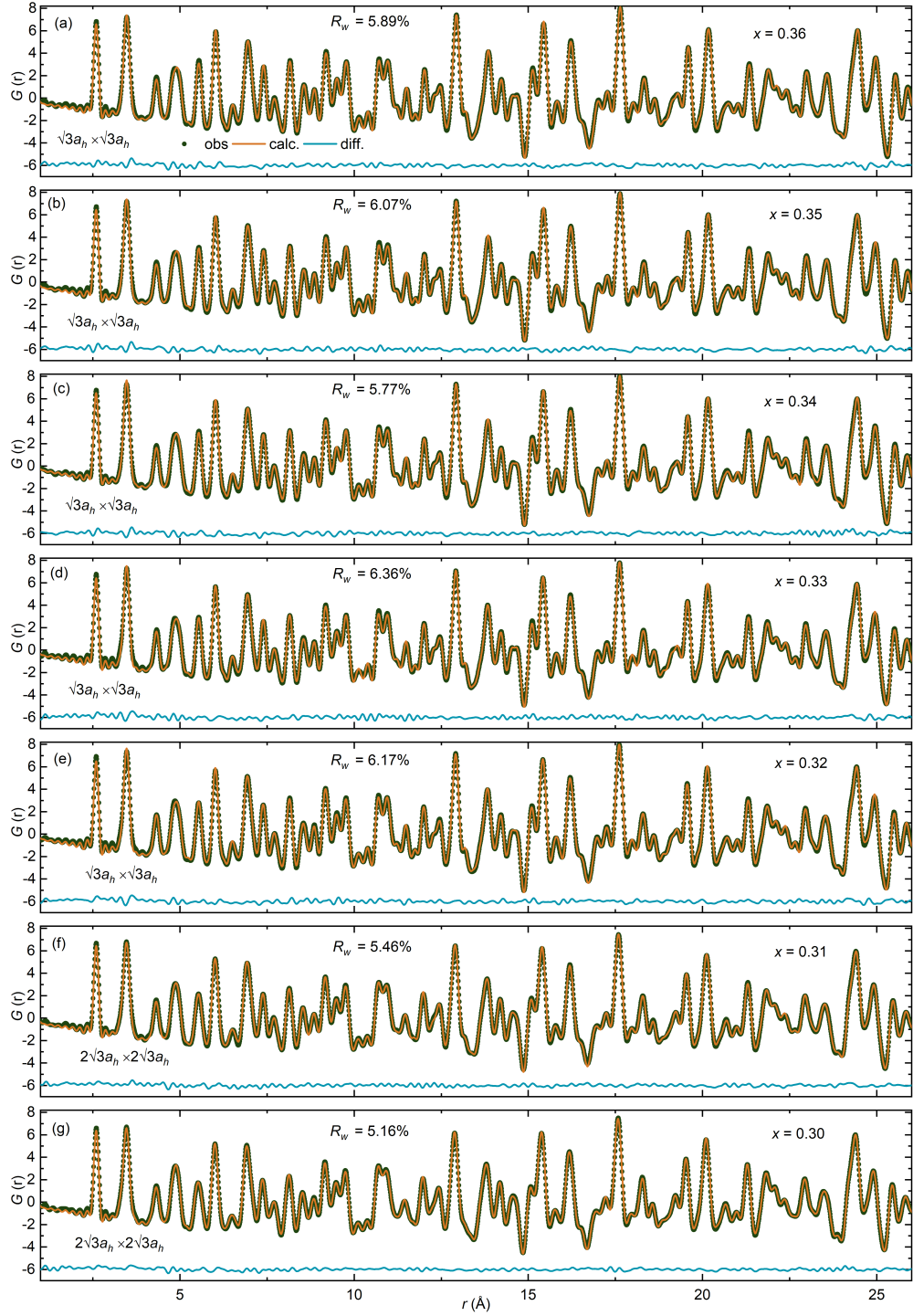


Figure 5.17: Small-box neutron powder pair distribution function analysis of air-quenched  $\text{Co}_x\text{NbSe}_2$  collected at 200 K. (a-e)  $x = 0.36$  to  $0.32$  are modeled with non-centrosymmetric only domains ( $\sqrt{3}a_h \times \sqrt{3}a_h$ ). (f-g)  $x = 0.31$  and  $0.30$  are modeled with the coexisting domain superlattice, indicating that  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains' stability at low intercalation ratios.



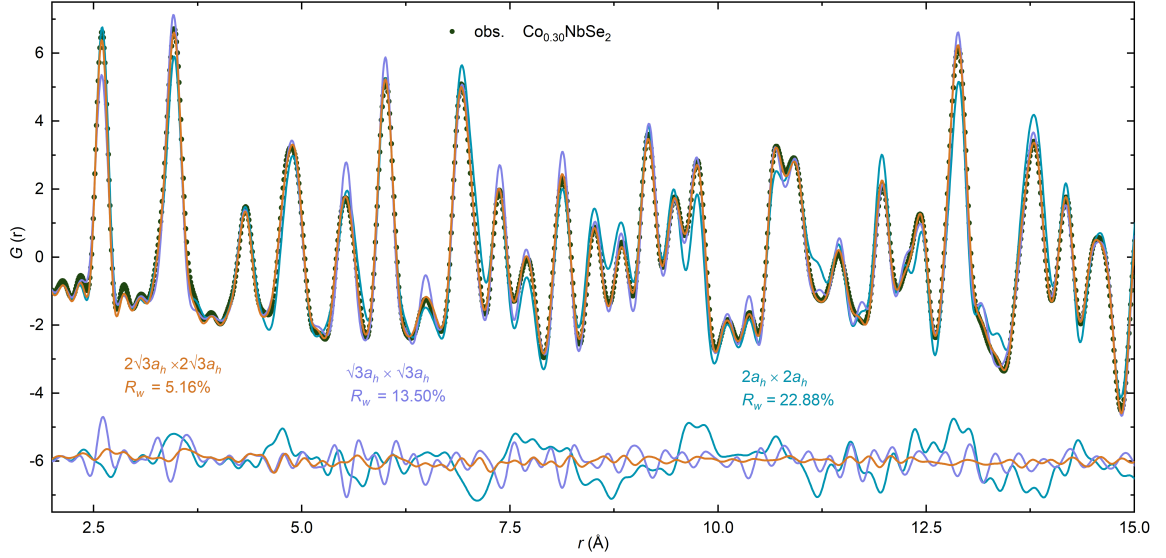


Figure 5.18: Small-box neutron powder pair distribution function analysis of air-quenched  $\text{Co}_{0.30}\text{NbSe}_2$  collected at 200 K. Data was modeled using the three space groups. Superlattice  $P6_322$  with  $2\sqrt{3}a_h \times 2\sqrt{3}a_h$  model with coexisting domains is shown in orange,  $P6_322$  with only  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains is shown in purple, and  $P6_3/mmc$  with  $2a_h \times 2a_h$  domains in blue.

host  $\text{NbSe}_2$  lattice, while preserving the idealized  $\text{NbSe}_2$  prism geometry leads to increased cobalt site disorder.

We then quantify the local domain formation by focusing on characteristic bond angles associated with each sublattice type. In the  $2a_h \times 2a_h$  configuration, cobalt atoms form interlayer Co-Nb-Co chains along the  $c$ -axis with an ideal  $180^\circ$  bond angle (Figure 5.20(e)). This geometry also has a characteristic intralayer angle near  $96^\circ$  as shown in the inset of Figure 5.20(f). Conversely,  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains are off-centered along the  $c$ -direction, with  $\sim 100^\circ$  angle between interlayered Co-Nb-Co. The total distribution of these three characteristic angles shows both domains coexisting in both samples, though with distinct preferences: air-quenched samples favor  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains, while furnace-cooled samples stabilize the  $2a_h \times 2a_h$  configuration. This is most clearly seen in Figure 5.20(f), where the distributions centered at  $96^\circ$  and  $100^\circ$  provide a useful ratio index to quantify

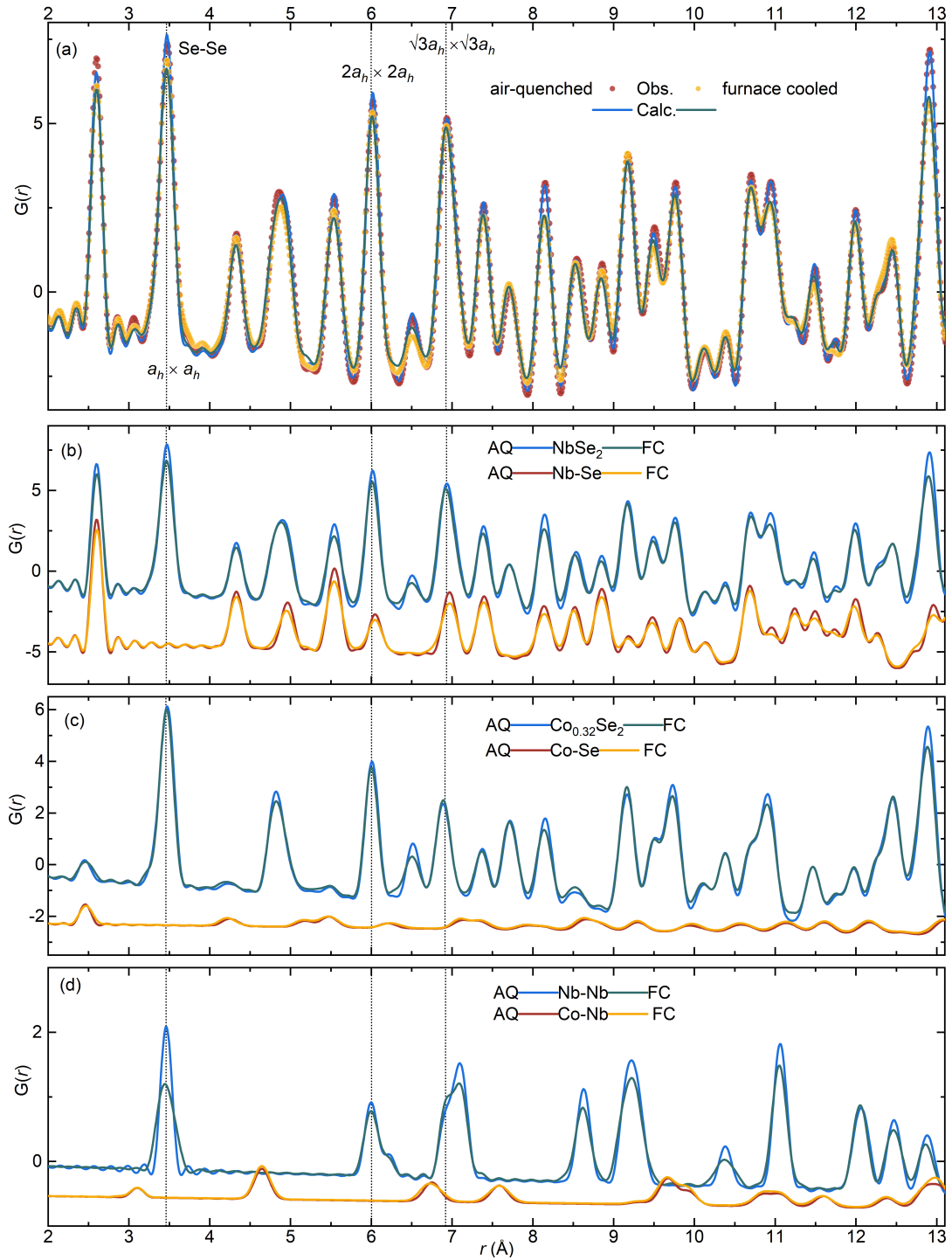


Figure 5.19: Small-box neutron powder pair distribution function analysis. (a) Total scattering fit of air-quenched (AQ) and furnace-cooled (FC)  $\text{Co}_{0.32}\text{NbSe}_2$ . (b) Calculated partials of  $\text{NbSe}_2$  host and Nb-Se pair. (c) Calculated partial of the  $\text{Co}_x\text{Se}_2$  layer and Co-Se pair. (d) Nb-Nb and Co-Nb pair partials. Co-Co is not shown as its contribution is small.



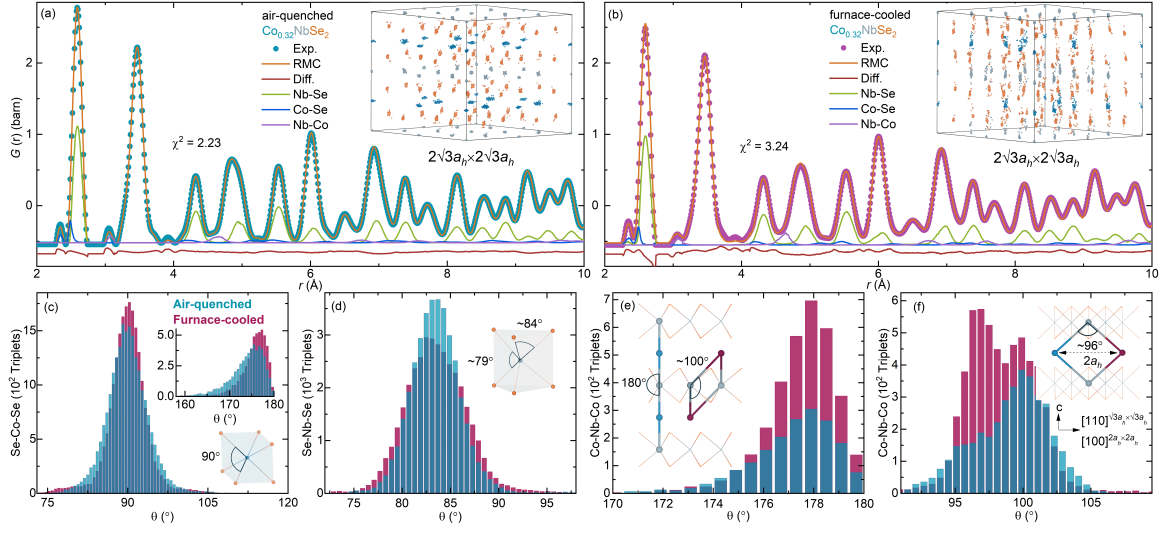


Figure 5.20: Big-box model fits of (a) air-quenched and (b) furnace-cooled real-space data. Inset structures show atomic distributions within a  $\sqrt{3}a_h \times \sqrt{3}a_h$  supercell. Bond-angle distribution of the Se-Co-Se octahedra (c) and Se-Nb-Se trigonal prism (d). Co-Nb-Co bond-angle distribution near  $180^\circ$  (e) and  $100^\circ$  (f). Search for the three pertinent bond-angles of Co-Nb-Co was performed in the  $2.96 \text{ \AA} \leq r_{ij} \leq 4.69 \text{ \AA}$  range.

each domain.

### 5.3.6 Insights from first-principles calculations

To further understand structure-magnetic properties relationships in  $\text{Co}_x\text{NbSe}_2$ , we perform DFT calculations using the ordered phases with  $x = 1/4$  and  $1/3$ , corresponding to the AM and near-frustrated spin-glass and SDW phases. Our simulated structures of these ratios result in reasonably sized unit cells due to fixed occupancies.

The crystal structure of  $\text{Co}_x\text{NbSe}_2$  consists of two  $1H$ -NbSe<sub>2</sub> layers intercalated with magnetic Co atoms forming two sublattices in the different  $z$ -plane. To identify the most favorable magnetic ordering, we first employ the supercell approach [118, 235]. Within this approach, we initialized magnetic moments of 8 Co atoms in a  $2 \times 2 \times 1$  supercell corresponding to a ferromagnetic (FM), and three antiferromagnetic (AFM1, AFM2, and AFM3) orderings (Figure 5.21). For  $\text{Co}_{1/4}\text{NbSe}_2$ , AFM1 (intralayer FM and interlayer

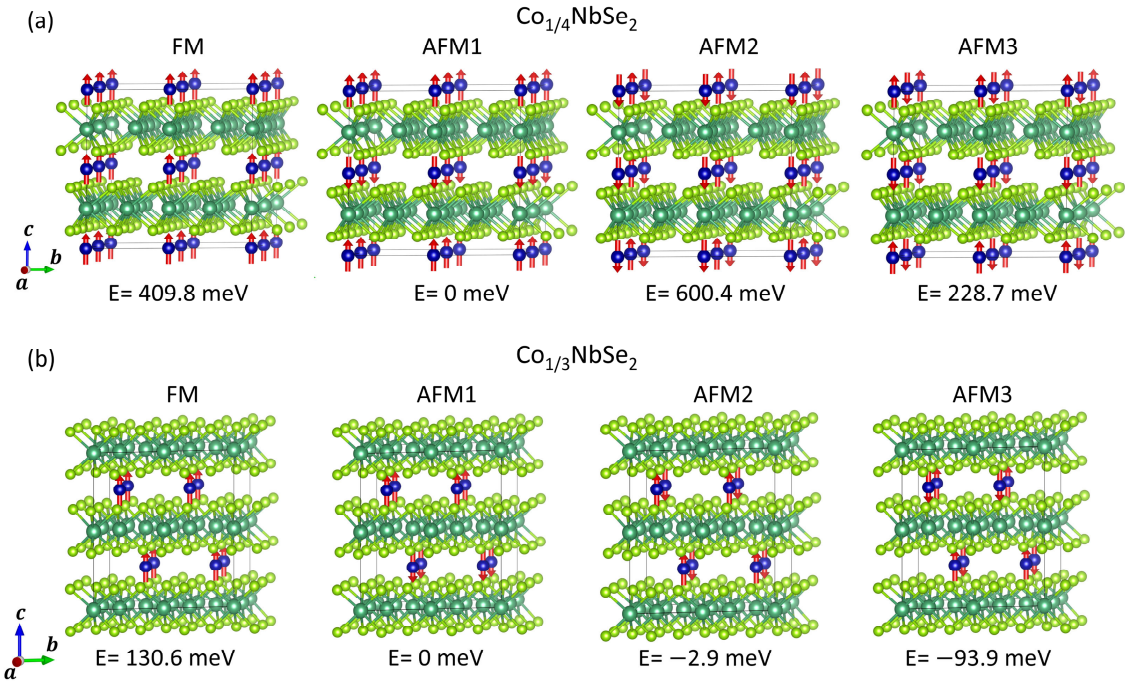


Figure 5.21: Crystal structures of (a)  $\text{Co}_{1/4}\text{NbSe}_2$  and (b)  $\text{Co}_{1/3}\text{NbSe}_2$  within a  $2 \times 2 \times 1$  supercell, illustrating different possible magnetic orderings. The total energies (calculated without spin-orbit coupling) for the ferromagnetic (FM) and three antiferromagnetic (AFM) configurations are shown. The energy of the AFM1 configuration—characterized by intralayer FM and interlayer FM alignment—is taken as the reference. AFM1 is the most energetically favorable ordering for  $\text{Co}_{1/4}\text{NbSe}_2$ . However, for  $\text{Co}_{1/3}\text{NbSe}_2$ , none of the illustrated AFM stackings correspond to the ground state (see Figure 5.9(c)).

AFM) is found to be the lowest energy magnetic structure. More specifically, the AFM1- $\text{Co}_{1/4}\text{NbSe}_2$  is altermagnetic with spin space group  $P^{-1}6_3/-1m^1m^{-1}c^{\infty m}1$ . Here, Litvin's notation is used, with superscripts placed in front of the spatial (nuclear) symmetry operation, indicating the spin part of the symmetry operation. A superscript of 1 (−1) means that the symmetry operation connects the same (opposite) spin sublattices[222].  $^{\infty m}1$  symmetry is pertinent to collinear magnets, denoting the infinite arbitrary spin rotations around the collinear spin axis and mirror reflection containing the collinear spin axis. The opposite spin sublattices are connected through  $C_{6z}$ ,  $m_z$ , and  $C_{2[210]}$ , leading to the  $g$ -wave even parity spin splitting qualitatively explained through the model Hamiltonian,  $H_g = \alpha k_z k_y (k_y^2 - 3k_x^2)$  (Figure 5.22). In the case of  $\text{Co}_{1/3}\text{NbSe}_2$ , the AFM1 configuration is higher in energy compared to the stripy AFM2 and AFM3 structures. AFM3 has the lowest energy among the three AFM structures, with the Co atom antiferromagnetically aligned to three nearest neighbor Co atoms and ferromagnetically aligned to the other three nearest neighbor Co sites within the  $z$ -plane. Note that this is a magnetically frustrated structure in which the intralayer nearest-neighbor exchange interactions between the 2D triangular array of Co spin sites cannot completely satisfy AFM ordering. Hence, stripy AFM3 may not be the most favourable ground magnetic state and requires an approach beyond the supercell method. Since our calculations show that the relativistic effects are negligible, we have obtained the exchange couplings  $J_{ij}$ , for the nonrelativistic Heisenberg model  $H = -\sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$  using the magnetic force theorem. Here,  $\mathbf{S}_i$  is the magnetic moment at the position  $r_i$ , and  $J_{ij}$  are the exchange coupling parameters between the magnetic moments at  $r_i$  and  $r_j$ . For the  $\text{Co}_{1/4}\text{NbSe}_2$ , the first nearest neighbor intralayer and interlayer  $J_{ij}$  are dominant ones, leading to intralayer FM and interlayer AFM ordering (Figure 5.23(a)). On the other hand, for  $\text{Co}_{1/3}\text{NbSe}_2$ , all intralayer  $J_{ij}$  values are relatively small. In particular,  $\text{Co}_{1/3}\text{NbSe}_2$  displays a weak FM (0.24 meV) coupling with the first nearest neighbor and AFM coupling (−0.35 meV) with the second nearest neighbor Co atoms within the same layer, resulting

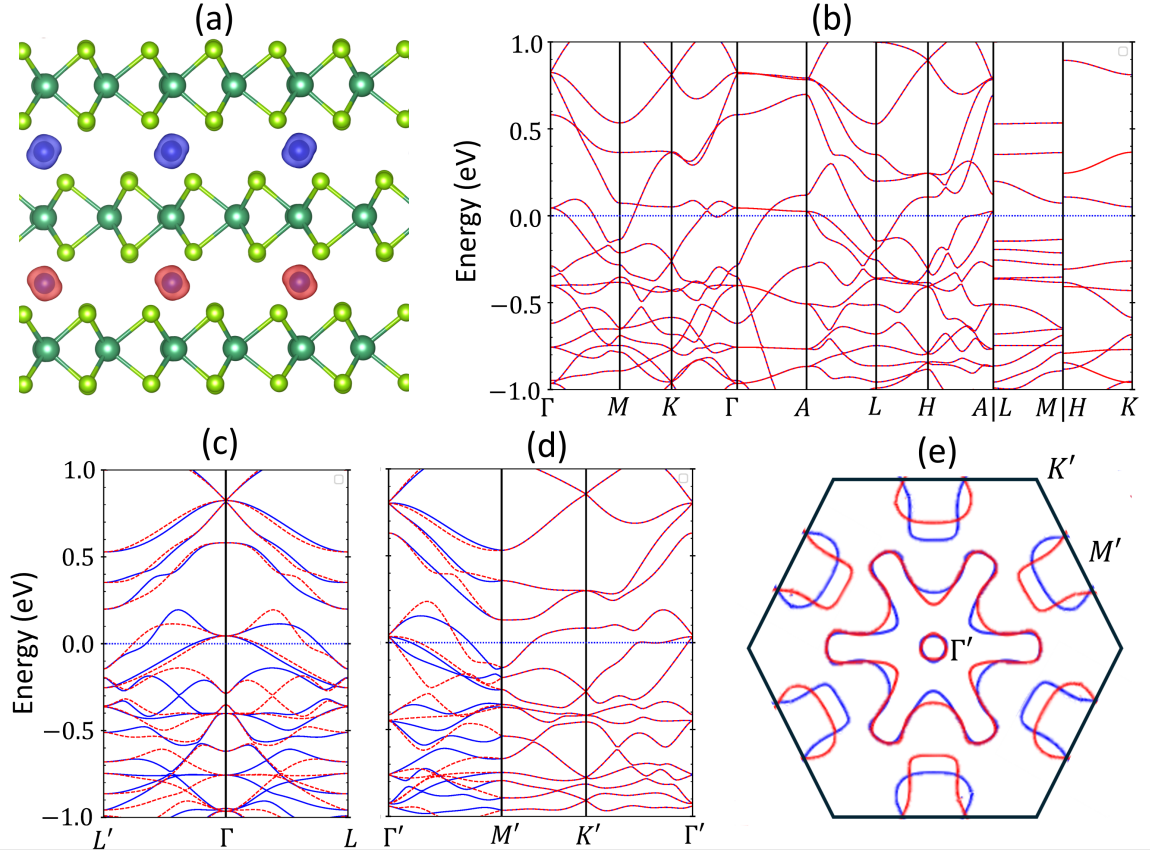


Figure 5.22: **Altermagnetism in  $\text{Co}_{1/4}\text{NbSe}_2$** . Crystal structure of  $\text{Co}_{1/4}\text{NbSe}_2$  with magnetization density distribution, with red and blue surfaces denoting spin-up and spin-down magnetization. The nonmagnetic crystal field ( $\text{NbSe}_2$  layers) distorts the magnetization density distribution from spherical symmetry, leading to nonrelativistic spin splitting at an arbitrary  $k$ -point. The bands are spin-degenerate along the (b) high-symmetry directions, and spin-split along (c)  $L' - \Gamma - L$  and (d)  $\Gamma' - M' - K' - \Gamma'$  directions. The  $\Gamma'$ ,  $M'$ , and  $K'$  are the midpoint of the  $\Gamma$  and A, M and L, and K and H, respectively. The L and  $L'$  are (0.5, 0, 0.5) and (-0.5, 0, 0.5), respectively. The  $\text{Co}_{1/4}\text{NbSe}_2$  is a  $g$ -wave altermagnet, and spin splitting can be explained qualitatively using the model Hamiltonian  $H_g = \alpha k_z k_y (k_y^2 - 3k_x^2) \sigma_z$ , where  $\alpha$  is the parameter signifying the strength of spin splitting. (e) The  $g$ -wave altermagnetic spin splitting is also evident from the spin-projected Fermi surface cross section in the  $\Gamma' - M' - K'$  plane. The nontrivial spin Laue group of  $\text{Co}_{1/4}\text{NbSe}_2$  is  $[E||C_{3v}] + [C_2||D_{6h} - C_{3v}](0, 0, 0.5)$ .

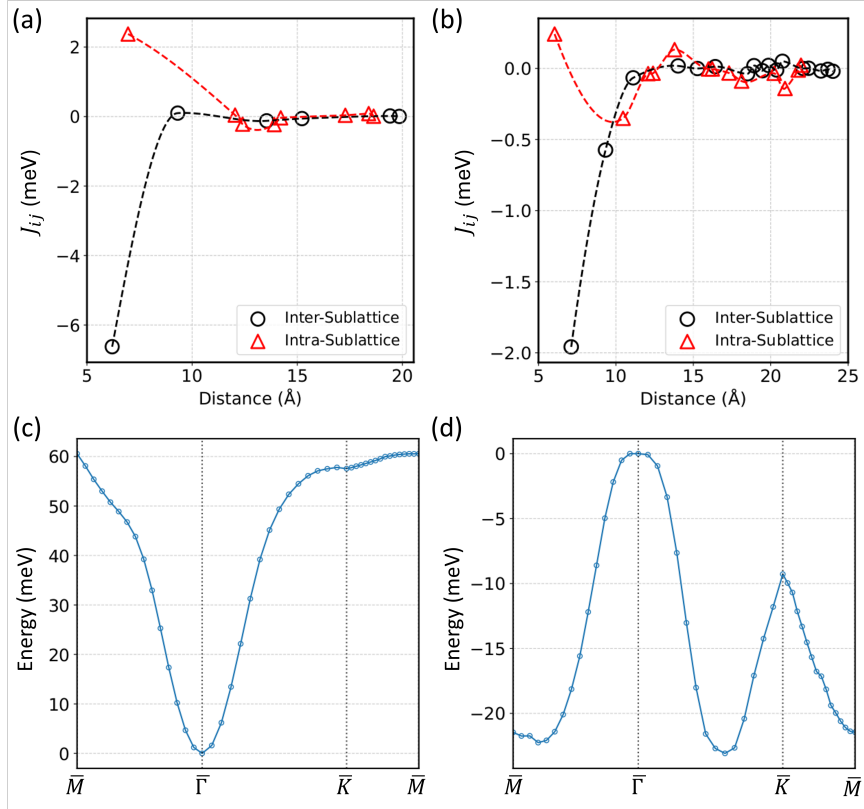


Figure 5.23: The DFT Heisenberg exchange ( $J_{ij}$ ) interactions for (a)  $\text{Co}_{1/4}\text{NbSe}_2$  and (b)  $\text{Co}_{1/3}\text{NbSe}_2$  as a function distance between Co atoms. The intra-sublattice and inter-sublattice  $J_{ij}$  represent the exchange interaction between Co atoms with the same and opposite spin magnetization from intralayer FM and interlayer AFM ordering, respectively. The positive and negative  $J_{ij}$  favor FM and AFM coupling, respectively. Dashed lines are a guide to the eyes. DFT obtained-magnon spectra of (c)  $\text{Co}_{1/4}\text{NbSe}_2$  and (d)  $\text{Co}_{1/3}\text{NbSe}_2$ . The  $\bar{\Gamma}$ ,  $\bar{M}$ ,  $\bar{K}$  are high symmetry points in the magnetic Brillouin zone, where  $\bar{\Gamma}$  corresponds to intralayer FM and interlayer AFM magnetic structure.

in magnetic frustration and spin density modulations (Figure 5.23(b)). The differences in exchange interaction strengths between  $\text{Co}_{1/4}\text{NbSe}_2$  and  $\text{Co}_{1/3}\text{NbSe}_2$  come from the interlayer stacking of the Co atoms as well as their intralayer distances. We attribute the strong interlayer AFM in  $\text{Co}_{1/4}\text{NbSe}_2$  to the stronger exchange interactions of Co-3d electrons through Nb- $d_{z^2}$  orbitals as they are directly on top of each other (Figure 5.24). However, the Co atoms in  $\text{Co}_{1/3}\text{NbSe}_2$  interact via different Nb atoms, since the interlayer Co atoms are also separated in the  $x-y$  plane. The stronger exchange interactions in  $\text{Co}_{1/4}\text{NbSe}_2$  lead to a higher Néel temperature (Figure 5.4(b)). To further understand the

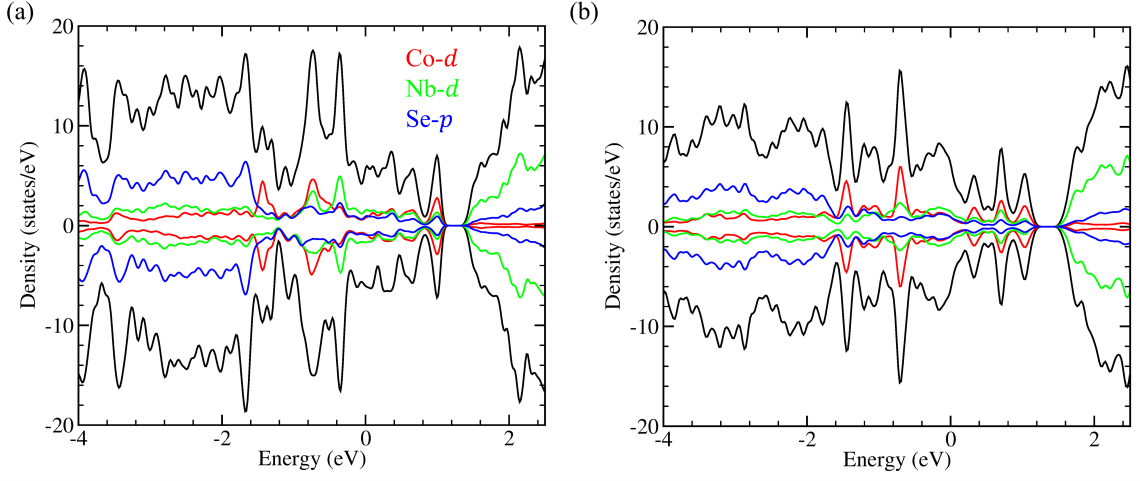


Figure 5.24: Spin polarized partial density of states of (a)  $\text{Co}_{0.25}\text{NbSe}_2$  and (b)  $\text{Co}_{0.33}\text{NbSe}_2$  projected over Co- $d$ , Nb- $d$ , and Se- $p$  orbitals. The projected density of states reveals that Co- $d$  orbitals contribute significantly near the Fermi energy, whereas Se- $p$  states are situated well below it, and Nb- $d$  states predominantly appear above the Fermi level. The states around the Fermi energy are mainly contributed by  $d_{xz}$ ,  $d_{yz}$ ,  $d_{xy}$ ,  $d_{x^2-y^2}$  of Co and  $d_{z^2}$ ,  $d_{xy}$ ,  $d_{x^2-y^2}$  of Nb.

periodicity of magnetic order, we simulate noncollinear spin spirals with a much larger magnetic unit cell, which have been studied mainly for ferromagnets[236, 237]. We use the generalized Bloch theorem to simulate the spin spirals with propagation vector ( $q$ ) that involves modulating the phase of the electron spinors by a factor of  $\pm q/2$ . We begin with the AFM1 to simulate the flat spin spirals using the DFT. The magnetizations on two Co sublattices at site  $r_i$  are given by

$$m_i^\pm = m(0, \mp \sin(q \cdot r_i), \pm \cos(q \cdot r_i)), \quad (5.1)$$

where  $m$  is the magnitude of spin magnetization on the Co atom. Figure 5.23(c and d) show the spin-spirals energy dispersion. As in the supercell approach, the most favorable magnetic ordering is AFM1 [ $q = (0, 0, 0)$ ] for  $\text{Co}_{1/4}\text{NbSe}_2$ . Whereas the  $\text{Co}_{1/3}\text{NbSe}_2$  have two energy minima around the  $\frac{2}{3}\bar{M}$  and  $\frac{1}{2}\bar{K}$  points in the magnetic Brillouin zone. The peak corresponding to  $q = \frac{2}{3}\bar{M} = (0, 1/3, 0)$  is also experimentally observed in  $\text{Co}_{1/3}\text{NbSe}_2$  (Figure

5.9(e)). Also, the generalized Bloch theorem is strictly defined without spin-orbit coupling (SOC), where the spin space and real space are decoupled. However, we have included SOC as a perturbation in first-order[238]. Our noncollinear DFT+TB2J simulations show that DMI interactions are an order of magnitude smaller than  $J_{ij}$  interactions in  $\text{Co}_{1/3}\text{NbSe}_2$ , while DMI interactions are forbidden in  $\text{Co}_{1/4}\text{NbSe}_2$  due to the presence of a center of symmetry. The weak SOC is also evident from the magnetocrystalline anisotropic energies (MCAE) of 141 and 229  $\mu\text{eV}/\text{Co}$  atom for  $\text{Co}_{1/4}\text{NbSe}_2$  and  $\text{Co}_{1/3}\text{NbSe}_2$ , respectively, with the easy axis of magnetization along the out-of-plane ( $z$ ) direction. The MCAE observed are much smaller than those reported for other intercalated TMDs, such as  $\text{Fe}_{1/3}\text{NbS}_2$ [239] (1.09 meV),  $\text{Fe}_{1/4}\text{TaS}_2$ [240] (15 meV),  $\text{Ni}_{1/4}\text{NbSe}_2$ [241] (0.9 meV),  $\text{Ni}_{1/3}\text{NbS}_2$ [67] (1.0 meV), and  $\text{Cr}_{1/3}\text{NbS}_2$  (0.8 meV)[242]. The small MCAE in  $\text{Co}_x\text{NbSe}_2$  makes it energetically less costly to tilt the magnetization away from the easy axis, favoring SDW and spin-glass behavior. Therefore, a confluence of two factors—magnetic frustration and very small MCAE—results in spin density modulations in  $\text{Co}_{1/3}\text{NbSe}_2$ .

## 5.4 Discussion

### 5.4.1 Synthesis-Dependent Magnetostructural Transitions

Compiling our experimental results, we construct a comprehensive phase diagram for each synthesis profile. From temperature-dependent magnetic susceptibility, we identify three distinct transition temperature regimes. Using powder X-ray and neutron diffraction in the paramagnetic region, we assign these magnetic transitions to the underlying structural phases. When  $\text{Co}_x\text{NbSe}_2$  is quenched, a centrosymmetric AM phase emerges with a relatively high  $T_N^A$ , coexisting with a non-centrosymmetric double- $q$  SDW phase, bridged by a spin glassy intermediate regime (Figure 5.25(a)). Furnace-cooling the same compositions yields four distinct phase regions. This series retains all phases found in the quenched

samples and includes an additional intermediate phase. The A-type AM structure persists at higher cobalt concentrations and coexists with the SDW phase, as shown in Figure 5.25(b).

Site occupancies and sublattice preference alter exchange pathways directly impacting the magnetic order[55]. The Curie-Weiss temperature serves as an indirect indicator of the magnetic interactions. We find that quenched samples exhibit weaker antiferromagnetic interactions compared to the furnace-cooled series for  $x < 1/3$  (Figure 5.26). Additionally, sublattice formation and polyhedral distortions along the  $c$ -axis may perturb the crystal field environment, thereby affecting the spin state and Co-Nb orbital hybridization[25, 26]. However, our local structure analysis finds no significant distortion of the octahedral environment, implying that intermediate exchange energy variations come from domain interactions. As previously discussed, slow-cooling favors the formation of  $2a_h \times 2a_h$  sublattices, which display strong AFM interactions mediated by Co-3d and Nb- $d_{z^2}$  orbital hybridization[32, 165]. In contrast, quenching kinetically traps  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains, leading to frustration and a spin-glass-like state.

#### 5.4.2 Local Domain Formation

Craig et. al.[29] have established that the  $\sqrt{3}a_h \times \sqrt{3}a_h$  sublattice will dominate at ratios above  $x = 1/4$  with locally ordered  $2a_h \times 2a_h$  domains through computational methods. Our local structure analysis here generally matches their conclusions as we find the  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains present in the whole air-quenched series (Figure 5.17), even where the average structure from diffraction shows no indication of these domains (Figure 5.18). Slow-cooling allows the intercalant to settle into configurations that maximize nearest-neighbour avoidance. Quenched samples will freeze in a state where nearest-neighbour avoidance is lower. However, we demonstrate the indifference of the antiferromagnetic phase to partial disorder and coexisting SDW phase by kinetically trapping  $2a_h \times 2a_h$  domains through



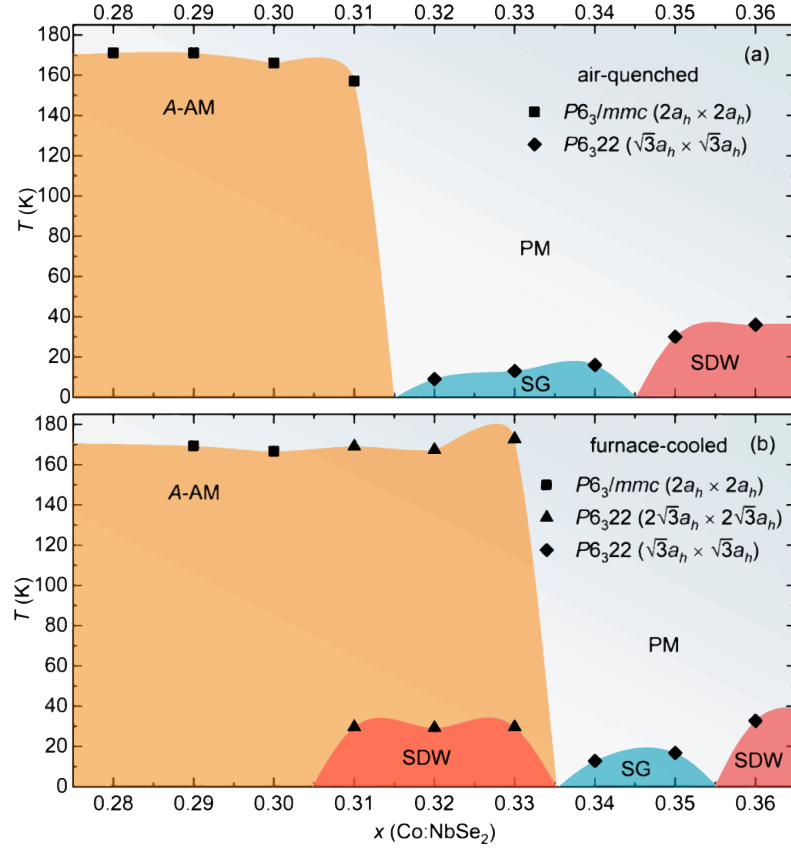


Figure 5.25: Nuclear and magnetic structure phase diagram of (a) air-quenched and (b) furnace-cooled  $\text{Co}_x\text{NbSe}_2$ .

slow-cooling. This phase may be stoichiometrically suppressed and thermodynamically freeze the  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains by quenching[165]. The  $c$ -axis parameter (Figure 5.6) indirectly demonstrates how nearest-neighbor avoidance is compensated by lattice expansion when the  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains are sealed through quenching.

### 5.4.3 Nature of Coexisting Magnetic Orders and Itinerant Magnetism

Considering that the diamagnetic term is constant in magnetic susceptibility, we assume that the temperature-independent term must change between different samples due to different amounts of Pauli paramagnetism[3, 177]. This term is approximated by fitting the modified Curie-Weiss law (4.1) in the paramagnetic region (Figure 5.27 and 5.28) and

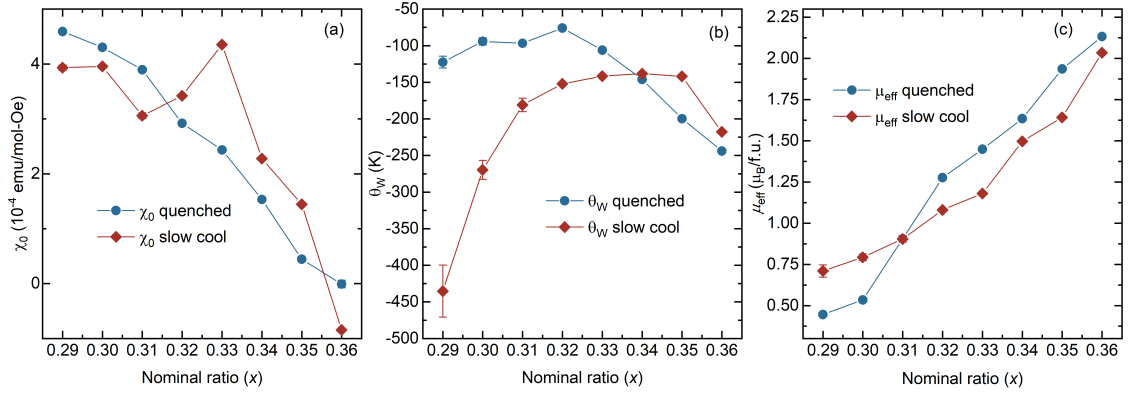


Figure 5.26: (a) Temperature-independent paramagnetic term ( $\chi_0$ ). (b) Curie-Wiess temperature constant and (c) Effective magnetic moment obtained from Curie-Wiess law fit from the paramagnetic region.

depends on the density of states at the Fermi energy[125, 204]. We find a significant Pauli paramagnetic term in samples with less cobalt (Figure 5.26). Increasing cobalt reduces this term significantly, indicating that the itinerant character of the moments begins to localize as  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains proliferate[32, 65, 243]. This observation is further corroborated by the large total moment at high cobalt concentrations.

The magnetic nature of the low-temperature transition in the coexisting regime remains unknown. This feature has been reported in both single-crystal and powder samples based on bulk property measurements, yet no long-range magnetic order is detected by neutron diffraction[1]. This phase comprises local SDW domain pockets that undergo an order-disorder transition, possibly reflecting local competition between the AM and SDW orders[58, 244]. This anomaly should not be associated with spin-glass behavior, as it lacks the ZFC-FC divergence typically seen in frustrated systems and exhibits a transition temperature  $T_N^S$  matching that of the isolated  $x = 1/3$  phase (Figure 5.28). We speculate that the SDW phase, which has a long period, when coexisting with the antiferromagnetic phase, is interrupted and becomes confined to a few layers. The length of the SDW is hence short

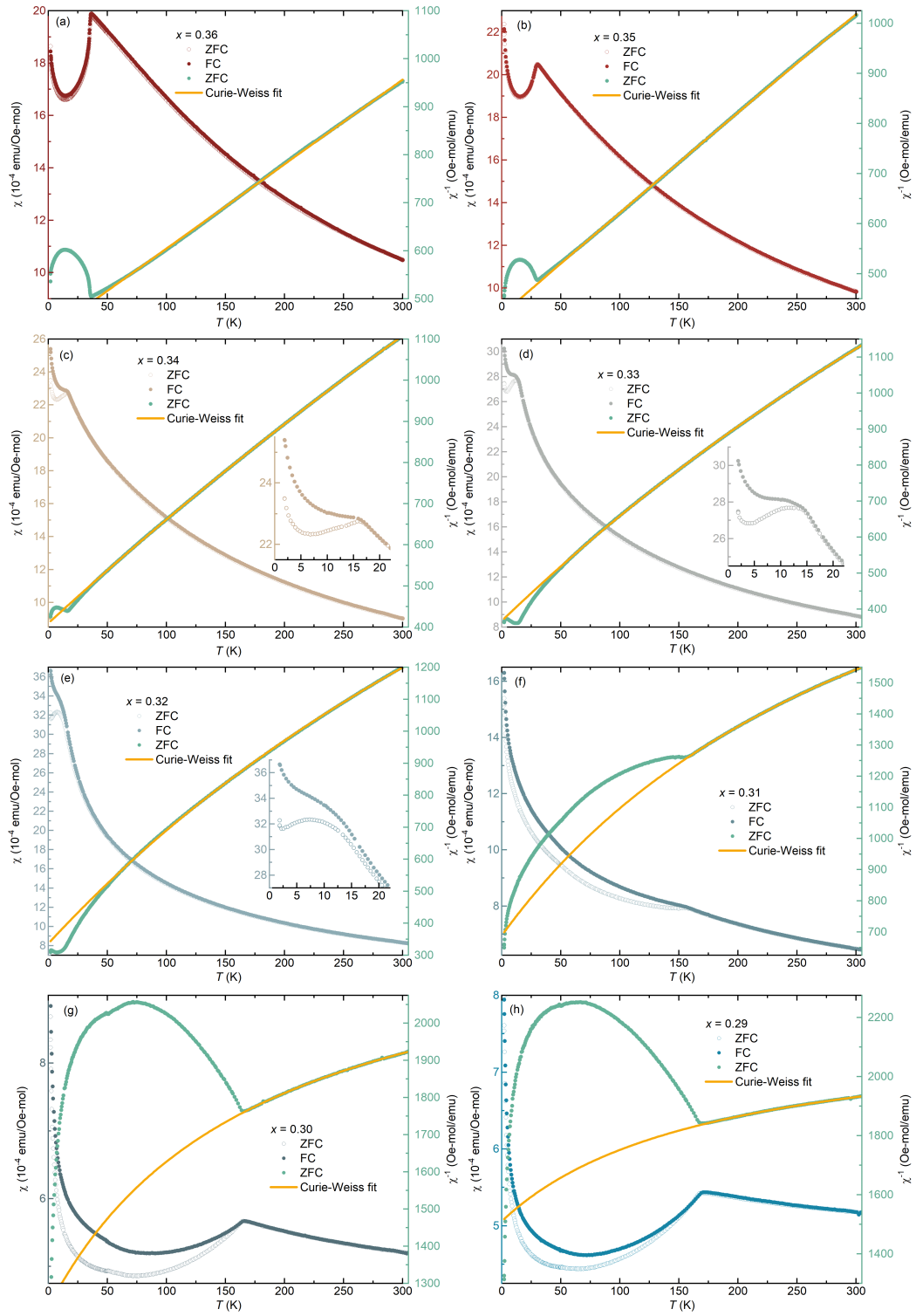


Figure 5.27: (a-h) Temperature-magnetic susceptibility ( $\chi$ ) of air-quenched samples. The paramagnetic region of inverse magnetic susceptibility is fitted to the modified Curie-Weiss law.

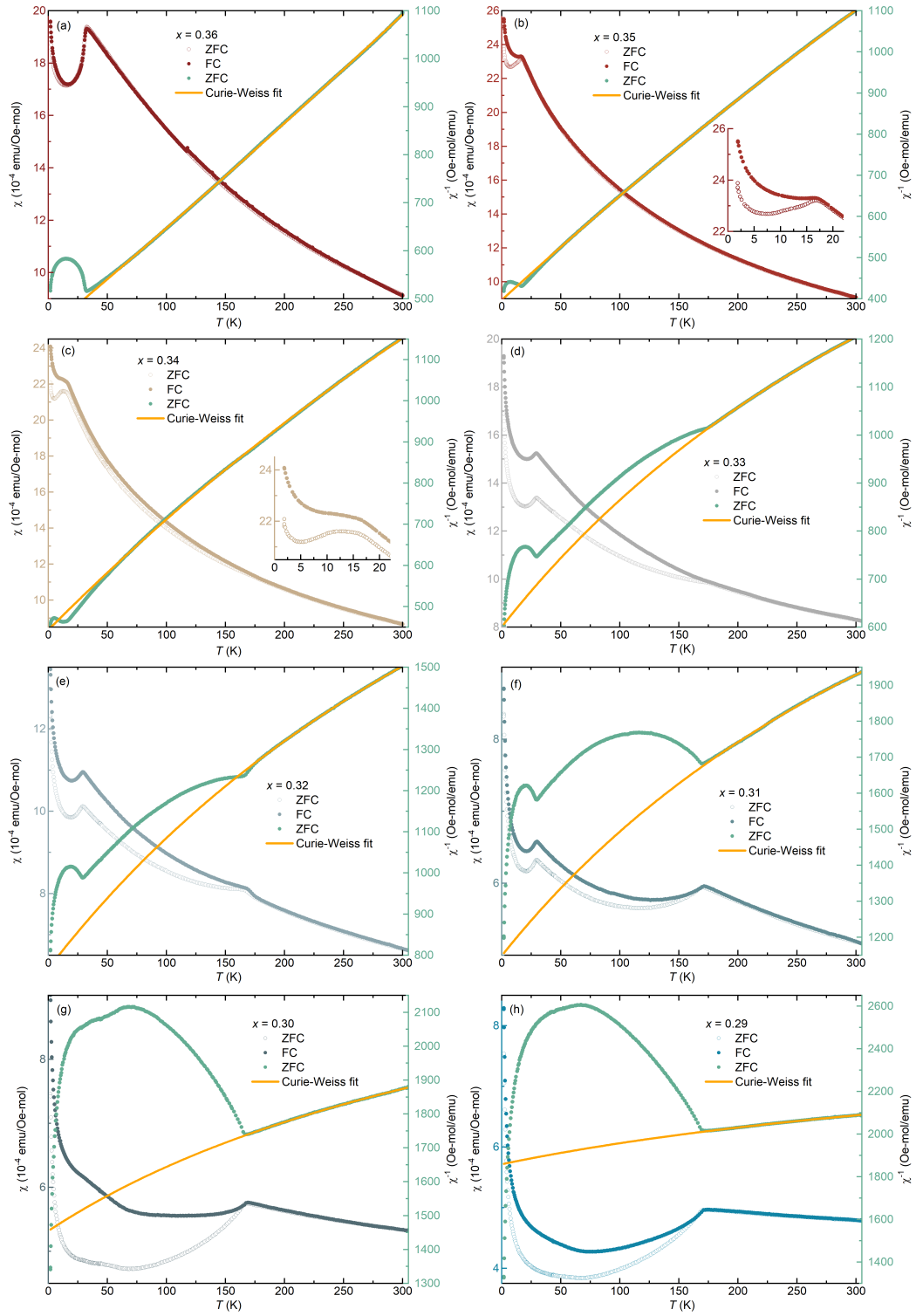


Figure 5.28: (a-h) Temperature-magnetic susceptibility ( $\chi$ ) of furnace-cooled samples. The paramagnetic region of inverse magnetic susceptibility is fitted to the modified Curie-Weiss law.

ranged and does not fully develop to produce magnetic Bragg reflections.

#### 5.4.4 Magnetic Frustration and Disorder

Exchange interactions in this system are driven mainly by conduction electrons through the RKKY mechanism. The Fermi surfaces of  $\text{Co}_{1/4}\text{NbSe}_2$  and  $\text{Co}_{1/3}\text{NbSe}_2$  are quasi-2D in nature, with Fermi sheets extending along the  $k_z$  direction[190, 227, 245]. This leads to strong conduction along the in-plane direction. Therefore, itinerant RKKY exchange interactions dominate along the in-plane direction, as evident by the oscillatory nature of the intra-sublattice exchange interactions (Figures 5.23(a and b)). The distance between the intercalants dictates the  $J_{ij}$ , and therefore the magnetic behavior strongly depends on the growth environment and structural domains (Figure 5.9). The triangular array of in-plane Co atoms satisfies ferromagnetic ordering in  $\text{Co}_{1/4}\text{NbSe}_2$ , leading to altermagnetic order. On the other hand, RKKY exchange interactions lead to highly frustrated magnetic layers in  $\text{Co}_{1/3}\text{NbSe}_2$ , driving the complex magnetic phase diagram containing SDW, spin-glass, and altermagnetic phases depending on the synthesis conditions (Figure 5.25).

### 5.5 Conclusions

We have systematically mapped the structural and compositional dependencies of  $\text{Co}_x\text{NbSe}_2$ , demonstrating that the synthesis profile, mainly cooling rate, governs the formation and interplay of two distinct cobalt sublattice arrangements:  $2a_h \times 2a_h$  and  $\sqrt{3}a_h \times \sqrt{3}a_h$ . These structural motifs underlie three emergent magnetic phases: altermagnetism (AM), spin-glass behavior, and a double- $q$  spin-density wave (SDW). Depending on the thermal history, these magnetic phases either emerge independently or coexist: quenching favors the isolation of domain types, while furnace cooling promotes their coexistence in off-stoichiometric compositions.

We directly quantified these domains through pair distribution function analysis by tracking characteristic Co-Nb-Co bond angles for each local domain arrangement. Slow cooling favors  $\sim 180^\circ$  triples, associated with the  $2a_h \times 2a_h$  sublattice hosting the AM phase. Because AM arises from non-relativistic spin splitting in a centrosymmetric environment, minimizing non-centrosymmetric disorder is critical for its formation. While both  $2a_h \times 2a_h$  and  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains are present across the phase diagram, our results show that slow cooling selectively localizes the  $2a_h \times 2a_h$  domains. In contrast, quenching enhances the proportion of  $\sqrt{3}a_h \times \sqrt{3}a_h$  domains entailing magnetic frustration, which correlates with the spin-glass phase.

Our first-principles calculation results reveal how these magnetic states emerge from the interplay between the local cobalt arrangement and conduction electron-mediated exchange interactions. The oscillatory nature of the RKKY mechanism favors in-plane ferromagnetic interaction for  $2a_h \times 2a_h$  domains, consistent with the observed AM structure. The tighter triangular cobalt sublattice in the  $\sqrt{3}a_h \times \sqrt{3}a_h$  domain induces frustration, giving rise to spin-glass and SDW phases depending on the structural disorder.

Overall, this work establishes a direct link between synthesis conditions, local structure, and emergent magnetism in Co-intercalated NbSe<sub>2</sub>. The strategies developed here offer a valuable guide for designing and understanding magnetostructural phases in other group-V transition metal dichalcogenides intercalated with divalent  $3d$ -ions.

## Chapter 6: Conclusions and future directions

### 6.1 Conclusions

This dissertation presents a systematic investigation of the magnetostructural consequences of intercalating group-V TMDs with a divalent cation. We focus on cobalt intercalation across a wide concentration range and place the resulting magnetochemical properties within the broader landscape of TMD intercalation chemistry. This class of materials offers exceptional flexibility for introducing a wide range of elemental and chemical species into the van der Waals gap, providing a tunable platform for engineering correlated electronic and magnetic states. Using this framework, we demonstrate how cobalt intercalation stabilizes distinct magnetic ground states and identify the compositional regimes in which altermagnetism, spin-glass behavior, spin density waves, and their coexistence emerge. To the best of our knowledge, we have here established the first comprehensive magnetic and structural phase diagram of a composition-dependent divalent intercalated TMD. Previous work had limited studies on disorder, and provided detailed observation on a single either ideal  $x = 1/4$  or  $x = 1/3$  phase. We establish clear trends and thermal effects during synthesis.

Intercalation limits and ordering constraints define the accessible magnetic phase space in cobalt-intercalated transition metal diselenides. Both  $\text{Co}_{1/4}\text{TaSe}_2$  and  $\text{Co}_{1/4}\text{NbSe}_2$  stabilize an altermagnetic phase at comparable ordering temperatures, indicating that the underlying TMD host lattice plays a secondary role in setting the energy scale for this phase. In contrast, the Ta-based analog saturates at  $x = 1/4$ , which restricts the accessible phase diagram

to a single ordered magnetic ground state. The Nb-based system exhibits substantially greater compositional flexibility, as  $\text{Co}_x\text{NbSe}_2$  can be stabilized beyond  $x = 1/3$ , thereby enabling access to regimes where chemical order, disorder, and phase coexistence can be manipulated. This extended tunability establishes  $\text{Co}_x\text{NbSe}_2$  as a particularly rich platform for investigating cooperative magnetic phenomena in low-dimensional intercalation compounds.

We’ve demonstrated how growth conditions and chemical control parameters govern the electronic character and magnetic coupling in cobalt-intercalated TMDs. We show that transport agents, thermal history, and intercalation ratios systematically tune the bulk magnetic and electronic responses. At low intercalation ratios,  $d$ -orbital hybridization between the Nb or Ta  $d_{z^2}$  orbital and Co  $3d$ -states promotes a more itinerant, metallic character. Increasing the intercalation level disrupts the Co–Nb–Co exchange pathways, decreases this itinerancy, and promotes localization of the magnetic moments. This evolution directly links local coordination geometry and chain connectivity to the balance between itinerant and localized magnetism, and it provides a transferable framework for interpreting magnetic behavior across the broader family of intercalated TMDs.

Beyond the intercalation of cobalt, we extend our exploration of chemically driven magnetism in TMDs to other intercalated  $3d$ -metals. We have initiated the synthesis and characterization of Mn-intercalated compounds, focusing in particular on  $\text{Mn}_{1/4}\text{NbSe}_2$ , whose magnetic structure remains unresolved by neutron diffraction. Prior work has proposed this composition to be a helimagnet; however, as outlined in the introduction, helimagnetism requires spin canting driven by the Dzyaloshinskii-Moriya interaction (1.2.1). At  $x = 1/4$ , the crystal structure is centrosymmetric, which nominally forbids this asymmetric exchange mechanism. This apparent contradiction positions  $\text{Mn}_{1/4}\text{NbSe}_2$  as a compelling test case for probing unconventional mechanisms of non-collinear magnetism in centrosymmetric intercalation compounds and motivates future diffraction-based studies to resolve its true



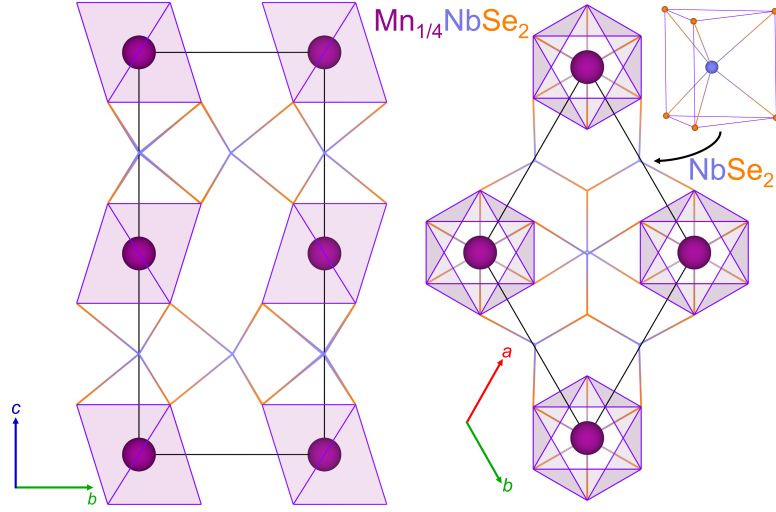


Figure 6.1: Crystal structure of hexagonal and centrosymmetric  $\text{Mn}_{1/4}\text{NbSe}_2$  viewed along the  $a$ -axis and  $c$ -axis.

magnetic ground state.

## 6.2 Ongoing Work

Centrosymmetric intercalated TMDs have so far presented collinear magnetic structures. However, previous magnetization studies on  $\text{Mn}_{1/4}\text{NbSe}_2$  have postulated this system as potentially having helimagnetic structure.[53] This compound is centrosymmetric with the  $2a_h \times 2a_h$  superlattice arrangement as shown in Figure 6.1.

To this point, no neutron studies had been performed in this compound. Most likely due to challenges in replicating the synthesis of a single crystal with the same composition exhibiting spin polarization. We are currently exploring the magnetic structure of this system under an applied magnetic field using powder samples.

The magnetic ground state structure of  $\text{Mn}_{1/4}\text{NbSe}_2$  orders in a single- $Q$  SDW (Figure 6.2). The magnetic Bragg reflections can be indexed by the magnetic propagation vector  $q_m = (\delta, 0, 0)$ , where  $\delta$  is almost commensurate with  $1/6$ . Refining the propagation vector as shown in Figure ??, we find it best fits to an incommensurate value of  $\delta = 0.1773(4)$ ,

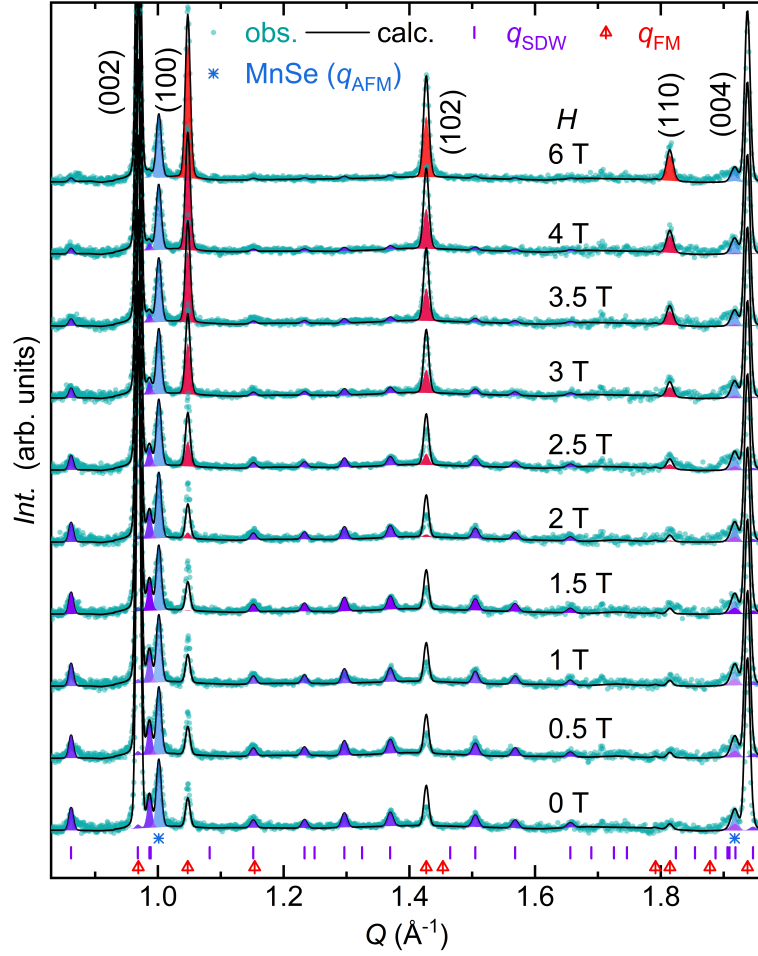


Figure 6.2: Refined neutron powder diffraction of  $\text{Mn}_{1/4}\text{NbSe}_2$  with applied magnetic field from 0 T (bottom) to 6 T (top). Bragg indices at the bottom correspond to the ferromagnetic state with  $q_{FFM} = (0,0,0)$ , incommensurate  $q_{SDW} = (0.177,0,0)$ , and the antiferromagnetic phase of impurity MnSe.

indicating that the pitch of the SDW is  $\sim 5.6$  unit cells long as illustrated in Figure ?? (a).

Notably, from the magnetization curve, the antiferromagnetic ground state undergoes a first-order metamagnetic transition. Neutron diffraction at an externally applied magnetic field up to 6 T, shown in Figure 6.2, indicates that this is a forced ferromagnetic state with  $q_{FFM} = (0,0,0)$ . Since the magnetic form factor is proportional to the perpendicular component of the scattering vector, we can gain an intuition of the direction at which the magnetic polarization occurs. Since none of the  $(002l)$  reflections have magnetic

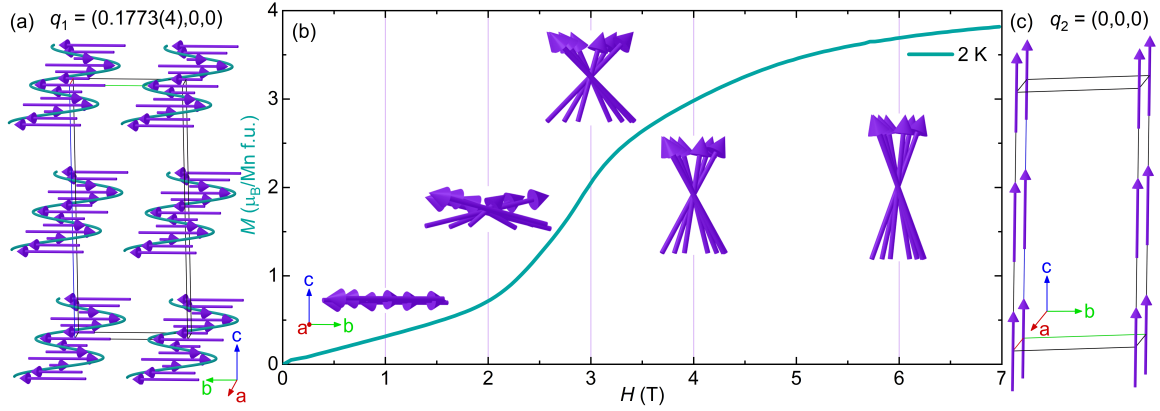


Figure 6.3: Structure association to bulk properties of  $\text{Mn}_{1/4}\text{NbSe}_2$ . (a) Spin density wave magnetic ground state structure (b) evolving to a polarized ferromagnetic state as a function of applied field. (c) single- $q$  magnetic structure of the forced ferromagnetic state.

contributions, we can only assume that the magnetic ordering occurs primarily along the  $c$ -direction. This is corroborated by the intensities of the in-plane reflections (100), (102), and (110) corresponding to the  $2a_h \times 2a_h$  superlattice increasing proportionally to the applied field.

Applying and incrementing an external magnetic field suppresses the incommensurate SDW and leads to the forced ferromagnetic state. Figure 6.2, has shows the neutron diffraction pattern at various fields from 0 T to 6 T at 0.5 T steps. The resulting double- $q$  structure ( $q_{SDW} + q_{FFM}$ ) as a function of magnetic field is shown Figure 6.3 (b). The SDW begins to polarize at 2 T, consistent with the magnetization; however, despite reaching 6 T, where the magnetization is near saturation, the SDW does not fully dissipate.

So far, we have found no evidence for a helimagnetic structure or the presence of solitons. Established rules of centro-symmetry have been followed; however, non-colinearity may still be present, for which polarized neutrons would be required. Yet, before that stage, obtaining a quality single-crystal sample is the present challenge. We expect to use our knowledge obtained from obtaining cobalt intercalation versions of this system to circumvent the current challenge.  $\text{Mn}_{1/4}\text{NbSe}_2$  represents an interesting corner of properties with the

group-V intercalated TMDs due to it possessing a metamagnetic transition while being centrosymmetric.

### 6.3 Future Directions

The compositions explored in this dissertation represent only a small fraction of the broader intercalation space available in TMDs. Significant opportunities remain for predicting and controlling the resulting electronic and magnetic ground states, particularly through deliberate manipulation of intercalant concentration and sublattice ordering. An outstanding challenge lies in achieving higher intercalation ratios in TaSe<sub>2</sub>, where we anticipate that compositions such as  $M_{1/3}$ TaSe<sub>2</sub> may be thermodynamically unfavorable. Nevertheless, guided by the chemical and structural trends established here, we speculate that such phases may be accessible under carefully chosen, although likely metastable, conditions. Non-equilibrium synthesis strategies, including metathesis, solvothermal, and other kinetically driven routes, therefore, can present a promising avenue for stabilizing these otherwise inaccessible compositions. Attaining such compositions would be interesting to explore to obtain a stronger spin-orbit interaction in the noncentrosymmetric structure arrangement. Performing an ion exchange as a metathesis route could serve as an alternative to tunnel through the activation barrier to form any of the  $M_{1/3}$ TaSe<sub>2</sub>. Both Li<sub>*x*</sub>TaSe<sub>2</sub> and Na<sub>*x*</sub>TaSe<sub>2</sub> where  $x \approx 2/3$ , reportedly exist.[246, 247] Using any of these two to react with a transition metal salt ( $MCl_2$ ) could prove advantageous to drive the reaction toward the desired phase. Of course, the reaction will only be as feasible as the stability of the counter salt.

A detailed investigation of anisotropic electronic transport in the altermagnetic phase constitutes another important direction for future work. In this study, we have identified altermagnetic candidates and performed Hall effect measurements with the magnetic field applied parallel to the easy *c*-axis. Based on symmetry considerations and the A-type

antiferromagnetic structures of  $\text{Co}_{1/4}\text{TaSe}_2$  and  $\text{Co}_{1/4}\text{NbSe}_2$ , these configurations are not expected to host an anomalous Hall effect. However, probing transport along the  $c$ -axis with  $H \perp c$  may provide new insight into charge carrier dynamics and interlayer coupling in the altermagnetic state. Such measurements are currently constrained by crystal morphology. Intercalated TMDs tend to grow as thin platelets, making wiring contacts difficult to attach in the vertical direction. Developing growth techniques that yield thicker crystals, thus, remains a critical experimental bottleneck.

Beyond transport signatures, altermagnetism is predicted to manifest through a distinctive deformation of the spin density with an intrinsic multipole character.[248, 249] Directly resolving this spin density distribution represents a compelling experimental challenge. We are actively pursuing polarized neutron scattering experiments to map the magnetic form factor and spatial spin texture of an altermagnet, which would provide a direct test of theoretical predictions and deepen our understanding of the local nature of this magnetic state.

Chiral transport phenomena may also emerge in related magnetic phases hosted in noncentrosymmetric lattices. In particular, the spin density wave (SDW) phase stabilized in  $\text{Co}_{1/3}\text{NbSe}_2$  is realized in a chiral crystal structure and may therefore support unconventional charge and spin transport responses. Although we have successfully grown single crystals of this compound, its electronic transport properties remain unexplored. The tunability of such an SDW texture raises the possibility of current-driven control mechanisms, analogous to those reported in  $\text{Ni}_{1/3}\text{NbS}_2$ . [199]

The low activation barrier for intercalating cations into interstitial sites enables exploration beyond single-species intercalation. Mixing magnetically active and non-magnetic cations, as well as combining divalent and trivalent species, introduces an additional degree of freedom for engineering exchange interactions and structural motifs. Distinctions between trigonal-distorting and non-distorting field cations are expected to play a balance-

breaking role in local coordination environments. Simultaneous intercalation of multiple  $3d$  transition metals naturally places these systems in the context of high-entropy materials, where competing interactions and chemical disorder may give rise to emergent magnetic phenomena. This multi-species intercalation then has two directions. (1) Introduce disorder via high-entropy intercalation of all accessible  $3d$ -cations; and (2) induce a longer-range order by selecting a trigonal-distorting and non-trigonal-distorting cation.

Mixing cations that are trigonal-distorting active and non-trigonal first-order could potentially lead to clustering of these cations. Such arrangements could stabilize long-range cation ordering with multiple magnetic sublattices or, alternatively, fragment the system into lower-dimensional motifs. For example, pairing a magnetically active, trigonal-distorting ion such as  $\text{Fe}^{3+}$  with a non-magnetic, non-distorting ion like  $\text{Zn}^{2+}$  may impose preferred structural arrangements within the van der Waals gap. The resulting exchange networks could support extended one-dimensional magnetic chains, frustration-driven spin-glass behavior, or complete suppression of long-range order in favor of a paramagnetic ground state. These outcomes remain unexplored and represent fertile ground for future investigation.

In addition to modifying the interstitial site, alloying the transition metal sublattice within the trigonal prismatic layers provides another route for tuning magnetic behavior. Intercalation into mixed-metal hosts in the form of  $M_x\text{Nb}_{1-y}\text{Ta}_y\text{Se}_2$  offers an opportunity to decouple intercalant-driven effects from those arising in the TMD framework itself. Substituting Nb with Ta introduces lattice distortions due to differences in ionic size while simultaneously tuning spin-orbit coupling through the heavier Ta ions. Naturally, this leads us to wonder about  $M_x\text{TS}_z\text{Se}_{2-z}$ . The interplay between structural strain, orbital hybridization, and relativistic effects may generate electronic and magnetic responses not accessible in either end member, opening a new parameter space for designing intercalated quantum materials.

The fact that there are yet many directions to explore this family of compounds is indicative of the vast flexibility and rich phases these systems host. However, as shown in Table 1.2, there remain a few parent  $M_xTQ_2$  compositions to explore. Filling in these magnetochemical property gaps is essential to complete the map of group-V intercalated TMDs in the magnetic scope.

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