

Magnetic properties of CoCr_2Se_4 using X-ray magnetic circular dichroism

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1. Introduction

Magnetic semiconductors are materials which have recently attracted attention due to their potential for use in spin-based electronics, or spintronics, which involves the manipulation of the spin of an electron in addition to its charge. Spintronics is an emerging field which has potential in improving magnetic storage devices by decreasing bit size, increasing bit manipulation speeds, and reducing electric power consumption (Wolf et al., 2010). Before magnetic semiconductors become a viable option for use in spintronic applications, however, a better understanding of the properties of these magnetic semiconductors is required (Zutic, 2004).

Previous studies have found that the resistivity of CoCr_2Se_4 decreases monotonically with temperature, indicating that CoCr_2Se_4 is semiconducting (Maciazek et al., 2006, Snyder et al., 1999). CoCr_2Se_4 was reported by Morris et al. (1970) to undergo antiferromagnetic ordering at 199 K. It will be shown here that CoCr_2Se_4 exhibits some magnetic character at room temperature, though the nature of this magnetism and the origin of the magnetic interaction is not understood. In spintronics, semiconductors with the ferromagnetic properties and a Curie temperature above room temperature would be ideal because they would produce a spin-polarized current at room temperature which would enable easy integration into modern semiconductor electronics (Wolf et al., 2010).

X-ray magnetic circular dichroism (XMCD) is a technique which can probe the difference in the number of spin-up and spin-down empty states in the valence bands of an atom. The technique is element specific and quantitative, so it can provide information about how much each of the cations in CoCr_2Se_4 contributes to its magnetic properties. A description of XMCD and its use in examining magnetic properties of CoCr_2Se_4 will be described.

2. Experimental

2.1 Synthesis

A total mass of 1g of CoCr_2Se_4 was mixed and pressed from stoichiometric amounts of Co (99.8%, CERAC Inc.), Cr (99.95%, CERAC Inc.), and Se (99.99%, Alfa Aesar) powders in an argon-filled drybox. The pallet was transferred in air to an evacuated silica tube, and sealed. It was heated for 24 hours at 800°C, before being quenched in cold water. The obtained sample was mixed with CrCl_3 powder in a 25:1 mass ratio, transferred in air to an evacuated silica tube, and sealed. The mixture was then placed in a tube oven in a temperature gradient with 900°C at one end and 750°C at the other end. The mixture was placed in the hot zone of the furnace, and by the end of the two-week period, some of the material had been transported towards the cold zone. The sample was oven cooled for three hours. Of the material that was transported toward the cold zone, single crystals with a flat, hexagon-like shape were selected for analysis.

2.2 Magnetization measurements

Magnetization measurements were collected using a Superconducting Quantum Interference Device (SQUID) magnetometer for temperatures between 2 K and 400 K in a 1 kG field in a zero-field cool/field-cool mode.

2.3 Synchrotron and STXM

XMCD measurements were performed using synchrotron radiation at the Canadian Light Source in Saskatoon, Saskatchewan using the Scanning Transmission X-Ray Microscope (STXM) at the Soft X-ray Spectromicroscopy beamline, 10ID-1. XMCD measurements require left and right circularly polarized x-rays, which were produced with an Apple II-type elliptically polarizing undulator.

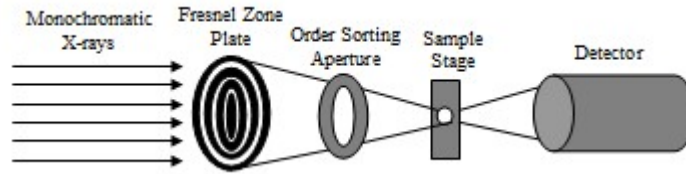


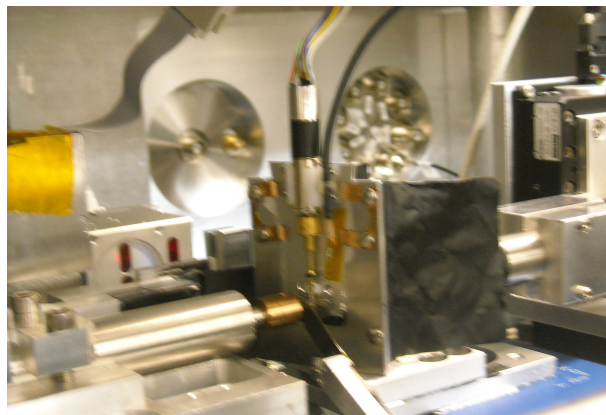
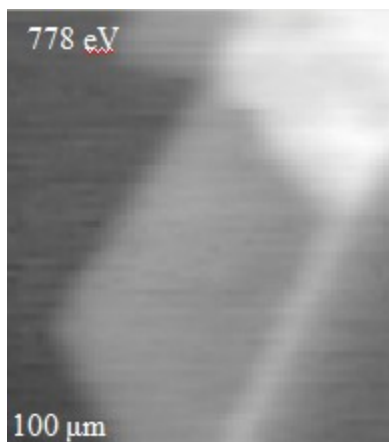
Figure 1. Schematic of the scanning X-ray transmission microscope at the Canadian Light Source.

Two types of measurements were performed with the STXM (see Figure 2), depending on the properties of the sample. For thinner samples (namely, single crystals ground into sub-micron sized particles using a mortar and pestle), transmission measurements were done by detecting the intensity of the transmitted light with a photomultiplier tube and a photon counting unit. The absorbance or the optical density, OD , of the sample is determined with the Beer-Lambert law, given in equation (1), where I_o is the incident intensity and I is the transmitted intensity.

$$OD = -\ln\left(\frac{I}{I_o}\right) \quad (1)$$

For thicker samples, including single crystals of CoCr_2Se_4 , transmission samples were not feasible since soft x-ray photons do not penetrate samples more than 1-2 μm thick. With these samples, total electron yield (TEY) measurements were done by detecting the emitted secondary electrons. The resulting spectra are derived from the measured current with equation (2).

$$\text{TEY} = \frac{I}{I_o} \quad (2)$$



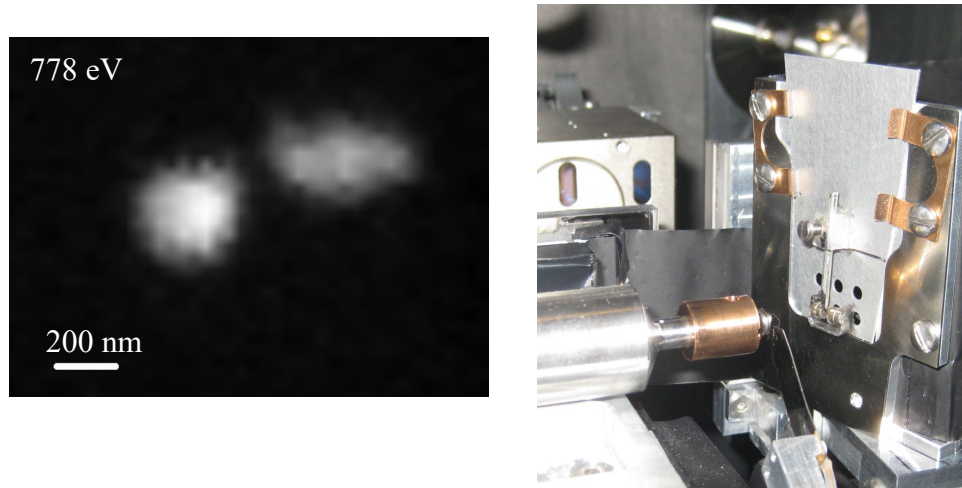


Figure 2. Above left: TEY image of a particle. Above right: Photograph of STXM in TEY mode. Below left: Transmission image of two particles. Below right: Photograph of STXM in transmission mode.

2.4 X-ray magnetic circular dichroism

Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy examines the structure and bonding of molecules of atoms with low atomic numbers by transitions between core and valence states near an absorption edge (Stohr, 1992). X-ray magnetic circular dichroism involves measuring the NEXAFS spectra with different circular polarizations of x-rays. If a magnetic field is applied in a direction parallel to the direction of the x-ray propagation, then the difference in absorption of left circularly polarized and right circularly polarized x-rays can be determined, and this difference is the x-ray magnetic circular dichroism or XMCD spectrum (Mason, 2007). Since the left and the right circularly polarized light transfer momentum to the electrons, core electrons will selectively be excited to spin-up or spin-down valence states in the valence band. Thus the difference of the absorption spectra taken with right and circularly

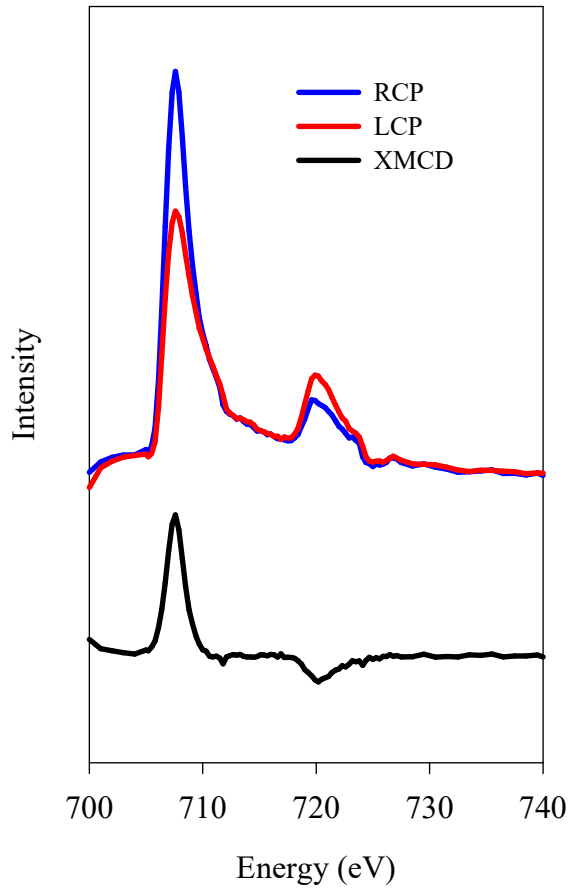


Figure 3. Fe 2p absorption spectra taken using left and right circularly polarized light and the associated XMCD spectrum.

polarized light gives quantitative information about the imbalance of spin-up and spin-down electrons in the valence band.

An example of an XMCD spectrum for the Fe 2p edge of FeGd (sample prepared by Eric Fullerton, Hitachi Global Storage Technologies, San Jose, CA), taken with the STXM in total electron yield (TEY) mode at the CLS in January, 2010 is shown in Figure 3 as an example.

The Fe 2p absorption spectra show transitions from excitations of electrons from the 2p orbital to the 3d orbital in FeGd. There are two peaks due to the spin-orbit coupling. The 2p orbital “splits” into two energies, corresponding to different values of the total quantum number, j , defined by equation (3) where l and s are vector quantities corresponding to the orbital angular momentum and the spin angular momentum of the electron, respectively.

$$\mathbf{j} = \mathbf{l} + \mathbf{s} \quad (3)$$

For the 2p orbital, $l=1$ and $m=\pm 1/2$, so $j=1/2$ or $j=3/2$. The $j=3/2$ state is at a higher energy than the $j=1/2$ state and thus is the peak on the left or the L_3 peak in Figure 3. The $j=1/2$ state is the peak on the right or the L_2 peak in Figure 3. The Fe 2p edge of this FeGd sample has a strong XMCD signal, indicating that iron is a large contributor to magnetism in the sample.

3. Results and Discussion

3.1 Magnetization Data

The CoCr_2Se_4 magnetization data taken using the SQUID magnetometer are shown in Figure 4. There is a relatively large separation of the magnetizations using the field cool and the zero field modes at 300 K. This difference indicates that the sample has some magnetic order at room temperature, though the origin of this magnetic order is not understood. The peak in magnetization at 50 K with the zero field cool is not related to the properties of the sample, but rather, is an artefact of oxygen in the SQUID.

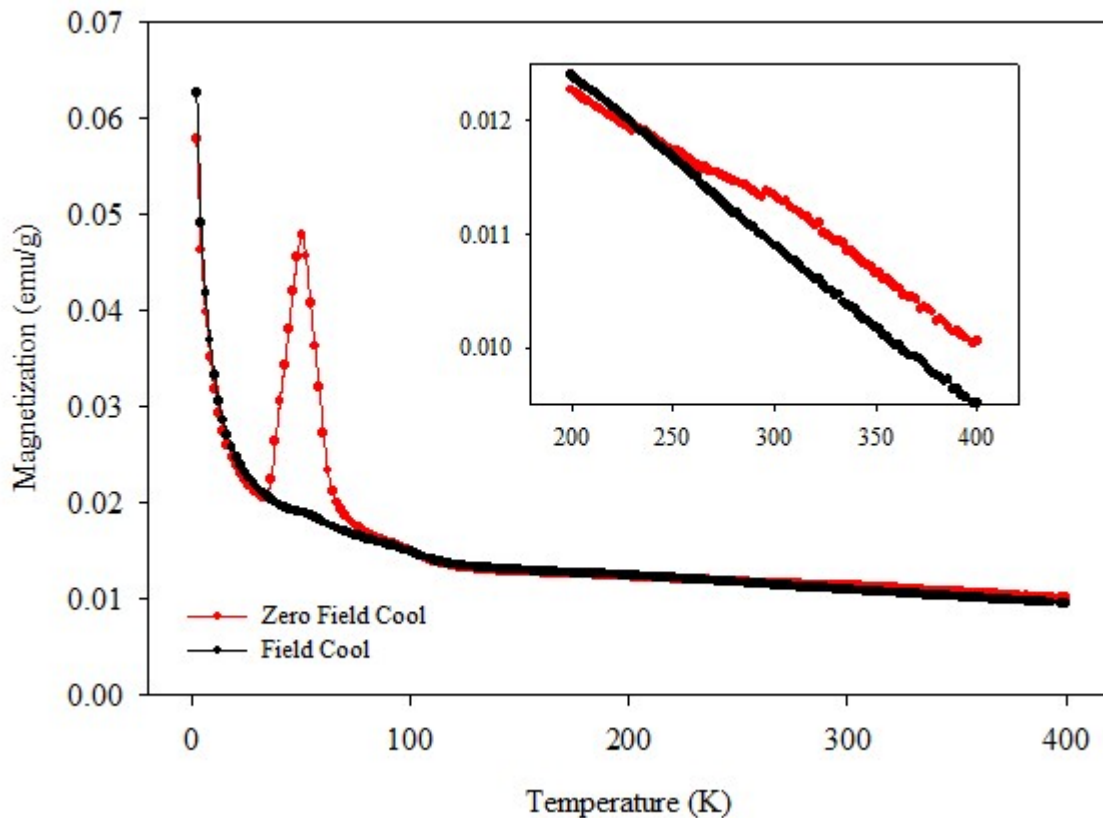


Figure 4. SQUID Magnetization data on CoCr_2Se_4 single crystal taken using a zero field cool/field cool mode. Inset: Magnetization data enlarged near room temperature.

3.2 STXM Measurements – Total Electron Yield Mode

Figure 5 below shows the XMCD spectra taken at the Cr 2p and Co 2p edges in TEY mode at the CLS in January, 2010. In both cases, the spectra taken using left and right circularly polarized x-rays overlap nearly perfectly, indicating very little or zero XMCD signal. However, this does not immediately imply that these crystals will not show XMCD. It was postulated that an oxide could have developed on the surface of the CoCr_2Se_4 crystals, so that when examining them in TEY mode, and hence studying only surface of the sample, the measurements would've reflected the properties of the oxide rather than the properties of the CoCr_2Se_4 . This hypothesis could be tested in transmission mode, which examines the bulk properties of particles rather than just surface properties.

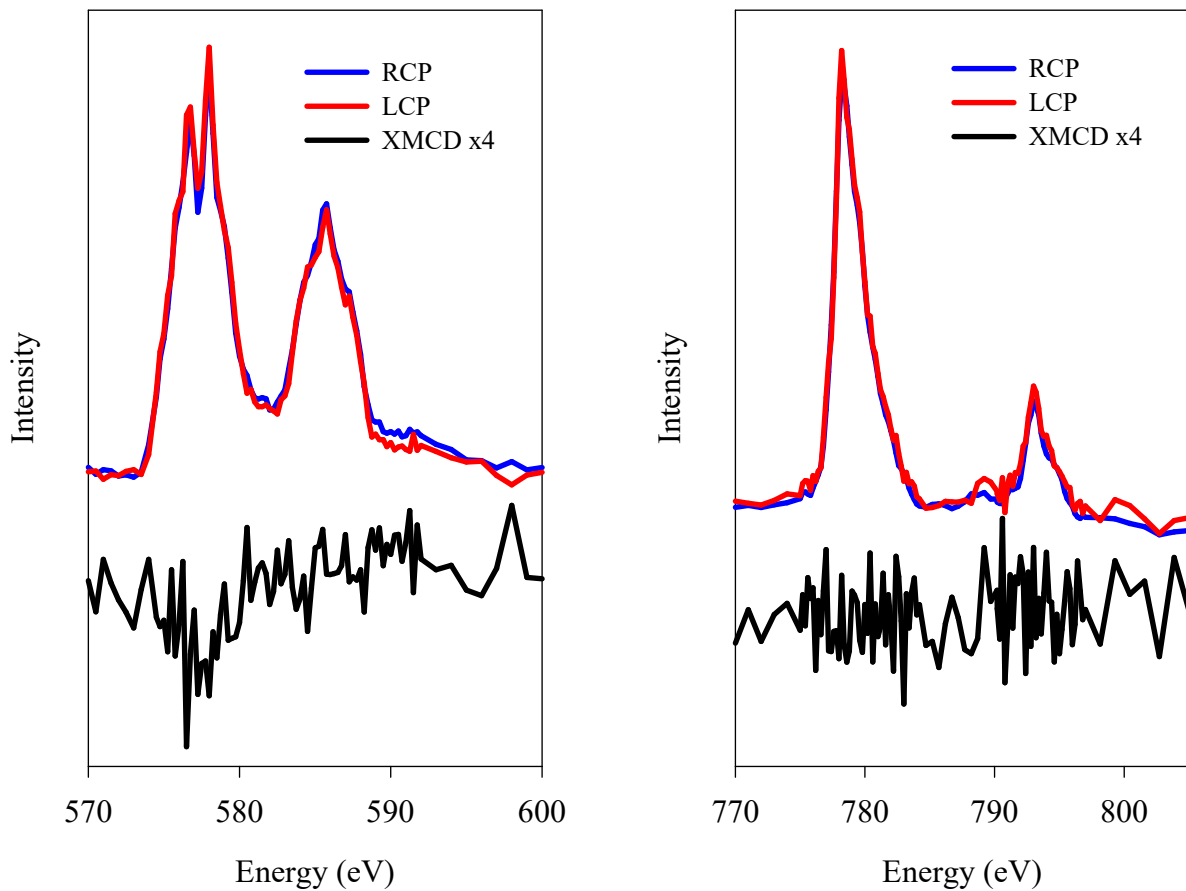
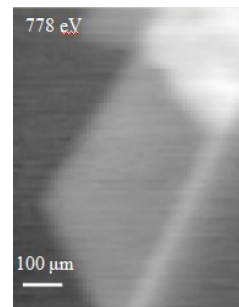


Figure 5. TEY spectra using left circularly polarized light (LCP) and right circularly polarized light (RCP), and the corresponding XMCD spectra (RCP-LCP) amplified by a factor of 4 at the Cr 2p edge (above left) and Co 2p edge (above right). Right: TEY image of the crystal being studied taken at 778 eV.



3.3 STXM Measurements – Transmission Mode

Figure 6 shows the XMCD spectra of parts of a particle taken at the Cr 2p and Co 2p edges in transmission mode at the CLS in February, 2010. The spectra taken with the different circular polarizations over the entirety of the particles showed very little difference, and thus no appreciable net XMCD. However, when areas were selected with high XMCD of a given polarity, the spectra at both edges show a distinct XMCD signal, especially on the L_3 peak. Notably, the XMCD signal is significantly stronger at the Co 2p edge, indicating that the magnetic properties of CoCr_2Se_4 are mostly due to the cobalt cations, with smaller contributions from the chromium cations.

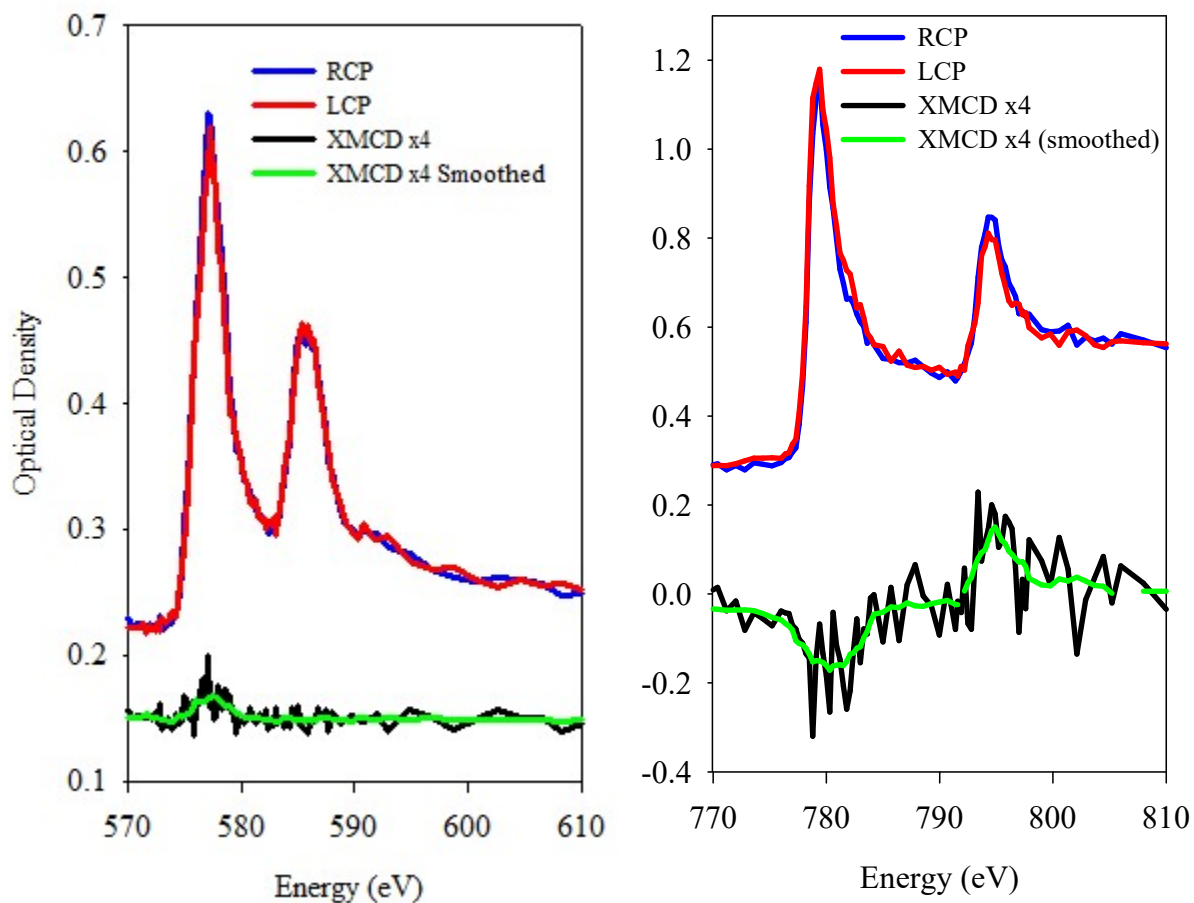


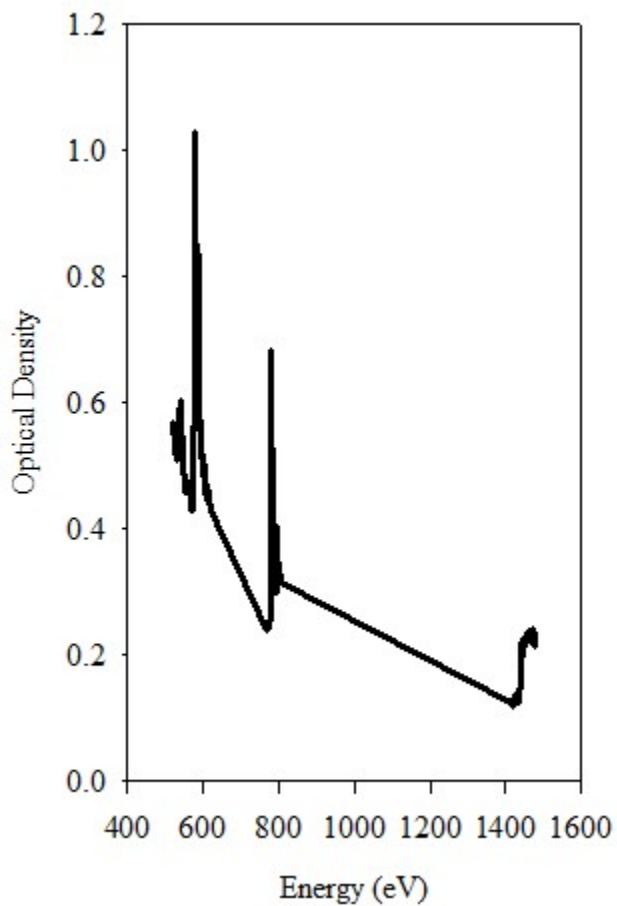
Figure 6. Transmission spectra using left circularly polarized light (from the green areas in the image on the left) and right circularly polarized light (from the blue areas in the image on the left), and the corresponding XMCD spectrum (RCP-LCP) amplified by a factor of 4 at the Cr 2p edge (above left) and Co 2p edge (above right) on a CoCr_2Se_4 , with transmission image shown on the left.

200 nm

To check that the CoCr_2Se_4 had the expected composition, spectra were taken in the energy ranges containing the Co 2p, Cr 2p, and Se 3p edges. The O 1s edge was also included to check for oxygen contamination. The appended spectra are shown in Figure 7. Though there is a peak at the oxygen edge suggesting that some oxygen is present, it is small compared to the peaks at the Co 2p and Cr 2p edges. It is likely that the transmission measurements, though

including some signal due to the oxide on the surface of the sample, are for the most part examining the properties of the oxygen-free bulk of the sample.

Figure 7. Transmission measurements on CoCr_2Se_4 . Shows peaks at the O 1s edge (540 eV), Cr 2p edge (580 eV), Co 2p edge (780 eV), and Se 3p edge (1440 eV).



Further transmission studies were done on another pair of particles. Figure 8 shows an image of these particles taken in transmission mode, as well as the transmission spectra and corresponding XMCD at the Co 2p edge for two regions in the particles which exhibit opposite XMCD polarity. The transmission image and the two XMCD plots taken together indicate that these particles are divided into two domains with opposite polarity.

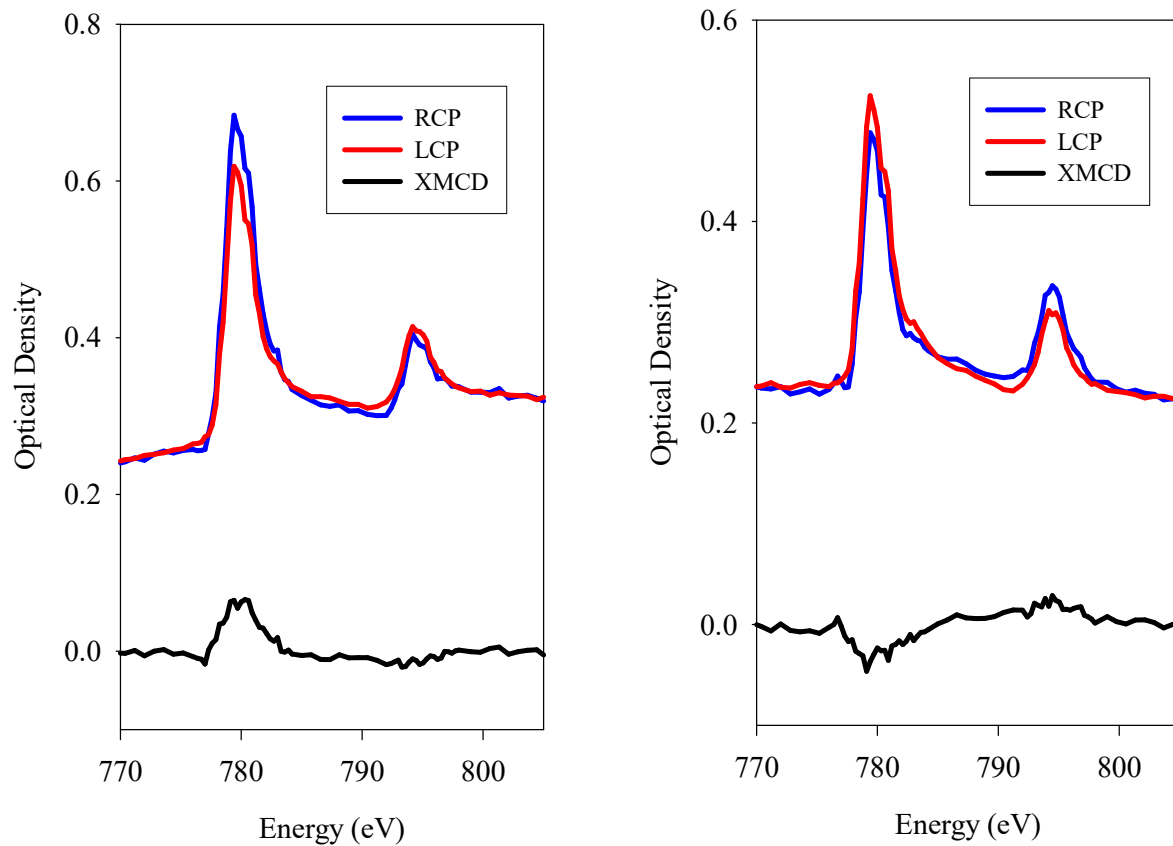
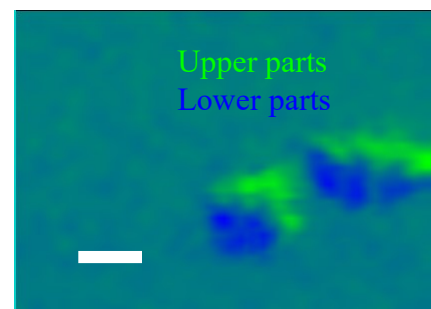


Figure 8. Transmission of CoCr_2Se_4 particles using right circularly polarized light (RCP) and left circularly polarized light (LCP), and the corresponding XMCD (RCP-LCP) at the Co 2p edge. The spectra of the upper parts of the particles, (indicated in green in the map on the right) are shown above left. The spectra of the lower parts of the particles (indicated in blue in the map) are shown above right.



These domains could be explained by a number of different possibilities. One is that the coercive field of approximately 2-3 kG in which the sample is placed is not strong enough to align the domains in the sample.

Another possibility is that the composition of the particles varies sufficiently to affect their properties on a large scale. A compositional map of the particles for which domain structure was found is given in Figure 9. The quantities of the different elements are shown by the intensities of the colour they are mapped by. From this map, it is evident that while the selenium is reasonably evenly distributed across the particles, cobalt and chromium have a much less equitable distribution. There are some areas that are very cobalt-rich and others that appear to be very low in cobalt. The same is true for chromium. Such compositional variations could have been created during initial synthesis or when the single crystals were crushed into smaller particles. Regardless of the origin of the compositional variation, it could be affecting how magnetic domains develop in the particles.

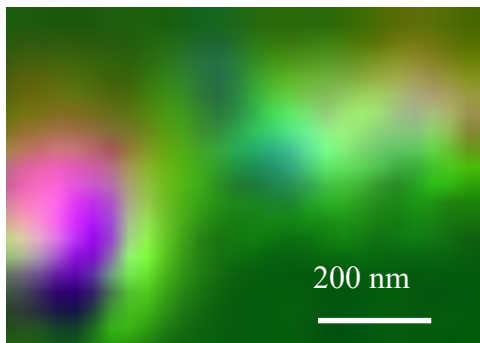


Figure 9. Compositional map of CoCr_2Se_4 particles where intensities give concentration of elements. Cobalt is shown in blue, chromium is shown in red, and selenium is shown in green.

3.4 Future Work

A major unanswered question in this project revolves around why magnetic domains were found. Two of the simplest possibilities were stated to be the possibility that the coercive field was not strong enough and compositional variation within the particles. XMCD measurements with a stronger magnetic field (created by modifications to the magnets mounted on the sample holder) could confirm that the magnetic field is not strong enough to align domains in the particles. It would be possible to examine the effects of variations in composition

by studying the spectra of un-ground single crystals (which would require TEY mode) and using a cleaning procedure to minimize oxidization. By comparing these spectra and the corresponding compositional maps of these crystals to the measurements on the smaller particles in TEY, we could extract more information about the origin of these domains.

Though progress has been made in determining what the elemental source of magnetism is in crystals of CoCr_2Se_4 , the character of the magnetic interaction has yet to be determined. This magnetism may be studied using the Muon Spin Relaxation (μSR) technique at TRIUMF in Vancouver, which would probe the magnetic fields inside the material.