Electronic and Magnetic Properties of MAX Phase \((\text{Cr}_{1-x}\text{Gd}_x)_2\text{AlC}\) and \(\text{Er}_3\text{AlC}\) Alloy

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Abstract

Bulk samples of \((Cr_{1-x}Gd_x)_2AlC\) with \(X = 0, 0.0025, 0.01, 0.025, 0.05\) and \(Er_3AlC\) compound were synthesized using the arc melting technique. The samples were characterized by X-ray diffraction, magnetic susceptibility, and four probe resistivity measurements to study their magnetic and electronic properties. Using Rietveld analysis for X-ray diffraction, it was determined that the parent compound \(Cr_2AlC\) exhibits a side phase of \(Cr_7C_3\). The substituted samples were found to have secondary phases of \(Cr_7C_3\) and \(GdCr_{3.5}Al_{8.5}\) which slightly increase on increasing substitution of \(Cr^{3+}\) by \(Gd^{3+}\). The change of the concentration of Gadolinium does not have any real effect on the lattice parameter of \((Cr_{1-x}Gd_x)_2AlC\). \(Er_3AlC\) contains secondary phases of \(ErAl_2\) and \(ErC_{0.6}\). The MAX phase \(Cr_2AlC\) and the Gadolinium substituted samples show complex magnetic behaviour. The magnetization measurements show that \(Cr_2AlC\) has an unusual magnetic behavior above 70 K which does not obey the Curie-Weiss law. The sample with \(X = 0.0025\) also does not obey the Curie-Weiss law at high temperature. The susceptibility data shows that samples with \(X = 0.01, 0.025, \) and \(0.05\) obey the Curie-Weiss law, and the magnitude of the effective magnetic moments decreases while increasing the value of \(X\). The susceptibility data of \(Er_3AlC\) obey the Curie-Weiss law; and the effective moment is \(9.1 \pm 0.005 \mu_B\). The resistivity measurement of the parent sample \(Cr_2AlC\) indicates metallic behavior. In the Gd-substituted samples, we observed a Kondo Effect from the resistivity data. The resistivity of Gd-substituted samples increases with increasing Gadolinium concentration. We also observed metallic behavior in the \(Er_3AlC\) resistivity.
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Chapter 1

Introduction-Background of MAX Phases and Er$_3$AlC Alloy

1.1 MAX phases

The MAX phase materials have the general formula M$_n$AX$_{n-1}$ (MAX) where $n = 2, 3$ or $4$, $M$ is an early transition metal, A is a p-element that is mostly from groups 13 and 14 in the periodic table, and X could be carbon and/or nitrogen. MAX phases can be classified into three groups depending on the $n$ value: “211” for M$_2$AX ($n=2$), “312” for M$_3$AX$_2$ ($n=3$), and “413” for M$_4$AX$_3$ ($n=4$), see Figure 1.1.

Elements that can create MAX phases can be seen in Figure 1.2. M elements which are early transition metals include Sc, Ti, V, Cr, Mn, Zr, Nb, Mo, Lu, Hf, and Ta. The A-group contains Al, Si, P, S, Ga, Ge, As, Cd, In, Sn, Ti, and Pb. Up to now, there are more than 70 MAX phases, but new ones are still left to be found. Most of the 70 MAX phases are 221 types, and only the Ti$_2$CdC phase has Cd as an A-group element [2].
Figure 1.1: Crystal structure of the 211 (n=2), 312 (n=3), and 413 (n=4) MAX phases [1].
The MAX phase alloys were synthesized for the first time in the 1960s by Hans Nowotny et al. in Vienna, Austria. They were known as H phase materials where H stands for a hexagonal close-packed structure [1]. In the middle of the 1990s, M. W. Barsoum and T. El-Raghy reported remarkable properties of Ti$_3$SiC$_2$, and they called these combinations MAX phases. This event increased scientific interest in these phases [1].

The MAX phase has the P63/mmc space group. In this hexagonal structure, there are $M_6X$ octahedral close-packed layers between the square planner slabs of the A-elements that are occupied in the center of trigonal prisms. The X atoms are located between M-atoms in the octahedral sites. Note that the trigonal prisms are larger than the octahedral sites, so they accommodate the A-atoms perfectly. The c-axis is longer than the a and b-axis in all three crystal structures. It can be seen in Figure 1.1 that for $n=2$ two M layers are separating each A layer, but for $n=3$ there are three layers separating the A-layer, while there are four M-layers for $n=4$. The MAX phase is anisotropic, and the
lattice parameter is usually around $a=3\text{Å}$ and $c=13\text{Å}$ for the 211 phases, $c=18\text{Å}$ for the 312 phases, and $c=23–24\text{Å}$ for the 413 phases [1]. Manoun et al. in 2006, for instance, stated that Cr$_2$AlC has a hexagonal structure and the P63/mmc space group, with the lattice constants $a=2.857\pm0.002\text{Å}$ and $c=12.81\pm0.002\text{Å}$ [3].

MAX phase materials have been useful in a wide variety of applications that require high temperature, chemical stability and thermal shock resistance due to their unique properties existing in both the ceramic and metallic form. Like metals, they are plastic at high temperature with good electrical and thermal conductivity, and they can be easily machined. They are similar to ceramics in being lightweight and in their hardness since they are harder than the parent metal, and resistant to oxidation at high temperature [4, 1]. These features are related to the structure and electronic properties of the nanoscale constituent atomic layers and the mix between the metallic covalent M-X bonds which are strong and the M-A bonds that are comparatively weak. Proper fireproof tubes, rockets, and cutting tools are examples of applications of MAX phases [1]. MAX phases may play an important role in the economy because they might decrease the expense and energy consumption of fuel-burning engines by improving their quality [5]. Nanolaminated and nanocomposite modifications of Ti$_3$SiC$_2$ are examples of MAX phase materials that have been used by some companies such as Sandvik/Kanthal, Seco Tools, IonBond, ABB, Impact Coatings, and Volvo AB [1]. Furthermore, the preparation of Cr$_2$AlC could be a successful way to recycle waste plastic. In 2018, a new technique using a simple chemical route at 800 °C to convert plastic waste to Cr$_2$AlC was reported [6]. Another 2018 study tested Cr$_2$AlC under gradient conditions using a burner ring [7]. They reported that Cr$_2$AlC can be useful in an application that requires high temperature, high heat fluxes, and oxidizing environments because it has an oxidation resistance. The compound survived after the accumulative time of 29 h at 1200 °C without detecting any damage due to the formation of an $\alpha$-Al$_2$O$_3$ layer, which is robustly bonded to the substrate [7].

Since MAX phases have been useful in many applications, there have been many theoretical and experimental reports on magnetic and electronic properties of Cr$_2$AlC and other MAX phase com-
pounds. In 2004, the first experimental results of Cr$_2$AIC were reported by Schneider et al. when they prepared the compound as a thin film [8]. They prepared it by using the magnetron sputtering process and discussed the result of their structure. They did not measure any magnetic properties. However, their theoretical calculation that was based on density functional theory (DFT) in conjunction with generalized gradient approximation (GGA) suggested that a paramagnetic or antiferromagnetic spin configuration state is more likely than the ferromagnetic configuration state. They also concluded that at room temperature the magnetism in Cr$_2$AIC may be curbed [8]. This agrees with the experimental Nuclear Magnetic Resonance (NMR) results that showed that MAX Phases are paramagnetic at temperatures over that of liquid nitrogen (around 80 K)[9]. However, another theoretical study in 2011 by Ramazan et al. found that the ferromagnetic ground state is most likely, and they reported some discrepancies of their results with previous studies [5]. They also suggested that the magnetic moment on each Cr atom is 0.9 µ by using the density functional calculation (DFT) based on generalized gradient approximation (GGA) and GGA+U calculation where (U) is a correction applied to GGA in order to improve the accuracy of the calculation. In 2013 Jaouen et al. prepared a bulk Cr$_2$AIC using hot isostatic pressing (HIP) [10]. They studied the Cr$_2$AIC structure and its magnetization using neutron powder diffraction and a Superconducting Quantum Interference Device (SQUID magnetometer) from room temperature to 1.8 K. They found that Cr$_2$AIC presents Invar-like behaviour at low temperatures. This behaviour is due to the rivalry between thermal expansion and magnetic interactions. Moreover, they found that Cr$_2$AIC has a very weak ferromagnetic moment, 0.002 µ per Cr-atom which is lower than the GGA+U prediction quoted above. They also found that magnetization in Cr$_2$AIC is suppressed at 100 K which is in agreement with the NMR study that is mentioned above [10].

Moreover, the tunable properties and the possibility of exchanging different elements have made the MAX phase an interesting topic for scientists due to their advantages over other materials. For instance, a different type of the MAX phase has been studied by substituting M atoms with iron transition group or other materials [11]. In 2011, another research by M. Dahlqvist et al. based on the DFT
calculation stated that \((\text{Cr}_{1-x}\text{Mn}_x)_2\text{AlC}\) compounds where \(X \geq 0.25\) can have a ferromagnetic behavior [12]. In 2014, A. Mockute et al. prepared \((\text{Cr}_{0.8}\text{Mn}_{0.2})_2\text{AlC}\) as thin film [13]. They found a magnetic response at least above room temperature, so they confirmed the previous theoretical prediction for a FM ground state of \(\text{Cr}_2\text{AlC}\) doped with Mn. They also prepared bulk \(\text{Cr}_2\text{AlC}\) with various levels of Mn-doping but they did not report FM or any other magnetic transition between 2 K and 300 K [13, 14]. In 2017, Hamm et al. prepared bulk \(\text{Cr}_2\text{AlC}\) by substituting Fe or Mn for Cr using microwave heating and spark plasma sintering [14]. They had a successful substitution of 10% Mn and 2% Fe incorporation, but they found many secondary phases that were observed in the X-ray diffraction data. The magnetic results of the Mn and Fe-substituted alloys showed a magnetic transition at low temperature but they did not show the ferromagnetic ground state. They agreed with A. Mockute et al. when they prepared bulk \(\text{Cr}_2\text{AlC}\) with various levels of Mn-doping [14].

One important issue related to the research of magnetic MAX phases is the quality of the samples. Bulk samples can be prepared in many ways: for example, hot isostatic pressing (HIP), hot pressing (HP), spark plasma sintering (SPS), and arc melting. Overall, despite all of the studies conducted about MAX phases, it is clear that there are discrepancies between theoretical calculations, thin film, and bulk magnetism results. The full potential of MAX phase properties is still unclear which means there is a need for more research about their magnetic properties.

### 1.2 The \(\text{Er}_3\text{AlC}\) alloy

Besides the \(\text{M}_n\text{AX}_{n-1}\) phase, another family including ternary antiperovskite carbides (space group pm3m) has attracted the attention of researchers because of the remarkable properties frequently observed in these compounds such as superconductivity, giant magnetoresistance (GMR), metal–insulator transition and magnetism [15]. The inverse perovskite or antiperovskite is a type of crystal structure similar to the perovskite structure, but the position of the cation is replaced by an anion
Figure 1.3: A unit cell of cubic antiperovskite: The blue atom at the body center and the green atoms at the corners are anions while the red atoms at the face-centers are cations [17].

and vice versa. The general formula of the perovskite structure is ABX$_3$, where A and B are cations and X is an anion. In antiperovskites, the general formula is switched. A and B sites are occupied by anions and the X site is occupied by the cation. Figure 1.3 exhibits an example of the simplest cubic antiperovskites structure, where the atom at the body center and atoms at the corners, are anions while face-centred atoms are cations [16, 17].

In the 1960s, a large group of R$_3$MC (R=La–Nd, Sm, Gd–Lu; M=Al, Ga, In) compounds were synthesized for the first time by Stadelmaier et al. and Rosens et al. [15]. In 1997, Gesing et al. studied the same materials where they found the lattice parameters of the material and compared them with existing literature studies [18]. Er$_3$AlC also was prepared for the first time successfully with the antiperovskite structure in 1967 by Buschow et al. [19]. In 1996, Pecharsky et al. also studied Er$_3$AlC experimentally, where they determined that Er$_3$AlC crystallizes in an antiperovskite structure [19]. Furthermore, they found that Er$_3$AlC may order antiferromagnetically, and this order can be easily transformed to a ferromagnetic one by a magnetic field of about 24600 Oe. Moreover, X-ray diffraction of Er$_3$AlC and Er$_3$AlC$_x$ (x=0.1, 0.25, 0.5) was investigated and it showed that Er$_3$AlC has a single-phase but other
compounds have another phase which is Er$_2$Al. Moreover, the heat capacity measurement was studied, and it showed that Er$_3$AlC and the carbide alloys have a $\lambda$ - type heat capacity anomaly at 3.1 K [19]. The magnetocaloric effect (MCE) of Er$_3$AlC were determined too. MCE of Er$_3$AlC$_x$ showed a maximum, then decreased as the $x$ value increased related to the reduction of the amount of Er$_3$AlC and the rise of Er$_2$Al [19]. They concluded that Er$_3$AlC could be used effectively in magnetic fields from 7 to 10 T in the temperature region between 20 K to approximately 1.5 K for magnetic cooling down to 1.5 K without using He$^3$ as a refrigerant [19]. Overall, in spite of the studies have been done about the Er$_3$AlC sample, there is a need for further studies of its magnetism.

The aim of this research is to study the magnetic and electronic properties of MAX phase (Cr$_{1-x}$Gd$_x$)$_2$AlC ($X=0.00$, 0.0025, 0.01, 0.025, 0.05) and Er$_3$AlC alloy. We substituted Gd with $S=2$ for Cr with $S=1$ in an attempt to study the effect of the rare earth element on the magnetic and electronic properties of MAX phase compounds and to create spin configurations that show magnetic order. The magnetic susceptibility and resistivity of the MAX phase and Er$_3$AlC as a function of both temperature and magnetic field are studied from 1.7 to 300 K.

In chapter two, the method of preparing samples and the X-ray results are discussed. In chapter three, magnetic properties results are presented. The resistivity measurement results are discussed in chapter four. In chapter five we present the conclusion and some possible future work on these compounds.
Chapter 2

Method of preparation and X-ray technique and results

2.1 Synthesis Method: Arc Melting

In the arc melting furnace, an electrical arc is used for melting the constituent elements under an inert argon gas atmosphere to make alloys. The arc melting furnace has two parts: (i) a hearth with a cup of one electrical polarity and (ii) a copper stinger with tungsten electrode that has opposite polarity. The arc occurs when electric current flows through an air gap between these two conductors. Materials have to be placed in the hearth plate which is made out of copper and the stinger is used to strike the arc in order to melt the material. The hearth plate is located in the base of a vacuum chamber. The top of the chamber has the stinger rod. The stinger rod is mounted into a swivel ball to allow vertical and angular movement of the electrode. The chamber has upper and lower water-cooling sections separated by a Pyrex observation tube. The cooling system is used to prevent the melting of the electrode as well as the copper hearth. There is an attached mechanical pump to evacuate before
back filling the inert gas. Additionally, the system is equipped with ports in order to inlet and outlet the inert gas (see Figure 2.1) [20]. Polycrystalline samples of MAX phases and Er$_3$AlC were prepared using the arc melting technique.

For the present study, MAX phase samples (Cr$_{1-x}$Gd$_x$)$_2$AlC were synthesized by mixing stoichiometric amounts of high purity Cr (99.99%), Al (99.5%), C (99.9995%), and Gd (99.9%) powders using a mortar and a pestle. This mixture was then pressed into pellets applying a force of approximately 5 tons using a 10 mm stainless steel dye. The pressed pellets were placed in the cup of the copper hearth. A small piece of zirconium is also placed in a small separate cup of the hearth to used as a getter. The furnace was then purged using the mechanical pump, followed by back filling with inert argon gas at a pressure of 1 bar that provided a fast way to evacuate oxygen from the chamber as well as acting as an ionizing gas. A 150 A current is required for melting the samples. Before melting the sample, the piece of zirconium was melted to remove any possible oxygen impurity. The specimen then was melted by moving the stinger around and over the materials to have a uniform and homogeneous melt. The specimen was turned over and remelted up to 6 times to ensure sample homogeneity. The sample was cleaned by aceton before each remelting. The arc is turned off by turn off the power supply. The furnace can reach temperatures above 3500 °C instantly. Melting points for Chromium, Gadolinium, Erbium, Aluminum, and Carbon are 1907 °C, 1312 °C, 1529 °C, 660.32 °C, and 3500 °C respectively. To control possible weight losses, the sample was weighed after each melting, which should be negligible to maintain the desired stoichiometrically. Er$_3$AlC was prepared by using high purity pieces: Er (99.9%), Al (99.999%), and graphite (99.9995%).

### 2.2 X-ray Diffraction Technique

To characterize the crystal structure of the samples, we carried out the X-ray measurements. In the X-ray diffraction technique, X-ray beams focus on the sample. Most of the rays are absorbed, and some of them are reflected. X-rays are reflected from surface layers and many planes because the
Figure 2.1: Complete view of the arc-melting furnace: chamber, power supply and Ar gas cylinder in the lab of Dr. F. S. Razavi at Brock University, 18 February 2018.
Figure 2.2: Diagram illustrating Bragg's law. The black arrows denote the path of the incident and reflected beams. $\Theta$ is the angle between the incident (reflected) beams, and the lattice planes, and $d$ is the distance between the atomic planes.

structure of a crystal is composed of many parallel planes. For most incident angles, the net reflection will be weak because the reflected rays are out of phase. However, there is a strong net reflection that could happen at a few specific angles for which the reflected rays are in phase. This reflection is known as X-ray diffraction. The Bragg condition, which is based on the condition of constructive interference, is given in equation 2.1 and can be extracted from the geometry shown in Figure 2.2:

$$n\lambda = 2d \sin \Theta \quad (2.1)$$

where $\lambda$ is the wavelength of the X-rays, $d$ is the spacing between the layers of atoms, $n$ is an integer number called the order of the reflection, and $\Theta$ is the incident angle which is the angle between the incident rays and the surface of the crystal [21].

In this work, X-ray powder diffraction was achieved on all samples by using the Rigaku Multiflex X-ray diffractometer, with Cu K$\alpha$ radiation to identify the samples and confirm their quality. This Cu K$\alpha$ tube is powered with 40 kV and 40 mA. After the arc melting, all samples were ball-shaped (see Figure 2.3). Therefore, for measuring X-ray diffraction, using the Precise Theta/2-Theta Scan (Bragg-Brentano
focusing), the alloy should be cut into a flat shape or crushed into powder. We found that increasing the percentage of Gadolinium in the MAX phase samples, decreases the hardness of the sample. Thus, \(\text{Cr}_2\text{AlC}\) was cut into a flat shape using a Precision Sectioning Saw (see Figure 2.4), but \((\text{Cr}_{1-x}\text{Gd}_x)\text{AlC}\) (\(X=0.0025, 0.01, 0.025, 0.05\)) was crushed into a black fine powder using a mortar and pestle. Note that \(\text{Er}_3\text{AlC}\) was crushed into powder as well. The scattered X-rays were measured for an angular range of \(2\Theta=10^\circ\) to \(80^\circ\). X-ray diffraction data were analyzed by using the PDXL software (Rigaku), which is an application software that has crystal structure analysis, Rietveld analysis, and phase identification. ICSD (Inorganic Crystal Structure Database), CIF (Crystal Information File), and VESTA (Visualization for Electronic and Structure Analysis) were used for obtaining crystal structure parameters.

2.3 X-ray Results of \(\text{Cr}_2\text{AlC}\)

X-ray diffraction data of \(\text{Cr}_2\text{AlC}\) alloys are shown in Figure 2.5. \(\text{Cr}_2\text{AlC}\) was measured as a flat sample, as well as a powder using the powder diffraction technique. The difference between \(\text{Cr}_2\text{AlC}\) as a flat alloy and as a powder can be seen in Figure 2.6, which indicates the presence of additional phase.
Figure 2.4: Flat Cr₂AlC, after having been cut using the Buehler Isomet Low Speed Sectioning Cut Off Saw with a diamond blade.
Figure 2.5: X-ray diffraction data of \( \text{Cr}_2\text{AlC} \).

Figure 2.6: X-ray diffraction of \( \text{Cr}_2\text{AlC} \) alloy compared to X-ray diffraction of \( \text{Cr}_2\text{AlC} \) powder.
Using Rietveld analyses and the PDXL software, it was found that the additional phase might belong to Cr$_7$C$_3$. The additional phase was clearer and easier to pinpoint in the powder sample. As expected, the parent compound Cr$_2$AlC has the hexagonal structure with the space group P63/mmc (see Figure 2.7). Crystal structure parameters for the sample as alloy and as powder were calculated from the powder patterns and presented in Table 2.1. Lattice parameters of Cr$_2$AlC agree with the reported values in Ref [14].

### 2.4 X-ray Results of (Cr$_{1-x}$Gd$_x$)$_2$AlC ($X = 0.0025, 0.01, 0.025, 0.05$ )

X-ray diffraction data of Cr$_2$AlC compared to Gd-substituted samples can be seen in Figure (2.8). The superimposed pattern of the parent compound Cr$_2$AlC and (Cr$_{1-x}$Gd$_x$)$_2$AlC can be seen in Figure (2.9). From the X-ray diffraction pattern for Gd-substituted samples, we detected some peaks that were not found in the X-ray diffraction pattern of Cr$_2$AlC. This indicates the presence of additional
phases. Using the PDXL software and Rietveld analysis, it was found that the additional phase was likely GdCr$_{3.5}$Al$_{8.5}$. In the Gd-substituted samples, Cr$_7$C$_3$ was presented as a minor phase, which is detected in the parent compound as well. The intensity of Cr$_7$C$_3$ and GdCr$_{3.5}$Al$_{8.5}$ peaks becomes stronger upon the substitution of Gd into Cr$_2$AlC. As an example, Figure 2.10 shows the Rietveld refinement including the impurity phases of Cr$_7$C$_3$ and GdCr$_{3.5}$Al$_{8.5}$ of the sample with X = 0.01 and the sample with the highest amount of Gd doping (X = 0.05).

The Refined unit cell parameters for our samples plus some previous studies are shown in Table 2.1. The substitution of Gd with Cr causes a small effect on the lattice parameters. Comparing the undoped sample with that of the highest level (X = 0.05) suggests a small increase in lattice parameters and volume with doping, see Figure 2.11. The R factors of the refinements $R_{wp}$ (weighted profile residual), $R_e$ (expected value of $R_{wp}$), and $S = R_{wp}/R_e$ (analytical accuracy) for the parent compound and the Gd-substituted compounds are presented in Table 2.2. The S value of the refinement is less than 2, indicating that the fitting results were credible. As S value indicates the goodness of fit and describes how much the fit deviates from the data.

My results are in agreement with the studies by C. M. Hamm et al. which stated that the substitution of Mn and Fe into Cr$_2$AlC affects the unit cell parameters marginally. Cr$_7$C$_3$ is also one of the additional phases they had in (Cr/Mn)$_2$AlC and (Cr/Fe)$_2$AlC [14]. Because the X-ray diffraction data does not give us any conclusion related to the successful substitution of Cr$_2$AlC with Gd, we need
Figure 2.8: X-ray diffraction data of (Cr$_{1-x}$Gd$_x$)$_2$AlC ($X = 0.00, 0.0025, 0.01, 0.025, 0.05$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{wp}$</th>
<th>$R_e$</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X=0$ (Alloy)</td>
<td>4.13</td>
<td>3.48</td>
<td>1.1873</td>
</tr>
<tr>
<td>$X=0$ (Powder)</td>
<td>7.89</td>
<td>5.94</td>
<td>1.3274</td>
</tr>
<tr>
<td>$X=0.0025$</td>
<td>9.01</td>
<td>5.77</td>
<td>1.5615</td>
</tr>
<tr>
<td>$X=0.01$</td>
<td>7.21</td>
<td>4.4</td>
<td>1.6352</td>
</tr>
<tr>
<td>$X=0.025$</td>
<td>8.17</td>
<td>6.14</td>
<td>1.3304</td>
</tr>
<tr>
<td>$X=0.05$</td>
<td>7.19</td>
<td>6.07</td>
<td>1.1832</td>
</tr>
</tbody>
</table>

Table 2.2: The final R factors for (Cr$_{1-x}$Gdx)$_2$AlC ($X = 0.00, 0.0025, 0.01, 0.025, 0.05$) and S values of the refinements.
Figure 2.9: The superimposed X-ray diffraction patterns of $(\text{Cr}_{1-x}\text{Gd}_x)_2\text{AlC}$ ($X = 0.00, 0.0025, 0.01, 0.025, 0.05$) in the $2\Theta$ range of $20^\circ$ to $70^\circ$. 
Figure 2.10: The superimposed patterns of Cr$_{1.98}$Gd$_{0.02}$AlC and Cr$_{1.9}$Gd$_{0.1}$AlC in 2Θ range of 30° to 80°.
Figure 2.11: Unit cell volume versus the concentration of Gadolinium in $(\text{Cr}_{1-x}\text{Gd}_x)_2\text{AlC}$ ($X=0.00, 0.0025, 0.01, 0.025, 0.05$).
Table 2.3: The Rietveld factors and the content of the additional phases of Er$_3$AIC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R$_{wp}$</th>
<th>R$_e$</th>
<th>S</th>
<th>Content (%) for the additional phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er$_3$AIc (A)</td>
<td>6.56</td>
<td>5.05</td>
<td>1.2965</td>
<td>ErAl$<em>2$(6.3), ErC$</em>{0.6}$(22.6)</td>
</tr>
<tr>
<td>Er$_3$AlC (B)</td>
<td>6.34</td>
<td>5.55</td>
<td>1.1416</td>
<td>ErAl$<em>2$(10), ErC$</em>{0.6}$(3.5)</td>
</tr>
</tbody>
</table>

2.5 X-ray Results of Er$_3$AIC

This experiment here is to investigate using the X-ray Diffraction technique. The Er$_3$AIC alloy, after cleaning with acetone, was found to have broken down into smaller pieces by itself and there were white layers covering the whole surface (see Figure 2.12). In the following, the Er$_3$AIC alloy after crushing the pieces using a mortar and pestle is referred to as sample A. Sample B refers to the sample A after having been left for 20 hours at room temperature. The X-ray diffraction of sample A and sample B is shown in Figure 2.13, and indicates the presence of two impurity phases. Using the PDXL software and Rietveld analysis for the powder diffraction pattern of sample A and sample B, Er$_3$AIC was found to be the main crystalline phase. Al$_2$Er, which has the fcc Laves phase structure (type C-15) as stated in Ref [22], and ErC$_{0.6}$ were present as minor phases. The concentrations of different phases calculated from the Rietveld analysis for both samples are shown in Table 2.3. The Rietveld refinement of the X-ray diffraction data yields the crystallographic data for samples A and B presented in Table 2.4. The lattice parameter (a) of Er$_3$AIC agrees well with the reported value of 4.8128 Å in Ref [19]. The crystal structure of Er$_3$AIC is shown in Figure 2.14. The R factors of the refinements can be seen in Table 2.3.
Figure 2.12: Er$_3$AlC alloy is broken down into parts by itself after cleaning it with acetone. On the left are the white layers after the separation.

Figure 2.13: X-ray diffraction of Er$_3$AlC alloy before and after the reaction with air.
Figure 2.14: Crystal structure of Er$_3$AlC sample: Aluminum is located at the corner of the cube, Carbon in the octahedral center, and Erbium is on the faces of the cube.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Space group</th>
<th>a(Å) = b(Å) = c(Å)</th>
<th>Volume(Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er$_3$AlC (A)</td>
<td>221: Pm-3m</td>
<td>4.8012 (3)</td>
<td>110.678(14)</td>
</tr>
<tr>
<td>Er$_3$AlC (B)</td>
<td>221: Pm-3m</td>
<td>4.8049(4)</td>
<td>110.930(18)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er</td>
<td>3c</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Al</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>1b</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 2.4: Crystallographic data for Er$_3$AlC.
Chapter 3

Magnetization

3.1 Magnetism

The source of magnetism comes from the spin and orbital motion and the interaction between electrons. The different types of magnetism characterize by how responsive a material is to the applied magnetic field. When a field (H) is applied to a material, the magnetization (M) is the collective response to the field. It is proportional to H by this equation:

\[ M = \chi H \]  

(3.1)

where \( \chi \) is the proportionality constant called the magnetic susceptibility. The effect of the interaction of an applied magnetic field on the orbital motion of electrons in an atom is known as diamagnetism. All materials exhibit a diamagnetic response, but only those that have no other magnetic behavior are classified as diamagnetic; this occurs when all atomic or molecular orbitals are either completely empty or filled leaving no net magnetic moment. Diamagnetism is usually a weak form of magnetism that is
only exhibited in the presence of an external magnetic field. Under the influence of an applied field (H), the electronic orbital movement changes. This motion is a type of electric current, and it produces a magnetization (M) in the opposite direction to the applied magnetic field (atomic version of Lenz’s law). The induced magnetic moment is a small negative number which is near -10^{-6} emu/mole. Another important characteristic behavior of diamagnetic materials is that the susceptibility is independent of temperature as seen in Figure 3.2 [23, 24]. On the other hand, materials with unpaired electrons can be classified into four categories depending on their magnetic moments order: paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism. Figure 3.1 shows these different kinds of magnetic materials schematically [23].
3.1.1 Paramagnetism

Paramagnetism refers to materials that have a small positive susceptibility to magnetic fields. In paramagnetic materials, each atom has a magnetic moment, which are only coupled in a weak manner. Hence, the magnetic moments are randomly aligned as a result of thermal fluctuation. When subjected to an applied magnetic field, the orientation of the atomic moments shifts slightly toward the field direction. Therefore, the total effect is to have a low magnetization in the same direction as the applied field. Generally, $\chi$ is between $10^{-3}$ and $10^{-5}$, and decreases with increasing temperature, as seen in Figure 3.3. This behavior known as the Curie-law and is given in this equation:

$$\chi = \frac{C}{T}$$

(3.2)

where $C$ and $T$ are the Curie constant and the absolute temperature respectively. This relation only holds for high temperatures, or weak magnetic fields [23]. In fact many paramagnetic materials follow a more general temperature dependence given by the Curie-Weiss law [23]:

Figure 3.2: Magnetization versus magnetic field and susceptibility versus temperature in diamagnetic materials [24].
3.1.2 Ferromagnetism

Ferromagnetic materials have a large positive susceptibility to the magnetic field. They display a strong attraction to the magnetic field and maintain their magnetic properties after an external magnetic field is removed. The atomic moments in ferromagnetic materials exhibit very strong interaction. This interaction is produced by electronic exchange forces and causes the unpaired electrons to line up parallel with each other in regions called domains. The exchange force is a quantum mechanical phenomenon caused by the relative orientation of the spins of two electrons. In the demagnetized state, the magnetization directions of different domains have different orientations and the net magnetic field
as a whole is zero. When a magnetic field is applied, all domains orient in the same direction to create a strong magnetic field. As ferromagnetic materials are heated, the alignment of the atomic magnetic moments will be decreased and the magnetization will decrease smoothly to become zero at a certain temperature which is called the Curie temperature $T_C$. Above $T_C$, ferromagnetic compounds become paramagnetic and obey the Curie-Weiss law, as seen in Figure 3.4 [23, 24, 27].

When a ferromagnet is magnetized in one direction, it will not demagnetizes completely if the field is removed. It can be demagnetized by applying a magnetic field in the opposite direction or applying heat. If the magnetic field changes periodically, the ferromagnetic materials magnetization will trace out a loop called a hysteresis loop. The lack of retraceability of the magnetization curve is an important feature of ferromagnetic materials which is related to the existence of magnetic domains in these materials. The magnitude of the magnetization when the magnetic field is zero is named the retentivity, and the strength of the magnetic field when the magnetization disappears, is called the coercivity (Figure 3.5) [23, 27].
3.1.3 Antiferromagnetism

In antiferromagnetic materials, the magnetic moments line up so the neighboring moments are aligned in opposing directions. Therefore, the atomic magnetic moments cancel each other, resulting in zero spontaneous magnetization. The temperature dependence of the susceptibility in polycrystalline antiferromagnetic materials is shown in Figure 3.6. The phase transition to the antiferromagnetic state is known as the Néel transition and happens at a temperature denoted by \( T_N \), called the Néel temperature. Below the Néel temperature, the susceptibility decreases with decreasing temperature, but above \( T_N \) an antiferromagnet is often paramagnetic and the susceptibility obeys the Curie-Weiss law \( \chi = C/(T - \theta) \) with \( \theta < 0 \) [23]. In a single crystal antiferromagnetic material, the temperature dependence of susceptibility has different behavior. The susceptibility in a single crystal antiferromagnet depends on whether the magnetic field is aligned with the magnetization direction or perpendicular to it [25].
Ferrimagnets are similar to antiferromagnets in having an opposite magnetic moment alignment. However, the net magnetization of ferrimagnetic materials is not zero due to the different magnitude of the magnetic moments. These materials break down into magnetic domains like ferromagnetic materials. They also behave similar to ferromagnetic materials, in that they have a spontaneous magnetization below some critical temperature $T_c$ even in the absence of an applied field. Nevertheless, ferrimagnets and ferromagnets have a very different magnetic ordering (Figure 3.4). Ferrimagnetism only happens in compounds that have more complex crystal structures than pure elements [23, 29].

3.2 Experimental procedure

DC Magnetization measurements were performed using the Quantum Design Magnetic Properties Measurements system (MPMS) magnetometer (see Figure 3.7). Measurements of the magnetiza-
tion as a function of temperature, magnetic field, or time can be carried out by this system. The main components of this system consist of the following:

1. Temperature control system for controlling the sample temperature in the range of 1.7 K to 350 K.

2. Magnet control system for providing the magnetic field from 0 to 5.5 T.

3. Superconducting Quantum Interference Device (SQUID) amplifier, which is the heart of the magnetic moment detection system.

4. Sample handling system for moving the sample automatically through the detection coils.

5. Liquid helium dewar mounted in its cabinet, supplying temperature down to 1.7 K.

6. Computer operating systems in order to automatically control all operating features of the MPMS [26].

For detecting the sample’s magnetization by using a SQUID, the sample has to move through the superconducting detection coil. This detection coil is located inside a superconductor magnet, and consists of three pick-up coils, two of which are wound clockwise and have a single turn. The third one consists of two turns in the opposite direction of the first two and is placed in the center between them (see Figure 3.8). This arrangement forms a second-order gradiometer. This second derivative coil is designed to eliminate the contribution from homogeneous fields such as the applying magnetic field. Therefore, only a signal due to second derivative or higher order term of changing magnetic field will be detected such as that is generating from magnetic moment of sample [30]. As the sample moves through the coils, the magnetic flux in the detection coils changes and that produce a change in the current. The detection coil is connected to the SQUID input coil via superconducting wires, and the SQUID works as a linear current to voltage converter. Therefore, this change in the current in the detection coil produce corresponding changes in the SQUID output voltage which is proportional to magnetic moment of the sample [30]. The output voltage is amplified and read out by the magnetometer’s electronics. By
Figure 3.7: The Magnetic Property Measurement System (MPMS) in the lab of Dr. F. S. Razavi at Brock University, 25 September 2019.
Figure 3.8: Schematic description of (a) the SQUID system in the MPMS, (b) a sample mounted in the plastic drinking straw and connected to the sample rod used for the magnetic measurement in the MPMS system [26].

observing the output voltage of the SQUID as a function of temperature, we can track the changes in the sample magnetization with the temperature [26].

The first step to determine the magnetic properties of a sample was to load it inside the MPMS system. Samples were pieces of alloy of irregular shape (approximately rectangular). The samples were weighed and mounted on a plastic drinking straw, whose diamagnetic moment was negligible. The sample was secured by making two horizontal cuts in the straw forming a strip that is pushed inside so the sample can be threaded through. Er$_3$AlC alloy was measured as a powder. Gelatin capsules were used to hold the sample. After the powder sample was weighed, the capsule was filled with the powder that was pressed down with a small amount of cotton to avoid movement during the magnetic measurement. The capsule containing the sample was secured in a plastic straw in the same way as securing the rectangular samples. After that, the straw containing the sample was attached to the end of the sample holder. The straw was moved vertically inside the system, and the sample was automatically centered in the SQUID pick up coils to make sure that the four coils sensed the magnetic moment of the sample. After that, the MPMS system was ready to run the sequence.
3.3 DC Magnetization Results

For measuring the magnetization of all samples, ZFC - FC (Zero Field Cooling-Field Cooling) sequences were chosen. First, the sample was cooled from \( T = 300 \) K to the minimum temperature \( T = 1.7 \) K in the absence of the magnetic field \( (H = 0) \). Then, the magnetic field was applied and the ZFC magnetization was recorded as a function of temperature while warming up to 300 K. Finally, the sample was cooled down slowly from room temperature to 1.7 K in the presence of the same magnetic field and then the FC magnetization was measured as a function of temperature upon warming up to room temperature.

3.3.1 Magnetic Results of \( \text{Cr}_2\text{AlC} \)

The ZFC and FC susceptibilities versus temperature of \( \text{Cr}_2\text{AlC} \) with an applied magnetic field of 500 Oe are shown in Figure 3.9. In this figure, the dc-susceptibility indicates a magnetic phase transition at 2.2 K. The magnetic dc-susceptibility of \( \text{Cr}_2\text{AlC} \) shows irregular temperature evolution between 70 K and 300 K. The dc-susceptibility increases as the temperature increases between 70 K and 300 K which is contrary to the Curie theory. In the Curie theory the magnetization will decrease as the temperature increases in the paramagnetic region, above the ordering temperature. Assuming \( \text{Cr}_2\text{AlC} \) to be antiferromagnetic with Néel temperature above 300 K, another experimental measurement of the magnetization with temperature above 300 K was done (Figure 3.9). As the sample warmed above 300 K, we did not observe any transition, however we observed a kink at 300 K. This kink could be seen clearly in the inverse susceptibility, as seen in Figure 3.10. This kink was also observed at 335 K previously in [14], and it was discussed that the kink might be because of a phase transition, likely in the structure of the sample.

Figure 3.11 (a) and (b) shows the ZFC and FC susceptibilities and reciprocal susceptibility versus
temperature of \( \text{Cr}_2\text{AlC} \) with applied magnetic field of 5000 Oe respectively. This plot also shows the magnetic phase transition at 2.2 K that was observed with lower field, and at around 70 K it shows the same unusual behavior that does not obey the Curie-Weiss law. In these magnetic dc-susceptibility results with 500 Oe and 5000 Oe in Figure 3.9 and 3.11 respectively, there is an increase of the magnetization with increasing temperature. This increasing of magnetization with temperature means that there is a magnetic ordering at high temperature and the magnetic moments align. This uncommon behavior could be due to spin canting of AFM sublattices as we assumed \( \text{Cr}_2\text{AlC} \) to be an antiferromagnet. This assumption was discussed in Ref [31]. At high temperatures in magnetic ordered system, the AFM interaction is low. The sublattices will bend more and aligned not parallel which makes a source of weak ferromagnetism in antiferromagnet, so the average of the magnetic moment increases [31]. Studying \( \text{Cr}_2\text{AlC} \) magnetization as a function of temperature in a high-temperature range above 400 K might give a valuable understanding of \( \text{Cr}_2\text{AlC} \) magnetic order. This study needs further research.

The Magnetization as a function of field at 1.7 K is presented in Figure 3.12. As the slope of the M-H curve does not show saturation even with 60kOe, the sample has antiferromagnetic behavior. However, the magnetization (M-H) curve has a non-linear behavior and has a small hysteresis as shown in the inset indicating the existence of weak ferromagnetism with a coercivity, \( H_c \), and a remnant magnetization, \( M_r \), of around 43 Oe and 309 emu/mole, respectively. According to the X-ray results, \( \text{Cr}_7\text{C}_3 \) is the only impurity identified, which is nonmagnetic [32]. Therefore, this weak ferromagnetic behaviour could be caused by a small concentration of impurities that is difficult to identify with X-ray diffraction.

### 3.3.2 Magnetic Results of \( (\text{Cr}_{1-x}\text{Gd}_x)_2\text{AlC} \) (X = 0.0025, 0.01, 0.025, 0.05)

The magnetic dc-susceptibility versus temperature of \( (\text{Cr}_{0.9975}\text{Gd}_{0.0025})_2\text{AlC} \) in a magnetic field of 5000 Oe is shown in Figure 3.13. It shows some differences from the parent compound \( \text{Cr}_2\text{AlC} \). At higher temperature between around 220 K and 300 K, it indicates the same unusual temperature behavior
Figure 3.9: Magnetic susceptibility as a function of temperature for Cr$_2$AlC in a magnetic field of 500 Oe. The blue and red lines represent the ZFC and FC curves, respectively. The inset is an enlarged view to show $\chi$ at low temperature. The black arrow indicates the magnetic phase transition.
Figure 3.10: The inverse of magnetic susceptibility as a function temperature for \( \text{Cr}_2\text{AlC} \) in a magnetic field of 500 Oe. This result shows unusual behavior of the magnetic susceptibility, which does not follow the Curie-Wiess law. It also indicates a kink at 300 K.
Figure 3.11: a) Magnetic susceptibility of Cr$_2$AlC in a magnetic field of 5000 Oe. The inset shows the magnetic susceptibility behavior at low temperature. The black arrow indicates the magnetic transition. (b) Reciprocal magnetic susceptibility of Cr$_2$AlC at 5000 Oe. The black arrow indicates the magnetic transition. This result shows unusual behavior of the magnetic susceptibility, which does not follow the Curie-Wiess law.
Figure 3.12: Magnetization versus Magnetic field for Cr$_2$AlC at 1.7 K. The curve does not show any saturation but it has a small hysteresis loop. The inset zoomed around the origin showing the hysteresis loop. The black arrows indicate the coercivity ($H_c$) and the remnant magnetization ($M_r$).
Figure 3.13: Magnetic susceptibility of \((\text{Cr}_{0.9975}\text{Gd}_{0.0025})_2\text{AlC}\) in a magnetic field of 5000 Oe. The black arrows indicate the magnetic transitions. The inset shows an enlarged view of the results in the range of 200 K to room temperature where the sample shows the unusual behavior in that the magnetic susceptibility increases with increasing temperature near 270 K.
Figure 3.14: Reciprocal magnetic susceptibility of (Cr$_{0.9975}$Gd$_{0.0025}$)$_2$AlC in a magnetic field of 5000 Oe. The result above around 170 K shows unusual behavior of the magnetic susceptibility, which does not follow the Curie-Weiss law.
that existed in the parent compound between 70 K and 300 K. This behaviour can be seen clearly in Figure 3.13-inset. As shown in the inset, as the sample is warmed above 200 K, the dc-susceptibility decreases slightly before it starts increasing at near 270 K. This behaviour might be related to canting of AFM sublattices. Additionally, as shown in Figure 3.13, we observed a transition that is indicated by a cusp at 6 K, and we also observed changes in the slope of the susceptibility at 70 K and 170 K. The second phase identified by X-ray diffraction, which is Gd$_{3.5}$CrAl$_{3.8}$, undergoes an antiferromagnetic transition with $T_N = 6.75$ K [33]. Therefore, this phase might be the reason we observe a transition at around 6 K in (Cr$_{0.9975}$Gd$_{0.0025}$)$_2$AlC. The transition at 70 K was observed in the parent compound, too, and was assumed to be explained in terms of canting of AFM sublattices. The transition at 170 K could be caused by impurities with a small concentration that are not detected with X-ray diffraction. We assumed this secondary phase to be GdAl$_2$ which is ferromagnetic with $T_c$ between 165 - 171 K [34, 35].

Figure 3.14 shows the temperature dependence of the inverse magnetic susceptibility $1/\chi(T)$ for (Cr$_{0.9975}$Gd$_{0.0025}$)$_2$AlC. The data at high temperature does not appear to obey the Curie-Weiss law. At temperatures between 70 K and 170 K, the relationship of $1/\chi$ vs $T$ obeys the Curie-Weiss law. By fitting the inverse susceptibility to the Curie–Weiss law ($\chi = C/(T - \theta)$) for temperatures between 70 K to 170 K, the following parameters were found; the Curie Constant $C$ is $0.304 \pm 0.003$ emu.k/mole.Oe and the Curie-Weiss temperature $\theta$ is $-242 \pm 2$ K. The experimental value of effective magnetic moment ($\mu_{eff}$) can be calculated in units of Bohr magnetons using the following formula (3.5):

$$\chi = \frac{C}{T} = \frac{\mu_{eff}^2 n N_A}{3 K_B T}$$  \hspace{1cm} (3.4)

where $N_A$ is the Avogadro’s number, $n$ is the number of atom, $K_B$ is the Boltzmann’s constant, and $\mu_{eff}$ is the effective magnetic moment. Thus:
Figure 3.15: Magnetization versus magnetic field for (Cr\(_{1-x}\)Gd\(_x\))\(_2\)AlC (X = 0.0025) (a), X= 0.01 (b), X= 0.025 (c), and X= 0.05 (d) at 1.7K. The non-linearity increases with increasing concentration of Gadolinium. The magnetization increases with increasing Gd concentration as the area of the hysteresis expands upon substituting more Gadolinium.

\[
\mu_{eff} = \sqrt{\frac{3k_B C_m}{nN_A}} = 2.82 \sqrt{C_m}
\]

(3.5)

where \(C_m\) is equal to the inverse of the slope of \(1/\chi\) versus T curve [30]. This value of the \(\mu_{eff}\) is 1.10 ± 0.01 \(\mu_B\). The negative Curie-Weiss temperature \(\theta\) is a sign of an antiferromagnetic interaction, so (Cr\(_{0.9975}\)Gd\(_{0.0025}\))\(_2\)AlC might undergo an antiferromagnetic phase transition.

The magnetization versus magnetic field of (Cr\(_{0.9975}\)Gd\(_{0.0025}\))\(_2\)AlC at 1.7 K is shown in Figure 3.15 (a). In this graph, the M-H curve does not show any saturation which indicates an antiferromagnetic behavior, but a weak FM interaction is clear by observing a small hysteresis. Therefore, the sample magnetization is complex and might have FM and AFM interactions.
Figure 3.16: a) Magnetic susceptibility of \((\text{Cr}_{0.99}\text{Gd}_{0.01})_2\text{AlC}\) in a magnetic field of 5000 Oe. The black arrows indicate the magnetic transitions. (b) Reciprocal magnetic susceptibility of \((\text{Cr}_{0.99}\text{Gd}_{0.01})_2\text{AlC}\). The solid green line represents a fit to a Curie-Weiss law, and the negative Curie-Weiss temperature is indicated by the black arrow.

The ZFC and FC susceptibilities versus temperature of \((\text{Cr}_{1-x}\text{Gd}_x)_2\text{AlC}\) \((X = 0.01, 0.025)\) with an applied magnetic field of 5000 Oe are shown in Figures 3.16 (a) and 3.17 (a) respectively. In these dc-susceptibility curves, we observed transitions at 6 K, 70 K, and 170 K. The results are almost the same as the doped sample with \(X = 0.0025\). However, these samples with \(X = 0.01\) and 0.025 of Gadolinium obeyed the Curie-Weiss law at high temperature and did not show the non-conventional temperature behavior that was observed in both the parent compound \(\text{Cr}_2\text{AlC}\) and \((\text{Cr}_{0.9975}\text{Gd}_{0.0025})_2\text{AlC}\).

At high temperature \((170 \text{ K} < T < 300 \text{ K})\), inverse susceptibility data was fitted to the Curie-Weiss law \((\chi = C/(T - \theta))\). The same method as for the \(X = 0.0025\) sample was used to calculate the effective magnetic moment. From the fit, we obtained the Curie constant \(C = 0.71 \pm 0.01\) emu.K/mole.Oe and the Curie-Weiss temperature \(\theta = -559 \pm 12\) K, giving an effective moment \(\mu_{eff} = 1.69 \pm 0.03\).
Figure 3.17: (a) Magnetic susceptibility of \((\text{Cr}_{0.975}\text{Gd}_{0.025})_2\text{AlC}\) in a magnetic field of 5000 Oe. The black arrows indicate the magnetic transitions. (b) Reciprocal magnetic susceptibility of \((\text{Cr}_{0.975}\text{Gd}_{0.025})_2\text{AlC}\). The solid green line in the inset represents a fit to a Curie-Weiss law, and the negative Curie Weiss temperature is indicated by the black arrow.
Figure 3.18: a) Magnetic susceptibility of (Cr$_{0.95}$Gd$_{0.05}$)$_2$AlC in a magnetic field of 5000 Oe. The black arrows indicate the magnetic transitions. (b) Reciprocal magnetic susceptibility of (Cr$_{0.95}$Gd$_{0.05}$)$_2$AlC. The solid green line represents a fit to a Curie-Weiss law, and the positive Curie-Weiss temperature is indicated by the black arrow.
for \((\text{Cr}_{0.99}\text{Gd}_{0.01})_2\text{AlC}\). For \((\text{Cr}_{0.975}\text{Gd}_{0.025})_2\text{AlC}\), we obtained the Curie constant \(C = 0.51 \pm 0.01\) emu.K/mole.Oe and the Curie-Weiss temperature \(\theta = -98 \pm 3\) K, giving an effect moment \(\mu_{\text{eff}} = 1.42 \pm 0.02\) \(\mu_B\). The transition at 6 K might be related to the second phase that is observed by the X-ray diffraction, which is \(\text{GdCr}_{3.5}\text{Al}_{8.5}\) with antiferromagnetic ordering at \(T_N = 6.75\) K [33]. The transition at 70 K could be related to the same transition we had in the parent compound \(\text{Cr}_2\text{AlC}\) that might occur due to AFM canting. Additionally, the transition at 170 K might be related to \(\text{GdAl}_2\) with \(T_c\) between 165 and 170K [34, 35]. Therefore, these two samples might also undergo an antiferromagnetic phase transition, hence the negative Curie-Weiss temperature \(\theta\).

Figure 3.15 (b) shows the magnetization as a function of field for \((\text{Cr}_{0.99}\text{Gd}_{0.01})_2\text{AlC}\). In the graph, the M-H curve does not show any saturation which indicates antiferromagnetic behavior, but the sample has a small hysteresis which indicates the existence of weak ferromagnetism. Figure 3.15 (c) shows the magnetization (M-H) curve for \((\text{Cr}_{0.975}\text{Gd}_{0.025})_2\text{Al}\). The curve shows a non-linear behaviour with small hysteresis that indicates the sample has a small amount of ferromagnetism. Therefore, these samples \((\text{Cr}_{1-x}\text{Gd}_x)_2\text{AlC}\) (\(X = 0.01, 0.025\)) are complex and might have a FM interaction as well as the parent compound and the sample with \(X = 0.0025\).

Figures 3.18 (a) and (b) show the dc-susceptibility \(\chi(T)\) and inverse magnetic dc-susceptibility \(1/\chi(T)\) versus temperature of \((\text{Cr}_{0.95}\text{Gd}_{0.05})_2\text{AlC}\) with an applied magnetic field of 5000 Oe respectively. As seen in the figure, the dc-susceptibility in this Gd-substituted sample with \(X = 0.05\) indicates transitions at 70 K and 170 K as in the other doped samples. However, in this sample we did not observe any transition at 6 K as for the other doped samples. The transition at 70 K might occur due to the canting of AFM moments, which can be seen as a slight sudden increase in the magnetic susceptibility between 70 K and 170 K (Figure 3.18(a)). The transition at 170 K is assumed to be related to \(\text{GdAl}_2\) which is ferromagnetic with \(T_c\) between 165 - 171 K [34, 35]. At high temperature (170 K < \(T < 300\) K), the inverse susceptibility data is fitted using a Curie-Weiss law \((\chi = C/(T - \theta))\). The same method as for the \(X = 0.0025\) sample was used in order to calculate the effective magnetic moment.
Figure 3.19: Magnetization as a function of magnetic field, $M(H)$ for $(\text{Cr}_{0.95}\text{Gd}_{0.05})_2\text{AlC}$ at four temperatures: 1.7, 30, 140, and 180 K. The inset is zoomed around the origin showing the hysteresis loop at 1.7 K. The black arrows indicate the coercivity ($H_c$) and the remnant magnetization ($M_r$).

From the fitting, we obtained the Curie constant $C = 0.45 \pm 0.01$ emu.K/mole.Oe and the Curie-Weiss temperature $\theta = 116 \pm 3$ K, giving an effective moment $\mu_{eff} = 1.34 \pm 0.02 \mu_B$. The positive Curie Weiss temperature $\theta$ is evidence of a ferromagnetic interaction, so $(\text{Cr}_{0.95}\text{Gd}_{0.05})_2\text{AlC}$ might undergo a ferromagnetic phase transition.

Magnetization isotherms of $(\text{Cr}_{0.95}\text{Gd}_{0.05})_2\text{AlC}$ over a temperature range of 1.7 K to 180 K were recorded after the sample was cooled in zero magnetic field. Figure 3.19 shows the magnetization versus magnetic field of $(\text{Cr}_{0.95}\text{Gd}_{0.05})_2\text{AlC}$ at 1.7, 30, 140, and 180 K. It is clear that the nonlinear behaviour decreases with increasing temperature until it is almost a line at 180 K, above the assumed $T_c$. The largest hysteresis is detected at 1.7 K which is however very small, with the coercivity, $H_c$ and the remnant magnetization, $M_r$ of around 29.5 Oe and 46 emu/mole, respectively. This small hysteresis shows that the sample magnetic ordering may be more complex than a simple FM structure and that
Figure 3.20: The zero field cooled magnetization as a function of temperature of $(\text{Cr}_{1-x}\text{Gd}_x)\text{AlC}$ ($X=0$, 0.0025, 0.01, 0.025, 0.05) under an applied field of $H=5000\text{Oe}$. The inset shows an enlarged view of the results in the range 1.7 K to 200 K for all samples to show clearly that the magnetization increases with increasing the amount of Gd concentration.
Figure 3.21: The magnetization as a function of the magnetic field, $M(H)$ for $(Cr_{1-x}Gd_x)_2AlC$ ($X = 0, 0.0025, 0.01, 0.025, 0.05$) at $1.7$ K. The inset shows an enlarged view of the result in the range $0$ Oe to $4000$ Oe to show clearly the increasing of magnetization with increase of the amount of Gadolinium concentration.
an AFM interaction could exist as in other doped samples. However, in this compound with the highest amount of Gadolinium (X = 0.05), the ferromagnetic order might dominate, which is not the same as for the other doped samples that were assumed to be dominated by antiferromagnetic order.

The magnetization behavior in these doped samples is complex, but it is clear that all of them have been affected by secondary phases and that the magnetization increases with increasing the concentration of Gadolinium. The temperature dependence of the zero-field cooled magnetization of (Cr\(_{1-x}\)Gd\(_x\))\(_2\)AlC (X = 0, 0.0025, 0.01, 0.025, 0.05) in 5000Oe is given in Figure 3.20. As shown in the graph, as the Gd concentration increases, the magnetization of the samples increases. Gd and Cr are respectively ferromagnetic and antiferromagnetic. Therefore, with increasing the concentration of Gd, we expect ferromagnetic ordering to gradually increase and replace the antiferromagnetic ordering.

Magnetization versus magnetic field for (X = 0, 0.0025, 0.01, 0.025, 0.05) at 1.7 K is shown in Figure 3.21. The figure inset shows clearly that with increasing Gadolinium the magnetization increases as the Gd atom brings an additional magnetic moment to the MAX Phase. Figure 3.15 shows that the FM interaction also increases with increasing Gd concentration as the area of the hysteresis expands upon substituting more Gadolinium.

All of the Gd-substituted compounds except the sample with X = 0.0025 of Gd obey Curie-Weiss law at high temperatures. At high temperature (170 K < T < 300 K), the data is fitted using the Curie-Weiss law (\(\chi = C/(T - \theta)\)). The fitting parameters: effective magnetic moment (\(\mu_{\text{eff}}\)), Curie Weiss temperature (\(\theta\)), and Curie constant (\(C\)) are summarized in Table 3.1. The experimental values for the effective magnetic moment \(\mu_{\text{eff}}\) are smaller than the theoretical value of \(\mu_{\text{eff}} = \sqrt{((1 - x)\mu_{Cr^{3+}})^2 + ((x)\mu_{Gd^{3+}})^2} = 3.83\ \mu_B, 3.78\ \mu_B,\) and 3.70\ \mu_B\ for X = 0.01, 0.025, and 0.05 respectively, where \(\mu_{Cr^{3+}} = 3.87\ \mu_B\) and \(\mu_{Gd^{3+}} = 7.94\ \mu_B\). This reduction in the value of \(\mu_{\text{eff}}\) might be due to the Kondo effect [36]. A signature of the Kondo effect is observed in the low temperature resistivity of (Cr\(_{1-x}\)Gd\(_x\))\(_2\)AlC (X = 0.0025, 0.01, 0.025) which will be discussed in chapter four in this thesis.
Table 3.1: Listing of parameters obtained experimentally in the paramagnetic region above all transitions from the susceptibility data for (Cr$_{1-x}$Gd$_x$)$_2$AlC ($x = 0, 0.0025, 0.01, 0.025, 0.05$). The effective moment was calculated from equation (3.5) with $n = 2$.

The magnetic results of (Cr$_{1-x}$Gd$_x$)$_2$AlC ($x = 0, 0.0025, 0.01, 0.025, 0.05$) are complex. Further understanding of the magnetism in these materials could be possible by studying neutron diffraction and knowing the exact nature of the competing ferromagnetic and antiferromagnetic interactions. This is a recommendation for a future study.

### 3.3.3 Magnetic Results of Er$_3$AlC

The ZFC and FC susceptibilities versus temperature of Er$_3$AlC with an applied magnetic field of 24600 Oe are shown in Figure 3.22. With the temperature increasing from 1.7 K, the susceptibility $\chi$ increases to a maximum value which is about 2.8 emu/mole.Oe at 2.5 K. Then, the value of $\chi$ decreases with increasing temperature above 2.5 K. The temperature dependence of the inverse magnetic susceptibility $1/\chi(T)$ is shown in Figure 3.23. By fitting the inverse susceptibility data to the Curie-Weiss law ($\chi = C/(T - \theta)$) for temperature between 100 K to 300 K, the following parameters were found: the Curie constant $C$ is $31 \pm 0.02$ emu.K/mole.Oe giving the effective moment $\mu_{e,f} = 9.05 \pm 0.01 \mu_B$, and the Curie-Weiss temperature $\theta$ is $-4 \pm 0.2$ K. The small negative Curie-Weiss temperature $\theta$ is evidence of an antiferromagnetic interaction, so Er$_3$AlC undergoes an antiferromagnetic phase transition at the Néel temperature $T_N = 2.5$ K. Our value of $T_N$ is close to 3.1 K which was reported in Ref [19] and Ref [37]. The value of the $\mu_{e,f}$ is $9.1 \mu_B$, which is 5% lower than the theoretical value for Er$^{3+}$ ion (9.58 $\mu_B$). This indicates that the crystalline fields might be weak in this compound and do not noticeably
Figure 3.22: Magnetic susceptibility of $\text{Er}_3\text{AlC}$ in a magnetic field of 24600 Oe. The blue and red lines represent the ZFC and FC curves, respectively. The inset shows the result below 5 K, and the arrow indicates the magnetic transition at 2.5K.

affect the orbital contribution to the moment [22]. The fitting parameters: effective magnetic moment ($\mu_{\text{eff}}$), Curie-Weiss temperature ($\theta$), and Curie constant ($C$) for $\text{Er}_3\text{AlC}$ are tabulated in Table 3.2.

The ZFC and FC susceptibilities versus temperature of $\text{Er}_3\text{AlC}$ with an applied magnetic field of 100 Oe show an interesting magnetization behavior (see Figure 3.24). The ZFC-FC behaviour separates around 55 K which is likely due to a weak ferromagnetic (FM) short-range ordering from the secondary phases $\text{ErAl}_2$ and $\text{ErC}_{0.6}$. According to the X-ray results, there are two extra phases in the $\text{Er}_3\text{AlC}$ sample. The first one is $\text{ErAl}_2$ which has FM order with $T_c = 14$ K [22]. The second is $\text{ErC}_{0.6}$, with ferromagnetic ordering at $T_c = 90$ K [38]. The ZFC magnetic susceptibility is lower than that of the FC due to the absence of magnetic field during cooling that causes lower ordering. Figure 3.24 clearly shows transitions at 3.1 K and 14 K. The lower one at 3.1 K is close to $T_N = 2.5$ K obtained from the dc-susceptibility in a magnetic field of 24600 Oe, but it is slightly shifted downward at higher field
Figure 3.23: Inverse susceptibility vs temperature for Er$_3$AlC. The solid red line represents a fit of a Curie-Weiss law. Inset shows an enlarged view of the graph to show the negative Curie-Weiss temperature which is indicated by the black arrow.
Figure 3.24: Magnetic susceptibility of $\text{Er}_3\text{AlC}$ in a magnetic field of 100 Oe. The blue and red lines represent the ZFC and FC, respectively. The inset shows the magnetic susceptibility behavior at low temperature. Black arrows indicate magnetic transitions.

as high fields commonly affect the magnetic transition. The transition at 14 K might be caused by the secondary phase that is identified by X-ray diffraction, which is $\text{ErAl}_2$. Therefore, the secondary phase might affect the magnetization properties of $\text{Er}_3\text{AlC}$, and there is a small ferromagnetic ordering in the sample.

The magnetization isotherms of $\text{Er}_3\text{AlC}$ at temperatures between 1.7 and 60 K were recorded after the sample was cooled in the zero magnetic field. Figure 3.25 shows the magnetization versus

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\mu_{\text{eff}}(\mu_B)$</th>
<th>$C$ (emu.K/mole.Oe)</th>
<th>$\theta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Er}_3\text{AlC}$</td>
<td>$9.05 \pm 0.01$</td>
<td>$31 \pm 0.02$</td>
<td>$-4 \pm 0.2$</td>
</tr>
</tbody>
</table>

Table 3.2: Effective magnetic moment ($\mu_{\text{eff}}$), Curie-Weiss temperature ($\theta$), and Curie constant ($C$) for $\text{Er}_3\text{AlC}$ that are determined experimentally in the paramagnetic region from the susceptibility data. The effective moment was calculated from equation (3.5) with $n = 2$. 

56
magnetic field of Er$_3$AlC at 1.7, 10, 20, and 60 K. The magnetization (M-H) curve for Er$_3$AlC at the lowest temperature (1.7 K) which is below $T_N$ is non-linear. The non-linearity decreases with increasing the temperature to 10 and 20 K but is still discernible. However, at 60 K the M-H curve becomes linear as expected for a paramagnet.

The magnetization (M-H) curve for Er$_3$AlC at 1.7 K (below first transition $T_N$) has a non-linear behavior and a small hysteresis as indicated in the inset (Figure 3.26). The hysteresis indicates the existence of weak ferromagnetism with the coercivity $H_c$ and the remnant magnetization, $M_r$ of around 100 Oe and 1047 emu/mole, respectively. Figure 3.26 shows both FM and AFM components of Er$_3$AlC at 1.7 K. To determine the FM component of the sample, a linear fit is done to the total magnetization (black curve) at high field which will give the paramagnetic contribution. By subtracting this linear contribution from the total data, we leave the FM curve and determine the saturation magnetization above 25 kOe which is close to $10 \mu_B/f.u.$

Figure 3.27 shows the magnetization as a function of magnetic field at 10 K (below the second transition) which shows a magnetic hysteresis, indicating the existence of weak ferromagnetism with the coercivity $H_c$ and the remnant magnetization, $M_r$ of around 60 Oe and 199 emu/mole, respectively. The area enclosed by the hysteresis is less than that at 1.7 K. It is clear that the isothermal M-H curves support the conjecture that the secondary phases we have detected by the X-ray diffraction might affect the magnetic properties of Er$_3$AlC. Therefore, there is a small ferromagnetic ordering due to the magnetic ordering of impurities in the sample.
Figure 3.25: The magnetization as function of magnetic field for Er$_3$AlC at four temperatures between 1.7 K and 60 K. The magnetization in all magnetic fields decreases with increasing the temperature. The non-linearity also decreases with increasing the temperature.
Figure 3.26: Magnetization versus magnetic field for Er$_3$AlC at 1.7 K (blue curve). The black curve shows the magnetization curve at 1.7 K extracted by subtraction of the linear (PM) contribution. The inset zoom around the origin shows the hysteresis loop. The black arrows indicate the coercivity ($H_c$) and the remnant magnetization ($M_r$).
Figure 3.27: Magnetization versus magnetic field for Er$_3$AlC at 10 K. The inset zoom around the origin shows the hysteresis loop. The black arrows indicate the coercivity ($H_c$) and the remnant magnetization ($M_r$).
4.1 Electrical Resistivity

The electrical resistivity characterizes the nature of electron-electron and electron-phonon interactions as well as changes in symmetry due to a structural phase transition [40]. By measuring temperature dependence of the electrical resistivity and analyzing the data, the difference between metals, insulators, and semiconductors is revealed. Some other properties of a material such as its energy gap ($E_g$) if applicable can be extracted by analyzing the resistivity data. Materials can be classified into three groups depending on their energy band structure: conductor, insulator, and semiconductor [40].

4.1.1 Metals

In metals, the conduction electrons are freely separated from their parent atoms and move through the lattice. The ability of the electrons to travel freely through the material, which is called conductivity, is reflected in its electrical resistivity. Resistivity which is the inverse of the conductivity...
is the ability to oppose the flow of electric current. The resistivity of a metal increases with increasing
the temperature. As the temperature increases the lattice vibrations which scatter moving electrons
increase and thus the resistivity also increases. The quantum lattice vibration is called a phonon, and
the number of phonons is not a fixed value [41]. The average number of phonons in a given mode is
given by the Bose-Einstein distribution:

\[
<n> = \frac{1}{\exp(h\omega/K_B T) - 1}
\]  \hspace{1cm} (4.1)

where \( \omega, K_B \), and \( h \) are the frequency of phonons, the Boltzmann constant, and the Plank’s constant,
respectively [25]. In the Debye model, the density of these modes is given by

\[
D(\omega) = \frac{V \omega^2}{2\pi^2 \nu^3}
\]  \hspace{1cm} (4.2)

where \( V, \omega, \) and \( \nu \) are the volume of the solid, the angular frequency, and the velocity of sound in the
material, respectively [25]. The total average number of phonons in the lattice is given by:

\[
<n_{total}> = \int D(\omega) <n> d\omega
\]  \hspace{1cm} (4.3)

For a unit volume

\[
<n_{total}> = \frac{3}{2\pi^2 \nu^3} \int_0^{\omega_D} \frac{\omega^2}{\exp(h\omega/K_B T) - 1} d\omega
\]  \hspace{1cm} (4.4)

where the factor 3 here is because there are three acoustic phonon branches ( 1 longitudinal and 2
transverse), and \( \omega_D \) is the maximum mode frequency that can be supported by the solid, and can be
expressed in term of Debye temperature ($\theta_D$) [25, 41]:

$$\hbar \omega_D = K_B \theta_D$$  \hspace{1cm} (4.5)

At very low temperature ($T \ll \theta_D$), $<n_{\text{total}}> \text{ goes as } T^3$, while at high temperature ($T \gg \theta_D$), $<n_{\text{total}}>$ goes linearly with $T$. As more vibrations make it harder for electrons to travel through a solid, the resistivity is proportional to $<n_{\text{total}}>$ [25, 41].

4.2 Magnetoresistance (MR)

Magnetoresistance refers to the change in resistance of a material under an applied magnetic field. The magnetoresistance ratio (MR) is the ratio of the change in resistance under the influence of an applied field to the resistance at zero field:

$$MR = \frac{R(H) - R(0)}{R(0)}$$

$$\quad = \frac{\Delta R}{R}$$  \hspace{1cm} (4.6)

Therefore, the MR effect can be negative or positive. If the material has a larger resistance in the presence of a magnetic field than in the absence of the field, the material is defined to have a positive magnetoresistance. On the another hand, the magnetoresistance is negative when the field reduces the resistivity. The phenomenon of magnetoresistance has been useful in many applications such as magnetic sensors, magnetic memories, and the read component in magnetic recording heads [23].
4.3 Experimental Procedure

The Quantum Design Physical Properties Measurements System (PPMS) was used to measure the AC electrical resistivity and magnetoresistance (MR), by using the AC Transport (ACT) option. The AC Transport option can be used to make four types of electrical current measurements: resistivity, Hall Coefficient, I-V curve, and electrical current. The AC Transport option carries out measurements using four or five contacts points on up to two channels at one time. The standard ACT puck contains five pads (I+, I-, VA+, VB+, and V-) on both channels (see Figure 4.1). The precision current source has a resolution of 0.02 μA and a maximum current of 2 A. The ACT option can supply an AC bias current from 1 Hz up to 1 kHz. The ACT option supports four-terminal alternating current resistivity measurements [42]. When the four-terminal method is used, the current is supplied via a pair of current leads. These generate a voltage drop as the current passes through the sample if the sample has any resistance to the electrical current (see Figure 4.2). The voltmeter has a very high impedance, so almost no current flows to the measuring instrument. Therefore, the current through the sample and the potential drop across the sample can be measured accurately. The effect of the leads and contact resistance can be virtually eliminated. Ohm’s law is used to calculate the sample resistance:

$$R = \frac{V}{I}$$  \hspace{1cm} (4.7)

where I is the current through the sample, and V is the measured potential drop across the voltage contacts. Knowing the dimensions of the sample, the resistivity ($\rho$) is calculated by this equation:

$$\rho = \frac{R \cdot A}{l}$$  \hspace{1cm} (4.8)

where $A$ is the cross-sectional area through which the current passes, and $l$ is the voltage lead sepa-
ration [42]. In this research, the resistivity measurements were done with rectangular shaped samples. To mount the sample on the standard ACT puck, the sample was placed near the center of the puck with a piece of Kapton tape, and 0.05 mm thick gold wires were used to connect the sample contacts to the desired channel input pads. All wires were attached to the sample using 16031 Colloidal Silver paint, and connected to the channel input pads by soldered gold wires. All of these connections were made under the microscope.

4.4 Resistivity Results of Cr$_2$AlC

The temperature dependence of the electrical resistivity for Cr$_2$AlC without magnetic field and with an applied magnetic field of 40kOe are shown in Figure 4.3. Starting from room temperature, the resistivity decreases with decreasing temperature showing metallic behavior which is a regular characteristic of all MAX phases due to the high density of states at the Fermi level of these compounds [44]. The resistivity of Cr$_2$AlC under 40kOe magnetic field shows the same trend with the increase of temperature. In order to investigate the magnetoresistance (MR) effect of the sample at different magnetic
fields, the change in resistance with magnetic field applied at 2.2 K is measured and plotted in Figure 4.4. MR values are calculated using equation 4.6. From the curve, we observe that the sample Cr$_2$AlC has a positive MR effect, reaching a value at 2.2 K of about 5% at 90kOe, the highest field investigated.

4.5 Resistivity Results of (Cr$_{1-x}$Gd$_x$)$_2$AlC (X=0.0025, 0.01, 0.025)

Figure 4.5 shows the electrical resistivity versus temperature with no magnetic field applied for (Cr$_{1-x}$Gd$_x$)$_2$AlC (x = 0, 0.0025, 0.01, 0.025). We can see from the figure that increasing the percentage of Gd substitution in the samples increases the electrical resistivity.

The temperature dependence of the electrical resistivity for (Cr$_{1-x}$Gd$_x$)$_2$AlC with X = 0.0025, 0.01, 0.025 was analyzed in Figures 4.6 to 4.8 respectively. The higher temperature electrical resistivity $\rho$ of these Gd-substituted samples (Figures from 4.6 to 4.8), suggests a metallic characteristic for the electrical resistivity, but below around 150 K, 100 K, and 50 K, respectively, the resistivity begins to increase with decreasing temperature.

The logarithmic temperature dependence of $\rho$ for (Cr$_{1-x}$Gd$_x$)$_2$AlC with X = 0.0025, 0.01, 0.025
Figure 4.3: Resistivity versus Temperature data for Cr$_2$AlC without magnetic field and with applied magnetic field of 40kOe.
can be seen in the $\rho$ vs $\ln T$ curve (Fig 4.6 - inset), (Fig 4.7 - inset), and (Fig 4.8 - inset) respectively. This low temperature behavior of the logarithmic decrease of the resistivity of the substituted samples may be attributed to the Kondo effect [45]. The Kondo behavior is visible from the linear region in Fig 4.6 - inset, Fig 4.7 - inset, and Fig 4.8 - inset for Gd-substituted samples with $X = 0.0025$, 0.01, 0.025 respectively. Kondo effect is an unusual scattering mechanism of the conduction electrons in a metal at low temperatures due to existence of localized magnetic moments on the impurity atoms [25]. Moreover, as seen in Figures 4.6 to 4.8, these Gd-substituted samples have an abrupt change in the slope of the resistivity curve at 258 K, 262 K, and 264 K respectively. Increased Gd doping leads to a shift in the transition peak to a higher value. This may be caused by the presence of pure elemental Gadolinium which has a sharp change in the slope between 291 to 292 K [46]. According to X-ray results, the overall trend of the increasing presence of secondary phases with further Gd doping is clearly observable even though the content of the secondary phases is too small to be determined by the Rietveld refinement.
Figure 4.5: Temperature dependence of the electrical resistivity of the parent compound Cr$_2$AlC and (Cr$_{1-x}$Gd$_x$)$_2$AlC (X = 0.0025, 0.01, 0.025) measured in zero magnetic field. Increasing the percentage of Gd substitution increases the electrical resistivity.
Figure 4.6: Temperature dependence of the resistivity of (Cr$_{0.9975}$Gd$_{0.0025}$)$_2$AlC. Black arrows show transitions at 7 and 258 K. The inset shows resistivity $\rho$ versus $ln(T)$, and the solid red line indicates a fit to a straight line.
Figure 4.7: Temperature dependence of the resistivity of ($\text{Cr}_{0.99}\text{Gd}_{0.01}$)$_2\text{AlC}$. Black arrows show transitions at 7 and 262 K. The inset shows resistivity $\rho$ versus $\ln(T)$, and the solid black line indicates a fit to a straight line.
Figure 4.8: Temperature dependence of the resistivity of $(Cr_{0.9975}Gd_{0.0025})_2AlC$. The black arrow shows the transition at 264 K. The inset shows resistivity $\rho$ versus $ln(T)$, and the solid blue line indicates a fit to a straight line.
However, the magnetic susceptibility does not show any anomaly at this temperature, so this feature might be related to the insulator to metallic transition. Additionally, \((\text{Cr}_{1-x}\text{Gd}_x)_2\text{AlC}\) with \(X = 0.0025\) and \(0.01\) as seen in Figures 4.6 and 4.7 exhibits a change in the slope around 7 K, close to the magnetic transition at 6 K obtained from susceptibility.

### 4.6 Resistivity Results of \(\text{Er}_3\text{AlC}\)

The zero-field resistivity of \(\text{Er}_3\text{AlC}\) increases with increasing temperature, typical of metallic behavior as seen in Figure 4.9. The resistivity exhibits sharp changes in slope around 3.4 K and 15 K (Fig. 4.9-inset), close to the transition temperatures of 14 K and 3.1 K determined by the \(\chi(T)\) curves in a magnetic field of 100 Oe (Figure 3.24). The temperature dependence of the resistivity with and without applying magnetic field are shown in Figure 4.10(a). As shown in this graph, the application of a magnetic field resulted in a large increase in electrical resistivity, and there is a slight downwards curvature above 70 K which usually happens because of the crystal electric field CEF effect [36]. Crystal electrical field is an electric field produced by neighboring atoms in the crystal [47].

The measurement of the temperature dependence of the resistivity with the magnetic field was repeated in order to be sure that the large increase in the resistivity upon application of a magnetic field is real. The repeated measurement result compared with the resistivity without applying a magnetic field is shown in Figure 4.10(b). As shown in this graph, the application of a magnetic field resulted in reducing the electrical resistivity \((\rho)\). This difference of the behavior of the electrical resistivity upon applying a magnetic field between the first and second measurement could be due to a time effect. Because initially the resistivity with field applied increased and then upon repeating it decreased, it suggests that the cause is extrinsic.
Figure 4.9: (a) Temperature dependence of the electrical resistivity of Er$_3$AlC. The inset displays a close-up of the low-temperature data with the magnetic transitions indicated by arrows at 3.4 K and 15 K.
Figure 4.10: (a) The temperature dependence of the resistivity for Er$_3$AIC measured with and without applied magnetic field. This second measurement (b) was done for the same sample that is presented in the first measurement (a), but after two days.
Chapter 5

Conclusion

The arc melting technique was used to prepare the MAX phase Cr$_2$AlC and its Gd-substituted analogs (Cr$_{1-x}$Gd$_x$)$_2$AlC (with X = 0.0025, 0.01, 0.025, 0.05) and Er$_3$AlC compound. Using the Rietveld analysis for XRD data, the content of some secondary phases was determined for each sample. The side phase is Cr$_7$C$_3$ in the parent compound Cr$_2$AlC, and secondary phases of Cr$_7$C$_3$ and GdCr$_{3.5}$Al$_{8.5}$ in the substituted samples. Er$_3$AlC has secondary phases of ErC$_{0.6}$ and ErAl$_2$. The substitution of Gd with Cr has minimal effect on the lattice parameter, and thus we could not conclusively prove the incorporation of Gd into Cr$_2$AlC by XRD. In the study of the magnetic properties, Er$_3$AlC exhibited an antiferromagnetic phase transition at the Néel temperature $T_N = 2.5$ K. However, Er$_3$AlC also showed ferromagnetic behaviour at low temperature and that was concluded to be associated with the presence of ferromagnetic secondary phases. Cr$_2$AlC shows non-conventional behaviour above 70 K which does not obey the Curie-Weiss law. This unusual behaviour might be attributed to the canting of antiferromagnet sublattices. Cr$_2$AlC might have a transition above 400 K. (Cr$_{1-x}$Gd$_x$)$_2$AlC (with X = 0.0025, 0.01, 0.025, 0.05) obeys the Curie-Weiss law except for the sample with X = 0.0025. The effective magnetic moments for all of the samples decrease with increasing value of X, ranging from $1.96 \pm 0.03 \mu_B$ for X = 0.01 to $1.34 \pm 0.02 \mu_B$ for X = 0.05. The experimental values of the effective magnetic moment are
smaller than the total theoretical calculated value for Gd\(^{3+}\) and Cr\(^{3+}\) ions. This reduction could be due to the Kondo effect that is observed in the resistivity data of the substituted samples as well. \(\text{Cr}_2\text{AlC}\) and the Gd-substituted samples have complex magnetic behaviour and may exhibited co-existence of ferromagnetic and antiferromagnetic order. The magnetization increases with increasing Gadolinium concentration because Gadolinium atoms introduce more magnetic moment to the MAX phase. Furthermore, the resistivity data shows that \(\text{Cr}_2\text{AlC}\) and \(\text{Er}_3\text{AlC}\) have metallic behaviour. The resistivity results of the Gd-substituted samples exhibit signatures of Kondo behaviour.

The results presented in this work make a valuable contribution to our understanding of these materials, but further work to investigate other physical properties of these compounds should be conducted. EPMA (Electron probe micro-analysis) is one of the recommended studies in order to prove the incorporation of Gd into the MAX phase. High temperature magnetic measurements for \(\text{Cr}_2\text{AlC}\) is also a recommended study because it will help to know the magnetic order and the exact transition temperature for this compound. Neutron diffraction measurements are another suggested study because they will help to establish the exact nature of the co-existence of ferromagnetic and antiferromagnetic order in \((\text{Cr}_{1-x}\text{Gd}_x)_2\text{AlC}\) (with \(X = 0, 0.0025, 0.01, 0.025, 0.05\)).
Bibliography


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