Near room temperature antiferromagnetic ordering with a potential low dimensional magnetism in AlMn$_2$B$_2$

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We present self flux growth and characterization of single crystalline AlMn$_2$B$_2$. It is an orthorhombic (space group Cmmm), layered material with a plate like morphology. The anisotropic bulk magnetization data, electrical transport and $^{11}$B nuclear magnetic resonance(NMR) data revealed an antiferromagnetic (AFM) transition at 313 ± 2 K. In the magnetization data, there is also a broad local maximum significantly above the AFM transition that could be a signature of low dimensional magnetic interactions in AlMn$_2$B$_2$.

INTRODUCTION

The Al$_x$T$_2$B$_2$ (T = Fe, Cr, Mn) system crystallizes in the orthorhombic, Cmmm structure and adopts a layer morphology with an internal structure of alternate stacking of Al atom planes and T$_2$B$_2$ slabs along the $b$-axis [1]. A representative unit cell of AlMn$_2$B$_2$ is shown in Fig. 1(a) to demonstrate this atomic structure. AlT$_2$B$_2$ compounds are interesting, specially for potential rare earth free magnetocaloric materials and soft magnetic materials. AlFe$_2$B$_2$ is ferromagnetic and studied for its magneto-caloric and anisotropic magnetic properties [2–4]. Understanding the magnetic properties of the neighbouring, isostructural compounds can provide further insight in to the series as well as how to tune the magnetocaloric property of the AlFe$_2$B$_2$ via substitution. We started this work to clarify the magnetic properties of AlMn$_2$B$_2$ since it was identified as a non-magnetic material [5]. In addition, some inconsistencies between bulk and local probe magnetic measurements in the Al(Fe$_{1-x}$Mn$_x$)$_2$B$_2$ were observed. A later first principle calculation suggested that AlMn$_2$B$_2$ should be an anti-ferromagnetic compound [6]. In a recent powder neutron study, AlMn$_2$B$_2$ is identified as a ceramic AFM compound [7] with Neel temperature around 390 K. A study of lattice parameters variation from room temperature to 1200 K revealed that there is a change in anisotropy nature in $a$ and $c$ lattice parameters around 450 K and a local minimum in $b$ lattice parameters around 400 K [8]. The lack of a clear description of the nature or number of magnetic phase transitions in AlMn$_2$B$_2$ led us to grow and systematically study single crystalline samples.

This paper reports the synthesis of bulk single crystals via high-temperature solution growth and their characterization via high and low temperature magnetization, NMR, and electrical resistance measurements. We find that AlMn$_2$B$_2$ is a metallic antiferromagnet with a transition temperature of $T_N = 313 \pm 2$ K. In addition we find that AlMn$_2$B$_2$ has features associated with pseudo-two-dimensional magnets.

FIG. 1. (a)AlMn$_2$B$_2$ unit cell showing Mn$_2$B$_2$ slabs stacked with Al layer (b) Concentrated NaOH etched AlMn$_2$B$_2$ single crystals

EXPERIMENTAL DETAILS

Crystal growth

Solution growth is a powerful tool even for compounds with high melting elements like B [3, 9, 10]. The major difficulty associated with solution growth is finding an initial composition that allows for growth of the single phase, desired compound. For example, CaKFe$_4$As$_4$ growth in single phase form presents an illustrative example [11]. Fortunately, with the innovation of fritted alumina crucibles sets [12] we can now reuse decanted melt and essentially fractionate the melt, as described below.

Al shot (Alfa Aesar 99.999%), B pieces (Alfa Aesar 99.5% metal basis) and Mn pieces (Alfa Aesar 99.9% metal basis) after surface oxidation cleaning as described elsewhere [13] were used for the crystal growth process. We started with an Al rich composition, Al$_{60}$Mn$_{22}$B$_{10}$, and arc-melted it at least 4 times under an Ar atmosphere. The button was then cut with a metal cutter and re-arcmelted if some not-reacted B pieces were found.

After the button appeared to be homogeneous, it was packed in a fritted alumina crucible set [12] and sealed under partial pressure of argon inside amorphous silica jacket to form a growth ampoule. The growth ampoule
TABLE I. Crystal data and structure refinement for AlMn$_2$B$_2$.

| Property                        | Value                                      |
|--------------------------------|--------------------------------------------|
| Empirical formula              | AlMn$_2$B$_2$                              |
| Formula weight                 | 158.48                                     |
| Temperature                    | 296(2) K                                   |
| Wavelength                     | 0.71073 Å                                  |
| Crystal system, space group    | Orthorhombic, Cmmm                         |
| Unit cell dimensions           | a = 2.9215(1) Å, b = 11.0709(6) Å, c = 2.8972(2) Å |
| Volume                         | 93.706(9) 10$^3$ Å                       |
| Z, Calculated density          | 2, 5.63 g/cm$^3$                           |
| Absorption coefficient         | 6.704 mm$^{-1}$                            |
| F(000)                         | 73                                         |
| θ range (°)                    | 3.693 to 29.003                            |
| Limiting indices               | -5 ≤ h ≤ 5, -22 ≤ k ≤ 22, -5 ≤ l ≤ 5      |
| Reflections collected          | 1467                                       |
| Independent reflections        | 270 [R(int) = 0.0401]                      |
| Completeness to theta = 25.242° | 98.5%                                      |
| Absorption correction          | multi-scan, empirical                      |
| Refinement method              | Full-matrix least-squares                  |
| Data / restraints / parameters | 270 / 0 / 12                               |
| Goodness-of-fit on $F^2$       | 1.101                                      |
| Final R indices [I>2σ(I)]      | R1 = 0.0362, wR2 = 0.0817                  |
| R indices (all data)           | R1 = 0.0387, wR2 = 0.0824                  |
| Largest diff. peak and hole    | 2.341 and -1.249 e.Å$^{-3}$                |

was then heated to 1200 °C over 2 h and soaked there for 10 h before spinning using a centrifuge. Due to high melting point of B containing compounds, homogeneous liquid was not formed at 1200 °C. Undissolved polycrystalline MnB and Al-Mn binary compounds were separated at 1200 °C via centrifuging. The catch crucible collected the homogeneous melt at 1200 °C was again sealed in a fritted alumina crucible sets under Ar atmosphere to form second growth ampoule. This second ampoule was heated to 1200 °C over 2 h, held there for another 10 h and cooled down to 1100 °C over 50 h and spun using centrifuge to separate the crystals. The second growth attempt produced a mixture of the targeted AlMn$_2$B$_2$ phase along with MnB crystals. So as to avoid this MnB contamination, the catch crucible of the second growth was used for a third growth and sealed again under a partial pressure of Ar. For this stage, to make sure there are no other nucleated crystals, the third growth was heated to 1200 °C over 2 h and soaked there for 2 h. It was then cooled down to 1100 °C over 1 h and stayed there for 1 h followed by slow cooling to 990 °C over 120 h and centrifuged to separate large, single phased AlMn$_2$B$_2$ crystals as shown in Fig. 1(b). The flux on the surface was removed via concentrated NaOH etching.

It should be noted that predominantly single phase AlMn$_2$B$_2$ crystals were grown in single growth attempt using initial Al$_{84}$Mn$_{8}$B$_{8}$ composition however the crystals were small, due to multiple nucleation sites.

**CRYSTAL STRUCTURE AND STOICHIOMETRY**

As grown single crystals were characterized using a scanning electron microscope (SEM), as well as both [a](fig:SEM_almn2b2_planar) and [b](fig:SEM_almn2b2_cross_sectional) SEM images of AlMn$_2$B$_2$ single crystalline sample along the planar view (with electron beam parallel to [010]) and in a cross sectional view with electron beam parallel to [100].

![SEM image of AlMn$_2$B$_2$ single crystalline sample](https://example.com/SEM_almn2b2_planar.png)

![SEM image of AlMn$_2$B$_2$ in a cross sectional view](https://example.com/SEM_almn2b2_cross_sectional.png)

**FIG. 2.** (a) SEM image of AlMn$_2$B$_2$ single crystalline sample along the planar view (with electron beam parallel to [010]). (b) SEM image of AlMn$_2$B$_2$ in a cross sectional view with electron beam parallel to [100].
powder and single crystal X-ray diffraction (XRD). Figures 2(a) and (b) show the planar and cross sectional backscattered SEM images of AlMn$_2$B$_2$ single crystals which show predominantly homogeneous compositions. The small linear grooves are the cracked layers associated with the SEM sample polishing. Being a layered material, it can be easily cleaved and deformed. Boron is difficult to account for correctly in electron dispersive spectroscopy (EDS), as a consequence of this we determined only the Mn:Al ratio for two different batches of single crystalline samples. In first batch, 13 spots were analyzed in EDS with Mn:Al ratio of 2.07 for all characteristics X-ray emissions. Similarly, an 8 spot analysis in the second batch provided the Mn:Al ratio to be 2.12 for characteristics K-lines for all elements. With the L-characteristics-lines analysis, a ratio of 2.51 was obtained for the second batch. Without the creation and use of Mn-Al-B based standards, further characterization by EDS is difficult.

Although the EDS results are qualitatively in agreement with the AlMn$_2$B$_2$ structure, to more precisely determine the composition and structure, multiple batches of AlMn$_2$B$_2$ were investigated using single crystal XRD technique. Single crystalline XRD data were collected with the use of graphite monochromatized Mo $K_\alpha$ radiation ($\lambda=0.71073$ Å) at room temperature on a Bruker APEX2 diffractometer. Reflections were gathered by taking five sets of 440 frames with 0.5° scans in $\omega/\theta$, with an exposure time of 10 s per frame and the crystal-to-detector distance of 6 cm. The structure solution and refinement for single crystal data was carried out using SHELXTL program package. Attempts to refine occupancies of each site indicated full occupancy($< 3\sigma$). The final stage of refinement was performed using anisotropic displacement parameters for all the atoms. The refinement metrics and atomic coordinates are presented in TABLE I and II respectively. The single crystalline refinement showed AlMn$_2$B$_2$ as a stoichiometric material.

Etched single crystals were finely ground and spread over a zero background silicon wafer sample holder with help of a thin film of Dow Corning high vacuum grease. Powder diffraction data were obtained using a Rigaku Miniflex II diffractometer within a 2$\theta$ range of 10 - 100° with a step of 0.02° and dwelling time of 3 seconds for data acquisition. The crystallographic information file from the single crystal XRD solution was used to fit the powder XRD data using GSAS [14] and EXPGUI [15] software packages. Figure 3 shows the Rietveld refined powder XRD pattern with R factor of 0.08. Being a relatively hard, layered material, texture is visible along the 001 direction although March Dollase texture correction was employed to account for this intensity mismatch.

To identify the crystallographic orientation of the AlMn$_2$B$_2$ single crystals, we employed the monochromatic X-ray diffraction from the crystallographic surfaces in the Bragg-Brentano geometry [8,16]. The direction perpendicular to the plate was identified to be [010] since a family of {020} lines were observed in the diffraction pattern as shown in blue curve in Fig. 4. The plate was held vertical and the family of {001} peaks were obtained as shown in red curve of Fig. 4. The monochromatic x-ray surface diffraction peaks were compared with powder
diffraction data to correctly identify their directions. A vertical line through the powder [110] peak was used as a reference point of comparison as shown in Fig. 4 Then the last remaining direction was identified to be [100] along the length of the crystals. A reference coordinate system is shown in Fig. 1(b) to demonstrate the crystallographic orientations of AlMn$_2$B$_2$ crystals.

![Graph showing temperature dependent normalized resistance and temperature derivative of AlMn$_2$B$_2$.](image)

**FIG. 5.** Temperature dependent normalized resistance (left axis) and temperature derivative (right axis) of AlMn$_2$B$_2$. The resistance is metallic in nature. The temperature derivative shows an anomaly at 313 ± 2 K consistent with an AFM phase transition.

![Graph showing susceptibility data along various crystallographic axes of AlMn$_2$B$_2$.](image)

**FIG. 6.** Low temperature (2 - 350 K) $M/H$ along various crystallographic axes of AlMn$_2$B$_2$ sample as outlined in the graph. The inset shows $d(M/H)/dT$ as a function of temperature.

**ELECTRIC AND MAGNETIC PROPERTIES**

The temperature dependent electrical resistance of AlMn$_2$B$_2$ was measured in a traditional 4 probe measurement on a NaOH etched, rod like sample using an external device control option to interface with a Linear Research, Inc. ac (1 mA, 17 Hz) resistance bridge (LR 700). Thin platinum wires were attached to the sample using DuPont 4929N silver paint to make electrical contact. Quantum Design Magnetic Property Measurement System (MPMS) was used as a temperature controller. The measured temperature dependent electrical resistance of AlMn$_2$B$_2$ is shown in Fig. 5 These data further confirm that our single crystals are essentially stoichiometric AlMn$_2$B$_2$; given that the residual resistivity ratio ($\frac{R(350\, K)}{R(2\, K)}$) is 28.5, there is relatively low disorder scattering. In addition, a very clear feature is seen in both R(T) and $\frac{dR(T)}{dT}$ at T = 313 ± 2 K. Such features are often related to a loss of spin disorder scattering at a magnetic transition. As such, these data are our first suggestion that AlMn$_2$B$_2$ may indeed have some form of magnetic order below 315 K.

The magnetic properties of AlMn$_2$B$_2$ were studied from a base temperature of 2 K to 700 K. Low temperature anisotropic magnetization data of single crystalline AlMn$_2$B$_2$ samples were measured within the temperature range 2 - 350 K using a MPMS. High temperature,

**FIG. 7.** (a) High temperature susceptibility data along various axes measured using VSM. There are shallow anomalies present around 313 ± 2 K for each directions. (b) Corresponding Curie Weiss plots identifying AlMn$_2$B$_2$ as an AFM material with $\theta_{100} = -815$ K, $\theta_{100} = -750$ K, and $\theta_{001} = -835$ K respectively.
anisotropic temperature dependent magnetization data were obtained using a Quantum Design VersaLab Vibrating Sample Magnetometer (VSM) over the temperature range 300 - 700 K in an oven option mode.

The low temperature anisotropic susceptibility data, with \( H = 3 \) T applied field, are presented in Fig. 6. Below 50 K, the magnetization data show a low temperature upturn as reported in a previous literature [5]. In all three directions, there is a clear anomaly in susceptibility data around 312 K. The inset shows \( \frac{d(M+T/H)}{dT} \) as a function of temperature showing a clear anomaly around 312 K identifying AlMn\(_2\)B\(_2\) as an AFM material. The observed anomaly in \( \frac{d(M+T/H)}{dT} \) coincides with the kink observed in \( \frac{dR}{dT} \).

Recently, AlMn\(_2\)B\(_2\) was reported to be AFM however Neel temperature was reported to be around 390 K [7]. To examine higher temperatures, our high temperature susceptibility data, obtained using our VSM are presented in Fig. 7(a) and (b). Although a broad local maximum of the susceptibility around 350 - 390 K for different axes, consistent to reference[7] was found, the \( \frac{d(M+T/H)}{dT} \) did not show any anomaly. The only clear and conclusive feature in the high temperature data associated with a magnetic transition is the feature at 313 ± 2 K. The broad local maximum in magnetization well above the transition temperature can be associated with low dimensional, or linear chain anisotropic Heisenberg antiferromagnetism [19–23]. The fitted Curie Weiss temperatures for various axes were obtained to be \( \theta_{010} = - \)

815 K, \( \theta_{100} = - 750 \) K, and \( \theta_{001} = - 835 \) K. From the average slope of Curie Weiss plot, the effective moment of Mn is found to be \( \sim 2.5 \mu_B/Mn \).

At low temperature, \( T \leq 50 \) K, in Fig. 6 there is a clear upturn in the \( M/H \) data, particularly for \( H \) along the [010] direction. In order to better understand this we measured the anisotropic field dependent magnetization at 2 K as shown in Fig. 8. For fields greater than 4 T the slopes of the \( M(H) \) plots are comparable for all three directions. For \( H \parallel [010] \), there is a roughly 0.02 \( \mu_B/Mn \) offset due to a rapid increase and saturation for \( H \leq 3 \) T. The origin of this small, anisotropic contribution is currently not known.

**NUCLEAR MAGNETIC RESONANCE STUDY**

To further investigate the magnetism of AlMn\(_2\)B\(_2\), we carried out \(^{11}\)B NMR measurements at various temperatures between 5 K and 457 K as presented in Figs. 9 - 11. To perform the NMR measurements for the temperature region of \( T = 5 - 295 \) K, crushed single crystalline powder was enclosed in a weighing paper folded closed cylindrical tube and inserted inside the NMR coil.
For the higher temperature NMR measurements up to 457 K from room temperature, the crushed powder was sealed under $\frac{1}{3}$ atmospheric pressure of Ar inside a $\sim$1 mm internal diameter amorphous silica tube. The NMR measurements were carried out using a lab-built phase coherent spin-echo pulsed NMR spectrometer on $^{11}$B (nuclear spin $I = \frac{3}{2}$ and gyromagnetic ratio $\gamma = 13.6552$ MHz/T) nuclei in the temperature range $5 < T < 457$ K. NMR spectra were obtained either by Fourier transform of the NMR echo signals, by sweeping frequency or by sweeping magnetic field. Magnetic phase transition was studied analyzing the full width at half maximum (FWHM) of $^{11}$B NMR spectra and spin-lattice relaxation rate $\frac{1}{T_1}$. The $^{11}$B $\frac{1}{T_1}$ was measured by the conventional single saturation pulse method.

Figure 7 shows the $^{11}$B NMR spectra obtained by Fourier transform of the NMR spin echo for temperatures in the range 315 - 457 K at $H = 7.4089$ T. Throughout the range of study, the FWHM $\sim$29 kHz is nearly independent of temperature. On the other hand, below 315 K, as shown in Fig. 10, the $^{11}$B NMR line broadens abruptly and has an almost rectangular shape at low temperatures. Since the rectangular shape is characteristic of NMR spectrum in AFM ordered state for powder sample, the results clearly indicate that the magnetic phase transition around 315 K is AFM. Similar rectangular NMR spectra in AFM state have been observed in BiMn$_2$PO$_6$ [24], NaVGe$_2$O$_6$ [25], CuV$_2$O$_6$ [26], and BaCo$_2$V$_2$O$_8$ [27].

In the low temperature range between 5 - 295 K, several $^{11}$B NMR spectra were measured at a frequency of $f = 44.32$ MHz by sweeping the magnetic field as shown in Fig. 11. The FWHM increases with decreasing temperature and shows nearly constant(\(\sim 0.06\) T) down to \(\sim 50\) K. Below 50 K, the FWHM slightly decreases, where the shape of the spectrum changes and the edges of the lines are smeared out. These results suggest a change in magnetic state around 50 K. Although it is not clear at present, it is interesting if the change relates to the strong enhancement of $\chi_b$ below 50 K as shown in Fig. 6. NMR measurements on single crystals could provide additional information in this issue. This is the future work.

Figure 12(a) shows the temperature variation of the FWHM of the $^{11}$B NMR spectra between 5 - 457 K. Since the FWHM of the powder NMR spectrum in AFM state corresponds to the twice of the hyperfine field($H_{hf}$) at the B site produced by Mn ordered moments, the temperature dependence of FWHM reflects the temperature dependence of the Mn sub-lattice magnetization. Therefore, one can obtain the critical exponent ($\beta$) of the order parameter using the formula $FWHM \propto (1 - \frac{T}{T_N})^\beta$. The maximum value of $\beta = 0.21 \pm 0.02$ with $T_N = 314$ K was obtained by fitting the data points in the range 295 - 315 K. This system exhibits a second order phase transition.
Structural, electrical transport and magnetic properties were studied on self flux grown single crystalline AlMn$_2$B$_2$ samples. All these measurements revealed that AlMn$_2$B$_2$ as an AFM compound with a transition temperature around 313 ± 2 K. At higher temperature broad hump, well above the transition temperature, could be the signature of low dimensional magnetic interaction in AlMn$_2$B$_2$ above the room temperature.

**CONCLUSIONS**

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