Synthesis and characterization of
AlM_2B_2 (M = Cr, Mn, Fe, Co, Ni)

Maxime Dottor
Abstract

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In this thesis the compounds AlM₂B₂ (M = Cr, Mn, Fe, Co, Ni) have been synthesized via arc melting, a high temperature synthesis technique. The structure for AlCr₂B₂, AlMn₂B₂ and AlFe₂B₂ are of AlFe₂B₂-type with the space group of Cmmm. The cell volumes were refined to be 96.40 Å³, 93.93 Å³ and 92.86 Å³ for AlCr₂B₂, AlMn₂B₂ and AlFe₂B₂ respectively. AlCo₂B₂ and AlNi₂B₂ are found to be metastable. AlCr₂B₂ and AlMn₂B₂ do not exhibit magnetic transition near room temperature.
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1 Introduction

Magnetism, the property of a magnet to influence other materials by attract or repulse them, is a phenomenon known for 2500 years through a mineral called magnetite, Fe₃O₄ [1-2]. Hundred years later, the mariner’s compass was created using magnetite, however, the magnetite needs a certain shape in order to float on water. The magnetite will rotate itself to point to north and south when the iron oxide floats on the water due to the earth magnetic field. This material was called lodestone in ancient English and means “guiding stone” in recent English.

Until the second half of the twentieth century, no important magnetic materials were discovered [3]. However, the study of magnetism was never interrupted due to numerous scientists such as Descartes, who showed that magnetism is a physical phenomenon and not metaphysical, Oersted and Ampère showed that electricity and magnetism are connected, and finally with Maxwell’s equations which linked electricity, magnetism and light [2].

The Magnetocaloric effect, MCE, were discovered in 1881 by Warburg [5]. A few decades later, Debye in 1926 [6] and Giauque in 1927 [7] independently showed the nature of MCE and its experimental use in cooling to low temperatures (few Kelvin) via an adiabatic demagnetization.

During the 1960s, where the first rare-earth elements started to be alloyed, the development of magnetic materials began to be important with for example, the synthesis of SmCo₅ [3]. This development led to the manufacturing of neodymium iron boride, Nd₂Fe₁₄B, which is the strongest magnetic material and the most used [4]. Permanent magnets is the application of these neo-magnets.

In these past decades, our society has changed into more energy aware. The compound Gd₅(Si₂Ge₂) in which the giant magnetocaloric effect were discovered 1997 [8]. This discovery had an impact on the utilization of magnetic materials in magnetic refrigeration, because this compound allows more cooling power for magnetic refrigeration. Even if Gd₅(Si₂Ge₂) has very good properties, especially near room temperature for magnetic refrigeration, this alloy has its weak points. The main weak point is the presence of gadolinium in this alloy. The mining to recuperate this element drag isotopes of uranium and thorium away with it [9]. Uranium is known to create damage on the environment, creation of mining pits, and release toxic substances during the extraction. Furthermore, the prize of rare-earth elements, such as gadolinium in this case, is expensive compared to non-rare-earth elements.

The study of non-rare earth elements have become essential in order to reduce environmental impact and economic issues. It is for this reason that all the alloys prepared with this thesis do not contain rare earth elements. Earlier study of AlFe₂B₂ [10-12], the crystal structure of AlFe₂B₂ is shown in figure 1, has shown that this compound is ferromagnetic and with a transition temperature near room temperature, which is necessary to have for a good magnetic refrigerant. Transition temperature is the temperature at which an abrupt change of properties appears such as a change of crystalline or phase structure. Earlier study of AlM₂B₂ (M=Cr, Mn) [13] did not show ferromagnetic properties. By this, the study of AlM₂B₂ (M= Cr, Mn, Fe, Co, Ni) becomes interesting.

![Figure 1. Crystal structure of AlFe₂B₂. Colour Scheme: Al: grey, Fe: red and B: blue [11].](image-url)
2 Theory

Magnetism resides in the random spin motions of unpaired electrons in d or more rarely in f-orbitals. The spin phenomenon called ferromagnetism is the most important for permanent magnets, because the magnetic properties of the material are given by ferromagnetism. Furthermore, other types of magnetism exist, such as antiferromagnetism or ferrimagnetism, shown in figure 2. The magnetic moments align themselves antiparallel to the neighboring moment for antiferromagnetism and neighboring magnetic moments of atoms or molecules align themselves in the opposite direction with different magnetic moments below \( T_C \) for ferrimagnetism. In a ferromagnetic material, the spins of the unpaired electrons are oriented in different ways according to the temperature. First, at high temperature scale, the spins of the electrons are randomly oriented in the material which is called paramagnetic region. Then a transition occurs at the Curie temperature, when the material is cooled down, and this leads to a transition to a ferromagnetic state because, when the temperature is decreased the magnetization is increased. Secondly, the spins of the electrons are oriented in the same direction due to this change. Consequently, a ferromagnetic material will lose its magnetization if the material is heated above its Curie temperature [2, 3, and 14].

![Figure 2. Schema of different types of magnetism.](image1.png)

For a permanent magnet to work the temperature needs to be below \( T_C \). However, \( T_C \) is not the only important property for its application. The magnetization, \( M \), of a ferromagnet is not proportional to the applied magnetic field, \( H \). In its place, the hysteresis loop of a ferromagnet, an \( M \) (\( H \)) curve, found in figure 3 shows the other properties a permanent magnet need to have. Figure 3 shows the magnetization in the compound, \( M \), as a function of the applied magnetic field, \( H \). The saturation magnetization, \( M_s \), is the first point which is interesting, this point is found by applying a magnetic field and corresponds to the maximum of magnetization of the decreased material. The magnetic field is then reduced and this decreased the magnetization. When the magnetic field is equal to zero during the decrease, the magnetization reaches a point called remanent magnetization, \( M_r \), which is the ability of a material to preserve magnetization. After that, the field is increased in the negative direction, a new point is reached where the magnetization equals to zero. \( H_C \) is the ability of a material to withstand an external magnetic field without becoming demagnetized. Negative further decrease of field results to another saturation, negative in this case. These three values \( M_s \), \( M_r \), and \( H_C \) are properties of the material.

![Figure 3. Hysteresis loop of a hard ferromagnet [14].](image2.png)

The magnetocaloric effect, MCE, is the reversible temperature change of a magnetic material as the result of the application or removal of a magnetic field [15]. Two parameters are used to quantify the MCE: \( \Delta S \), entropy change per mass unit, which is a measurement of its disorder and \( \Delta T_{ad} \), temperature change of the material during an adiabatic magnetization or demagnetization. The thermodynamics of the MCE for a ferromagnet near
its Curie temperature, $T_C$ (the magnetic ordering temperature for a magnet) is illustrated in figure 4. An optimal material needs to show large $\Delta S$ and $\Delta T_{ad}$, in combination with s small hysteresis.

Figure 4. The S-T diagram. The solid lines show the total entropy in two different magnetic fields: $H_0$ is zero magnetic field and $H_1$ is a non-zero magnetic field. The horizontal arrow shows $\Delta T_{ad}$ and the vertical arrow shows $\Delta S_M$ when the magnetic field is changed from $H_0$ to $H_1$. The dashed lines show the magnetic entropy in the two fields. $S_0$ are zero field entropy and temperature, $S_1$ and $\Delta T_1$ are entropy and temperature at an elevated magnetic field $H_1$ [16].

Figure 5 shows the refrigeration cycle of a magnetocaloric system. The magnetic moments are randomly oriented (1). Then when a magnetic field is applied, the magnetic moments orient parallel to that field, which decreases the magnetic entropy, and thus increases the temperature of the material, this process is an adiabatic magnetization and this is an exothermic reaction (2). A heat transfer, such as water, air or helium, is used to remove the heat (3) from the material. Afterwards, an adiabatic demagnetization process occurs, when the magnetic field is removed, the magnetic moments will disorder which increases the magnetic entropy of the compound, therefore the temperature decreases below the initial temperature because the disorder requires energy, this is an endothermic reaction (4). This final step is to use the heat transfer fluid through the material in order to cool the contents of the refrigerator.

Figure 5. Magnetic refrigeration cycle. The arrows represent the magnetic moment. The red, green and blue represent temperature above room temperature, room temperature and below room temperature respectively [17].

3 Aim

The aim of this thesis is to synthesize and examine the effect of substituting chromium, manganese, cobalt and nickel on the iron site in the ferromagnetic compound $\text{AlFe}_2\text{B}_2$. By using X-Ray diffraction and SQUID,
Superconducting Quantum Interference Device the crystal structure and magnetic properties of these alloys were examined. The plan of this thesis can be found in figure 6.

![Diagram](image)

**Figure 6.** Template (or work flow chart) followed for this thesis.

### 4 Experimental

#### 4.1 Synthesis

In this thesis four different alloys, $\text{AlM}_2\text{B}_2$ ($\text{M} = \text{Mn, Fe, Co, Ni}$), were prepared in two steps. Firstly, stoichiometric amounts of manganese (Institute of Physics, Polish Academy of Sciences, purity 99.999 %), iron (Leico Industries, purity 99.995 %), cobalt (Johnson Matthey, purity 99.999 %), nickel (ESPI Metals, purity 99.995 %), boron (Wacker Chemie, purity 99.995 %) were mixed to form master alloys of MnB, FeB, CoB and NiB. Secondly the final compounds were synthesized from stoichiometric amount of the master alloys and aluminum (Gränges SM, purity 99.999 %), however, extra aluminum of 50 % was used to obtain the ternary phase and to minimize the content of byproduct according to paper [10, 11 and 13]. The additional phases were etched away in diluted HCl (1:1) (Hydrochloric acid 35 %, Technical, CAS: 7647.01.09). However, one alloy $\text{AlCr}_2\text{B}_2$ was prepared, at the end, in two steps, arc melting with a stoichiometric amount of aluminum, boron and chromium (Alfa Caesar, purity 99.995 %) and annealing after, because some blacks traces appeared during the synthesis of the others. Arc melting was used as a high temperature synthesis technique to get the final alloys. The final alloys were crushed, milled and pressed into pellets; these pellets were put into the silica ampoules, which were washed in aqua regia and were evacuated for 30 minutes and then closed off. These silica tubes were annealed for 14 days at 900°C in a pit furnace. After the heat treatment, the ampoule was quenched in cold water. A quick cooling is performed in order to keep the phase formed at 900°C [18-22].

#### 4.1.1 Arc melting
Figure 7. (a) The actual arc furnace used to synthesize all of the alloys. (b) The schematic view of the arc furnace used.

The arc furnace, figure 7, used in this thesis was equipped with a tungsten cathode and a water cooled copper plate in where both sample and a titanium getter is placed. The melting was done under argon atmosphere. A titanium getter was melted prior to the samples to remove possible oxygen residuals, afterwards the samples were melted.

The master alloys containing a stoichiometric amount of manganese, iron, nickel, cobalt and boron were synthesized using the arc furnace. The samples were melted and remelted five times to ensure homogeneity. The final alloys AlM₂B₂ (M=Mn, Fe, Co, Ni) were obtained with stoichiometric amounts of the master alloys and aluminum. The alloy, AlCr₂B₂, was prepared in one step. Moreover, two other compounds, AlCo₂B₂ and AlNi₂B₂, were arc melted one time with stoichiometric amounts of aluminum, boron, cobalt and nickel respectively.

4.2 Characterization

During this thesis two types of properties were studied, the structural properties and the magnetic properties.

4.2.1 X-Ray Diffraction

X-Ray diffraction, XRD, is a technique used for the characterization of the crystal structure. The X-rays are sent to the sample, where they scattered off the surface of a sample, some of them will give diffracted X-Rays at certain angles and this will give a pattern with certain intensity at certain angles. Each crystal structure will generate peaks at certain angles due to scattered X-rays. This phenomena is described by Bragg’s law

\[ n \lambda = 2d_{\text{hl}} \sin \theta \]

where \( n \) is an integer, \( \lambda \) is the wavelength of the radiation, \( d_{\text{hl}} \) is the distance between two adjacent parallel lattice planes and \( \theta \) is the diffraction angle, see in figure 8.

The setup used for this project was a Bruker D8 diffractometer equipped with a LynxEye XE position sensitive detector 4° opening using CuKα- radiation (\( \lambda = 1.54056 \) Å). The samples were grinded and suspended in ethanol before being applied to a sample holder. Diffraction data were collected for \( 2\theta = 10-90^\circ \).

The software DiffracPLUS Eva was used to identify the phases of the samples. The intensity of the peaks is compared at different angles with a database to know the composition of the sample. Unit cell parameters a, b and c and the corresponding volume were refined using the software Checkcell [23].
4.2.2 SQUID, Superconducting QUantum Interference Device

A Superconducting QUantum Interference Device (SQUID) magnetometer was used to determine the magnetization of the alloys.

In this thesis, the setup used to determine the magnetic moment was performed through a Quantum Design MPMSXL 5T SQUID magnetometer. The magnetization has been studied as a function of temperature and a function of magnetic field. The study of the magnetization as a function of temperature is performed at a constant magnetic field. In return, the study of the magnetization as a function of applied magnetic field is performed at a constant temperature.

5 Results

5.1 X-Ray Diffraction

In this section, the five alloys will be divided into two groups: AlM$_2$B$_2$ (M = Cr, Mn and Fe) and AlM$_2$B$_2$ (M = Co and Ni) because Al$_2$B$_2$ is known to be isostructural to AlFe$_2$B$_2$ contrary to AlM$_2$B$_2$ as reported by previous research [10-13 and 18-22].

5.1.1 AlM$_2$B$_2$ (M = Cr, Mn and Fe)

The diffraction pattern for AlCr$_2$B$_2$, AlMn$_2$B$_2$, AlFe$_2$B$_2$ are shown in figure 9, 10 and 11 respectively. The three samples crystallize in an orthorhombic lattice, in the AlFe$_2$B$_2$-type structure (space group Cmmm) [10-13, 18-20 and 25].

In the case of AlCr$_2$B$_2$, figure 9, the impurities consist of zeta-CrB, Cr$_2$B$_3$, an orthorhombic structure, Al$_{13}$Cr$_2$, a monoclinic structure and B$_3$Si$_{11}$, a rhombohedral structure after annealing. After the process of etching, many impurities of zeta-CrB, Cr$_2$B$_3$, B$_3$Si$_{11}$ still remain and Al$_{13}$Cr$_2$ is removed. The ternary phase AlCr$_2$B$_2$ is present in relatively low yield compared to the situation before etching. However, a peak at 48 ° cannot be identified with the software.

For AlMn$_2$B$_2$, figure 10, the impurities are MnB, an orthorhombic structure, Al, a cubic structure and of AlB$_2$, a hexagonal structure after arc furnace. After annealing, the impurity of MnB disappears and after etching, a small amount of impurities of AlB$_2$ and of Al are left.

A significant amount of Al$_{13}$Fe$_4$, an orthorhombic structure, is present as impurity of AlFe$_2$B$_2$ until the treatment with acid, figure 11, as expected from earlier report [10, 11 and 13]. Furthermore, the ternary phase AlFe$_2$B$_2$ is present in relatively low yield after etching.
Figure 9. Summary of the X-Ray diffraction patterns for AlCr$_2$B$_2$. The black line and the red line represent the diffraction patterns of AlCr$_2$B$_2$ after annealing and AlCr$_2$B$_2$ after etching respectively. The bars at the bottom represent the binary and ternary phases found for AlCr$_2$B$_2$. The red bar, the pink bar, the dark red bar, the orange bar and the blue bar represent the phases AlCr$_2$B$_2$, Al$_{13}$Cr$_2$, Cr$_2$B$_3$, zeta-CrB and B$_{31}$Si$_{11}$ respectively.

Figure 10. Summary of the X-Ray diffraction patterns for AlMn$_2$B$_2$. The black line, the red line and the blue line represent the diffraction patterns of AlMn$_2$B$_2$ after arc melting, after annealing and AlCr$_2$B$_2$ after etching respectively. The bars at the bottom represent the phases found for AlMn$_2$B$_2$. The red bar, the pink bar, the green bar and the blue bar represent the phases AlMn$_2$B$_2$, AlB$_2$, Al and MnB respectively.
Figure 11. Summary of the X-Ray diffraction patterns for AlFe$_2$B$_2$. The blue line, the black line and the red line represent the diffraction patterns of AlFe$_2$B$_2$ after arc melting, after annealing and AlCr$_2$B$_2$ after etching respectively. The bars at the bottom represent the phases found for AlFe$_2$B$_2$. The blue bar and the green bar represent the phases AlFe$_2$B$_2$ and Al$_{13}$Fe$_4$ respectively. (A part of the diffraction pattern is missing for values of 10 to 20 theta from the blue line).

Cell parameters $a$, $b$ and $c$, showed in table 1, were obtained from the refined data. The volume of the ternary phase of AlT$_2$B$_2$ ($T = \text{Cr, Mn and Fe}$) was calculated by using the refined parameters $a$, $b$ and $c$.

Table 1. Cell parameters and the volume for the compounds refined by using the diffraction patterns are presented. Standard deviation is showed in parenthesis.

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCr$_2$B$_2$</td>
<td>2.969(2)</td>
<td>11.053(7)</td>
<td>2.938(2)</td>
<td>96.40(1)</td>
</tr>
<tr>
<td>AlMn$_2$B$_2$</td>
<td>2.923(1)</td>
<td>11.075(4)</td>
<td>2.902(1)</td>
<td>93.93(1)</td>
</tr>
<tr>
<td>AlFe$_2$B$_2$</td>
<td>2.928(1)</td>
<td>11.044(3)</td>
<td>2.872(3)</td>
<td>92.86(1)</td>
</tr>
</tbody>
</table>

5.1.2 AlM$_2$B$_2$ ($M = \text{Co and Ni}$)

The diffraction pattern for AlCo$_2$B$_2$ and AlNi$_2$B$_2$ are showed in figure 12 and 13. As expected from three references [13, 21 and 22], the two samples after annealing and etching provide only known binary phases.

Three binary phases and one ternary phase are provided by the material AlCo$_2$B$_2$, figure 12. Before annealing, the ternary phase AlCo$_2$B$_2$, with the same structure as AlFe$_2$B$_2$ (figure 1), is present but disappears after the heat treatment. Before the acid washing AlCo, a cubic structure is present. Al$_{13}$Co$_4$, a monoclinic structure and Co$_2$B, a tetragonal structure are present for the entire synthesis step.

The material AlNi$_2$B$_2$, figure 13, contains two different binary phases and one ternary phase. Before annealing, the ternary phase AlNi$_2$B$_2$, with the same structure as AlFe$_2$B$_2$ (figure 1), is present but disappears after the heat treatment. During all the procedure AlNi, a cubic structure and NiB, an orthorhombic structure, are present.
Figure 12. Summary of the X-Ray diffraction patterns for AlCo$_2$B$_2$. The black line, the red line and the blue line represent the diffraction patterns of AlCo$_2$B$_2$ after arc melting, after annealing and AlCo$_2$B$_2$ after etching respectively. The bars at the bottom represent the binary and ternary phases found for AlCo$_2$B$_2$. The red bar, the blue bar, the green bar and the orange bar represent the phases AlCo$_2$B$_2$, Co$_2$B, AlCo and Al$_3$Co$_4$ respectively. (A part of the diffraction pattern is missing for values of 10 to 20 theta from the black line).

Figure 13. Summary of the X-Ray diffraction patterns for AlNi$_2$B$_2$. The dark line, the red line and the blue line represent the diffraction patterns of AlNi$_2$B$_2$ after arc melting, after annealing and AlNi$_2$B$_2$ after etching respectively. The bars at the bottom represent the binary and ternary phases found for AlNi$_2$B$_2$. The blue bar, the green bar and the dark red bar represent the phases AlNi$_2$B$_2$, NiB and AlNi respectively. (A part of the diffraction pattern is missing for values of 10 to 20 theta from the black line).

The diffraction pattern for the bottom and the top of the whole piece of AlCo$_2$B$_2$ and AlNi$_2$B$_2$, which were arc melted one time, are shown in figure 14 and 15. As expected from two references [21 and 22], the top of the whole piece of the two samples don’t show any ternary phases, but only known binary phases. Furthermore, the bottom of the whole piece of AlCo$_2$B$_2$ and AlNi$_2$B$_2$, where a faster cooling occurs, show a ternary phase and binary phases.
The whole piece of AlCo$_2$B$_2$, figure 14, provides four binary phases and one ternary phase. Two binary phases, CoB, an orthorhombic structure, and Al-Co are present at the top and the bottom of the whole piece. However, the binary phase Al$_{0.52}$Co$_{0.48}$, a cubic structure, and the ternary phase AlCo$_2$B$_2$, an orthorhombic structure, are present only at the bottom of this whole piece. Moreover, the binary phase Al$_{0.47}$Co$_{0.53}$, a cubic structure is present only at the top of this whole piece.

Two different binary phases and one ternary phase are present for the whole piece of AlNi$_2$B$_2$. The two binary phases, AlNi, a cubic structure, and NiB, an orthorhombic structure, are present at the top and the bottom of the whole piece. However, the ternary phase AlNi$_2$B$_2$, an orthorhombic structure, is present only at the bottom of this whole piece.

Figure 14. Summary of the X-Ray diffraction patterns for the whole piece AlCo$_2$B$_2$ after one arc melting. The dark line and the red line represent the diffraction patterns of the bottom and the top of AlCo$_2$B$_2$ respectively. The bars at the bottom represent the binary and ternary phases found for AlCo$_2$B$_2$. The red bar, the blue bar, the dark red bar, the green bar and the yellow bar represent the phases AlCo$_2$B$_2$, CoB, Al-Co, Al$_{0.52}$Co$_{0.48}$ and Al$_{0.47}$Co$_{0.53}$ respectively.
Figure 15. Summary of the X-Ray diffraction patterns for the whole piece AlNi$_2$B$_2$ after one arc melting. The dark line and the red line represent the diffraction patterns of the bottom and the top of AlNi$_2$B$_2$ respectively. The bars at the bottom represent the binary and ternary phases found for AlNi$_2$B$_2$. The red bar, the blue bar and the pink bar represent the phases AlNi$_2$B$_2$, AlNi and NiB respectively.

Cell parameters $a$, $b$ and $c$ of the bottom of the compound AlM$_2$B$_2$ (M = Co and Ni) can be found in table 2. The volume of the ternary phase of AlM$_2$B$_2$ (M = Co and Ni) was calculated by using the refined parameters $a$, $b$ and $c$.

Table 2. Cell parameters and the volume for the compounds refined by using the diffraction patterns are presented. Standard deviation is showed in parenthesis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCo$_2$B$_2$</td>
<td>2.959(4)</td>
<td>10.900(15)</td>
<td>2.860(3)</td>
<td>92.24(2)</td>
</tr>
<tr>
<td>AlNi$_2$B$_2$</td>
<td>2.908(4)</td>
<td>10.899(15)</td>
<td>2.877(8)</td>
<td>91.22(2)</td>
</tr>
</tbody>
</table>

5.2 SQUID

The magnetization of the AlCr$_2$B$_2$ was measured as a function of temperature with applied magnetic field of 0.005 and 1 Tesla, presented in figure 16. The magnetization decreases when the temperature increases, however no inflexion point can be found.
Figure 16. Temperature dependence of magnetic susceptibility for AlCr$_2$B$_2$ measured under applied magnetic field of 1 Tesla. (Emu/g is the same as A.m$^2$.kg$^{-1}$).

The magnetization of the AlMn$_2$B$_2$ was measured as a function of temperature with different applied magnetic fields, presented in figure 17a, and as a function of magnetic field with a constant temperature, showed in figure 17b. The temperature dependence of magnetic susceptibility of AlMn$_2$B$_2$ exhibits a small inflexion point at an interpret temperature of 21 K (figure 17a). Moreover, the magnetization decreases when the temperature increases. Figure 17b shows that AlMn$_2$B$_2$ does not exhibit a huge hysteresis loop, where $H_C = 0.04$ T and $M_r = 0.04$ A.m$^2$.kg$^{-1}$ at 5K.

Figure 17. (a) Temperature dependence of magnetic susceptibility for AlMn$_2$B$_2$ measured under several applied magnetic fields. (Emu/g is the same as A.m$^2$.kg$^{-1}$). (b) Magnetization versus magnetic field at a constant temperature of five kelvin. $H_C = 0.04$ T and $M_r = 0.04$ A.m$^2$.kg$^{-1}$.

6 Discussion

From the XRD patterns and the refinements in figures 9 and 10, impurities are present during all the step of the process in each sample. These impurities are created during are melting of the final compounds and/or because of the reorganization of the atoms during the heat treatment. However the impurity concentration has been reduced after annealing and etching in general. It can be seen that for the compound AlCr$_2$B$_2$, Al$_{13}$Cr$_2$ has been removed during the acid washing. Furthermore, it can be noticed that a strange product B$_{31}$Si$_{11}$ is obtained after annealing and stayed after the etching, due to a contamination of the silica tube which has reacted with the alloys during annealing. Also, a peak at 48 ° for the diffraction pattern of AlCr$_2$B$_2$ cannot be identified by the database of the software due to an incomplete database and the etching process reduces the presence of the ternary phase because AlCr$_2$B$_2$ has reacted with the acid more than expected. The final alloy AlMn$_2$B$_2$ contained a majority of the ternary phase AlMn$_2$B$_2$ as expected, according to earlier report [13], but small contamination by AlB$_2$ and contamination of Al is found as reported earlier [13]. Furthermore, the process of annealing and etching lowered
the quantity of Al present in the compound and the disappearance of the binary phase MnB after annealing can be explained by the reorganization of the atoms due to the high temperature procedure. In figure 11, it can be seen that soaking of AlFe2B2 removed the impurity of Al13Fe4 as expected [10, 11 and 13], but the acid treatment has reduced the ternary phase.

Volume of AlMn2B2 and AlCr2B2 increased during the substitution of the iron site by manganese and chromium respectively. This seems in agreement with the previous values reported [13, 20 and 26], see table 3. Also, the unit cell parameters refined AlFe2B2 from the XRD data agree well with those reported by two independent sources [20 and 26], so the synthesis route of this compound was well performed.

Table 3. Unit cell parameters and volume of AlM2B2 (M = Cr, Mn, Fe) synthesized during this project and other values found in the references.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
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<th>c (Å)</th>
<th>V (Å³)</th>
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<td>11.053(7)</td>
<td>2.938(2)</td>
<td>96.40(1)</td>
</tr>
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<td>AlCr2B211</td>
<td>2.949(6)</td>
<td>11.10(1)</td>
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<td>AlMn2B2</td>
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<td>11.075(4)</td>
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<td>93.93(1)</td>
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<td>2.912(8)</td>
<td>95.06(1)</td>
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<td>AlFe2B2</td>
<td>2.928(1)</td>
<td>11.044(3)</td>
<td>2.8720(3)</td>
<td>92.86(1)</td>
</tr>
<tr>
<td>AlFe2B220</td>
<td>2.923</td>
<td>11.034</td>
<td>2.870</td>
<td>92.58</td>
</tr>
<tr>
<td>AlFe2B2</td>
<td>2.923</td>
<td>11.046</td>
<td>2.875</td>
<td>92.83</td>
</tr>
</tbody>
</table>

Figure 12 and 13 showed that the ternary phase can only be formed before the annealing for these two compounds, during this synthesis route, AlCo2B2 and AlNi2B2 as expected [13, 21 and 22]. This means that AlCo2B2 and AlNi2B2 may not be stable at high temperature, so metastable because the two compounds change their own structure according to the temperature. This is confirmed when arc melting was performed just one time for AlCo2B2 and AlNi2B2, it can be seen that the ternary phase AlCo2B2 and AlNi2B2 are present respectively at the bottom of the whole piece and not at the top of these samples, figure 14 and 15 respectively. The presence of the two ternary phases is confirmed by looking at the refined cell parameters [26], but other studies needs to be performed to ensure that the ternary phases are present. It is because the cooling rate is higher at the bottom of the piece, and therefore these two compounds are metastable, thermodynamics unstable at high temperature as studied earlier [21 and 22]. It can also be seen in figure 12 that for the compound AlCo2B2, AlCo has been removed during the etching. Furthermore, figure 14 indicates the ratio of aluminum and cobalt for the AlxCo1-x phase decreases (x change of 0.05) but, this small change of ratio cannot appear as a visible shift for an XRD measurement, the exact composition is not known, so no conclusion can be made.

Volume and unit cell parameters refined for the bottom of the whole piece of AlCo2B2 and AlNi2B2 from the XRD data are shorter than the three other compounds, see table 1 and 2. Moreover, the volume of AlCo2B2 is close to the volume of AlNi2B2. This seems in agreement with increasing the volume of the crystal structure when a substitution of an atom by a bigger atom takes place (rCo > rMn > rFe > rCo = rNi). AlCr2B2, figure 16, does not exhibit a magnetic transition under different applied fields no inflexion point can be found, agreement to reference [13]. The magnetic response of AlMn2B2, with Hc = 0.04 T and Ms = 0.04 A.m².kg⁻¹, is very low, so AlMn2B2 is a soft magnet. However a different cusp, 21 K instead of 52 K, is found in the thesis due to the impurities present in the compound [13].

7 Conclusion

A synthetic route has been developed for all the compounds but a low yield is found at the end for all the compounds. The etching process reduced a lot of sample mass, so another method needs to be performed in order to obtain a high yield of the ternary phases. However, only AlFe2B2 has been formed without impurity at the end. The five compounds AlM1B2 (M = Cr, Mn, Fe, Co, Ni) exhibit a change of volume during the substitution on the iron site as expected. Two compounds, AlCr2B2 and AlNi2B2, have been determined as metastable, but one need to be careful with this because other studies need to be performed to ensure this result. The magnetic response of AlCr2B2 and AlMn2B2 shows that this compound cannot be used for magnetic refrigeration.

8 Future investigations
A new synthesis route is required to form without impurity at the end the compounds AlCr$_2$B$_2$ and AlMn$_2$B$_2$ and also to obtain a high yield of the ternary phases. Also, additional techniques of characterization for the compounds need to be performed, such as energy-dispersive X-ray spectroscopy (EDS) to determine the actual composition of these compounds. As indicated in the literature [13], a new synthesis route can be performed. The final alloy is mixed together, after placed into an alumina crucible, covered with a piece of silica wool and sealed into a silica tube under vacuum. The reaction is heated up in a pit furnace and then slowly cooled down. The ampoule is quickly taken out of the furnace, flipped down and placed into a centrifuge to remove the unreacted aluminum. Single crystals of AlCr$_2$B$_2$ and AlMn$_2$B$_2$ can be picked up manually after because the crystals are distinguishable.

A mix of AlCo$_{2-x}$M$_x$B$_2$ or AlNi$_{2-x}$M$_x$B$_2$ (M = Mn, Fe) could be interesting to try because AlCo$_2$B$_2$ and AlNi$_2$B$_2$ are metastable, and these compounds might become stable during the entire synthesis route. Also, a study of the magnetic properties should be performed.

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References


Appendices