

## Original Paper

Syntheses and Properties of MgAlB<sub>14</sub>-type Compounds from Al-self FluxShigeru OKADA<sup>1,\*</sup>, Toetsu SHISHIDO<sup>2</sup>, Takao MORI<sup>3</sup>, Kiyokata IIZUMI<sup>4</sup>,  
Kunio KUDOU<sup>5</sup>, Kazuo NAKAJIMA<sup>2</sup><sup>1</sup>Faculty of Science and Engineering, Kokushikan University, 4-28-1 Setagaya, Setagaya-ku, Tokyo 154-8515<sup>2</sup>Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577<sup>3</sup>National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044<sup>4</sup>Faculty of Engineering, Tokyo Polytechnic University, 1583 Iiyama, Atsugi 243-0297<sup>5</sup>Faculty of Engineering, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama, 221-8686Al-セルフフラックスから MgAlB<sub>14</sub>-タイプ化合物の合成と性質岡田 繁<sup>1,\*</sup>, 宍戸統悦<sup>2</sup>, 森 孝雄<sup>3</sup>, 飯泉清賢<sup>4</sup>, 工藤邦男<sup>5</sup>, 中嶋一雄<sup>2</sup><sup>1</sup>国士舘大学理工学部, 154-8515 東京都世田谷区世田谷 4-28-1<sup>2</sup>東北大学金属材料研究所, 980-8577 仙台市青葉区片平 2-1-1<sup>3</sup>物質・材料研究機構, 305-0044 つくば市並木 1-1<sup>4</sup>東京工芸大学工学部, 243-0297 神奈川県厚木市飯山 1583<sup>5</sup>神奈川大学工学部, 221-8686 横浜市神奈川区六角橋 3-27-1

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LEAlB<sub>14</sub> (orthorhombic, *Imam*) (LE = Li, Mg) crystals were grown using metal salts (Li<sub>2</sub>CO<sub>3</sub>, LiF, LiI, MgO, MgF<sub>2</sub>, MgI<sub>2</sub>) and crystalline boron from a high-temperature aluminium metal flux. The growth conditions for growing LEAlB<sub>14</sub> were established using the starting mixtures of B/LE = 2.0 (atomic ratio), and Al metal was added to each mixture at a mass ratio of 1:15-20. LEAlB<sub>14</sub> crystals from the Al-self flux using metal salts could be obtained from all the different salts. The maximum dimensions of LiAlB<sub>14</sub> and MgAlB<sub>14</sub> crystals were approximately 18 mm and 12 mm respectively for the crystals obtained from LiF and MgF<sub>2</sub>. The unit-cell parameters of as-grown LEAlB<sub>14</sub> are as follows: for LiAlB<sub>14</sub> obtained from LiF, *a* = 0.5846(2) nm, *b* = 0.8144(2) nm, *c* = 1.0355(3) nm, *V* = 0.4930(2) nm<sup>3</sup>; for MgAlB<sub>14</sub> obtained from MgF<sub>2</sub>, *a* = 0.5845(2) nm, *b* = 0.8114(2) nm, *c* = 1.0330(4) nm, *V* = 0.4899(3) nm<sup>3</sup>. Microhardness, oxidation resistance and magnetic susceptibility of these materials are described in detail.

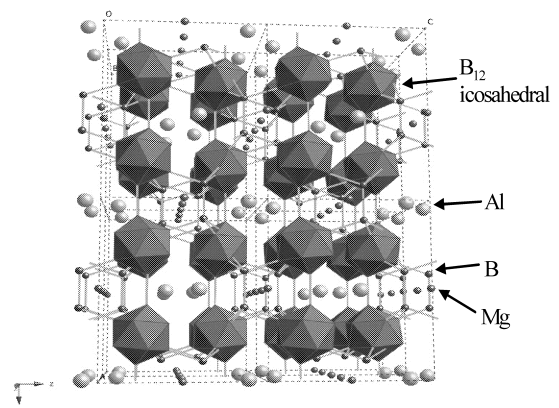
Key Words: LiAlB<sub>14</sub>, MgAlB<sub>14</sub>, Metal Salts, Vickers Microhardness, Magnetic Susceptibility

## 1. Introduction

Higher borides consisting of B<sub>12</sub> icosahedra are of great interest because of their remarkable physical and chemical properties[1], which in many cases are of potential interest for applications of thermoelectric, photodetectors and neutron shelters[2]. The boron-rich compounds of Li or Mg and Al have been reported as MgAlB<sub>14</sub>-type compounds (orthorhombic, *Imam*)[1,3]. The structure of MgAlB<sub>14</sub> type is made up to four B<sub>12</sub> icosahedra and eight single boron atoms per unit cell. The icosahedra are centered at 0, 0, 0; 1/2, 1/2, 0; 0, 0, 1/2 and 1/2, 1/2, 1/2, and were oriented so as to have one their mirror planes parallel to the (100) plane. The Al and LE (Li or Mg) atoms are accommodated in the large holes outside the icosahedra. Figure 1 shows a perspective view of the MgAlB<sub>14</sub>-type structure where the boron icosahedron unit is depicted as a cluster. The largest and the second largest atoms correspond to the Li or Mg and Al atoms, respectively. However, there is very little information about the physical and chemical properties of MgAlB<sub>14</sub>-type compounds.

Recently, we successfully prepared single crystal of LiAlB<sub>14</sub> from the aluminium-self flux using Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> or Li metal and boron powder as starting materials[4]. Another, crystal of MgAlB<sub>14</sub> is obtained by adding relatively large amount of Mg metal in high

temperature Al flux[3]. However, until now there have been no reports on the growth of LEAlB<sub>14</sub> (LE = Li, Mg) crystals from Al-self metal flux using metal salts (Li<sub>2</sub>CO<sub>3</sub>, LiF, LiI, MgO, MgF<sub>2</sub>, MgI<sub>2</sub>), instead of LE metal, and boron powder as starting materials

Fig.1 The crystal structure of MgAlB<sub>14</sub>-type compound.

by slowly cooling under an argon atmosphere.

In this paper, we report the experimental conditions for growing relatively large crystals of LEAlB<sub>14</sub> (LE = Li, Mg) from metal salts (Li<sub>2</sub>CO<sub>3</sub>, LiF, LiI, MgO, MgF<sub>2</sub>, MgI<sub>2</sub>), instead of LE metals, and boron powder as starting materials. The metal salts are more suitable as the source of LE elements than LE metals that have high vapor pressure, because of relatively high chemical stability in air atmosphere, and low reactivity for an alumina crucible at high temperature. The present study of LEAlB<sub>14</sub> crystals growth is the first to successfully utilize metal salts (Li<sub>2</sub>CO<sub>3</sub>, LiF, LiI, MgO, MgF<sub>2</sub>, MgI<sub>2</sub>) and boron powders as starting materials in Al self-flux. The size, morphology and crystallographic data of the crystals were determined. Vickers microhardness at room temperature, oxidation resistance heated in air up to 1473 K and magnetic susceptibility measurements at low temperatures were investigated.

## 2. Experimental details

### 2.1 Sample syntheses

The reagents used to prepare the samples were metal salts (Li<sub>2</sub>CO<sub>3</sub> (purity 99 %), LiF (purity 99.9 %), LiI (purity 99.9 %), MgO (purity 99.9 %), MgF<sub>2</sub> (purity 99 %), MgI<sub>2</sub> (purity 99.9 %)), crystalline boron powders (purity 99 %) and aluminium metal chips (purity 99.99 %). The growth conditions for growing LEAlB<sub>14</sub> were established using the starting mixtures of B/LE = 2.0 (atomic ratio), and Al metal was added to each mixture at a mass ratio of 1:15-20. The mixture of starting materials was heated at a rate of 300 K·h<sup>-1</sup> and held at soaking temperature 1673 K for soaking time 5 h, and then cooled to room temperature at a rate of 50 K·h<sup>-1</sup>. The ingot was removed by breaking the crucible. The crystals were separated by dissolving excess Al in dilute hydrochloric acid (6N-HCl). The obtained crystals were removed, rinsed, and dried. Figure 2 shows the flow chart of the syntheses of the crystals. LEAlB<sub>14</sub> crystals were selected under a stereomicroscope for the measurements of chemical analyses, X-ray diffraction, microhardness, oxidation resistance and magnetic susceptibility. Phase analysis and determination of unit-cell parameters were carried out by a powder X-ray diffractometer (XRD, Rigaku, RINT). The morphology, size and the impurity content of the crystals were observed by a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray detector (EDX, Horiba, EMAX-2770), and the electron probe microanalysis (EPMA, JEOL,

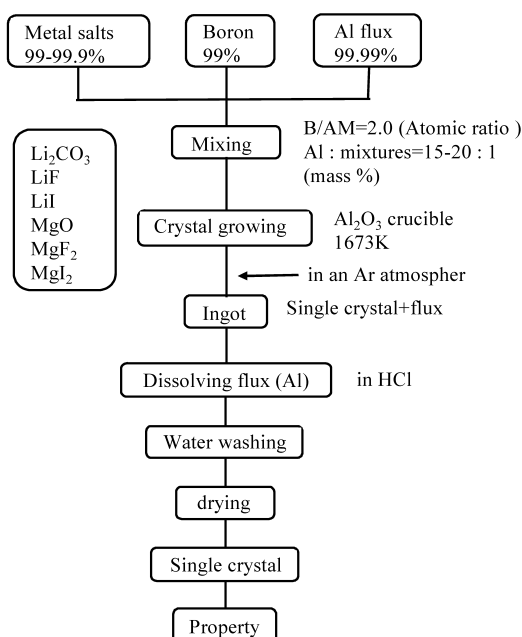


Fig.2 Flow chart for experimental condition of LEAlB<sub>14</sub> (LE = Li, Mg) crystals.

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### 2.2 Characterization

As-grown LEAlB<sub>14</sub> crystals were measured using a Vickers diamond indenter at room temperature. A load of 2.94 N was applied for 15 s and seven impressions were recorded for each sample. The obtained values were averaged and the experimental error was estimated. Pulverized samples of approximately 25 mg were heated between room temperature and 1473 K in air at a rate of 10 K·min<sup>-1</sup> by TG-DTA analyses[5]. Magnetic susceptibility of pulverized compounds was measured by using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) in the temperature range of 2 to 300 K, with a palladium sample used as a standard.

### 3. Results and Discussion

The results of the phase analysis are listed in Table 1. As seen from Table 1, four types of structure, namely LEAlB<sub>14</sub>, AIB<sub>2</sub>, α-AIB<sub>12</sub> and β-AIB<sub>12</sub>-type compound were identified, while crystals of γ-AIB<sub>12</sub>, MgAlB<sub>22</sub>, and binary compounds of magnesium-boron and lithium-boron[1,6,7] were not detected by XRD. For the Al-self flux growth using metal salts LEAlB<sub>14</sub> crystals could be obtained from all the different salts. However, the other phases are always obtained as AIB<sub>2</sub>, α-AIB<sub>12</sub> and β-AIB<sub>12</sub>-type compounds. We find that the large size of LiAlB<sub>14</sub> and MgAlB<sub>14</sub> crystals, with maximum dimensions of approximately 18 mm and 12 mm, are obtained when LiF and MgF<sub>2</sub> are used as the starting materials. But the LEAlB<sub>14</sub> crystals prepared with the other metal salts (Li<sub>2</sub>CO<sub>3</sub>, LiI, MgO, MgI<sub>2</sub>) had maximum dimensions of 50-150 μm, and not always sufficiently large for some property measurements.

Table 1 Typical growth conditions of LEAlB<sub>14</sub> (LE = Li or Mg) crystals.

Metal salts	Soaking temp. (K)	Soaking time (h)	Atomic ratios (B/LE=n)	Phases identified
Li <sub>2</sub> CO <sub>3</sub>	1673	5	2.0	LiAlB <sub>14</sub> , AIB <sub>2</sub> , α-AIB <sub>12</sub> , β-AIB <sub>12</sub> -type
LiF	1673	5	2.0	LiAlB <sub>14</sub> , AIB <sub>2</sub> , α-AIB <sub>12</sub> , β-AIB <sub>12</sub> -type
LiI	1673	5	2.0	LiAlB <sub>14</sub> , AIB <sub>2</sub> , α-AIB <sub>12</sub> , β-AIB <sub>12</sub> -type
MgO	1673	5	2.0	MgAlB <sub>14</sub> , AIB <sub>2</sub> , α-AIB <sub>12</sub> , β-AIB <sub>12</sub> -type
MgF <sub>2</sub>	1673	5	2.0	MgAlB <sub>14</sub> , AIB <sub>2</sub> , α-AIB <sub>12</sub> , β-AIB <sub>12</sub> -type
MgI <sub>2</sub>	1673	5	2.0	MgAlB <sub>14</sub> , AIB <sub>2</sub> , α-AIB <sub>12</sub> , β-AIB <sub>12</sub> -type

Therefore, the metal salts of Li<sub>2</sub>CO<sub>3</sub>, LiI, MgO, and MgI<sub>2</sub> probably do not have optimum solubility in the aluminium flux at high temperature. The MgAlB<sub>14</sub> and LiAlB<sub>14</sub> crystals obtained have well-developed {001} and {010} faces, and were black (for MgAlB<sub>14</sub>) and reddish black (for LiAlB<sub>14</sub>) with metallic luster. Single crystals having the typical crystal form are shown in Fig. 3 (MgAlB<sub>14</sub> (A) (for MgF<sub>2</sub>) and LiAlB<sub>14</sub> (B) (for LiF)). The LiAlB<sub>14</sub> crystals were enclosed by two large {100} faces, two large {010} faces and two large {001} faces. Although the impurity content of the LEAlB<sub>14</sub> crystals was not analyzed chemically, the EDX established the occurrence of traces of silicon and iron while aluminium was found to lie below the detection limit (< 0.05 %). Consequently the solid solubility of aluminium in LEAlB<sub>14</sub> is

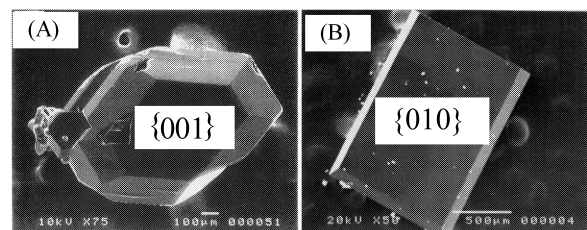


Fig.3 SEM photographs of MgAlB<sub>14</sub> (A) (for MgF<sub>2</sub>) and LiAlB<sub>14</sub> (B) (for LiF) crystals.

extremely small. No evidence was obtained for the presence of oxygen or fluorine-containing phases in the crystals, as concluded from EDX and EPMA analyses of as-grown crystals.

Unit-cell parameters for  $\text{LiAlB}_{14}$  were collected in Table 2. The unit-cell parameters of these compounds are in relatively good agreement with data published previously[4,7]. The values of unit-cell parameters are strong resemblance to ionic radii (Li (+1), 0.076 nm; Mg (+2), 0.072 nm) having coordination number 6[8].

Table 2 Unit-cell parameters of  $\text{LEAlB}_{14}$  (LE = Li or Mg) crystals.

Metal salts	Compounds	Unit-cell parameters (nm)			V ( $\text{nm}^3$ )	References
		a	b	c		
LiF	$\text{LiAlB}_{14}$	0.5846(2)	0.8144(2)	1.0355(3)	0.4930(2)	This work
$\text{Li}^*$	$\text{LiAlB}_{14}$	0.58469(9)	0.81429(8)	1.03542(6)	0.49297(8)	[4]
$\text{MgF}_2$	$\text{MgAlB}_{14}$	0.5845(2)	0.8114(2)	1.0330(4)	0.4899(3)	This work
$\text{Mg}^{**}$	$\text{MgAlB}_{14}$	0.5848(1)	0.8112(1)	1.0312(1)	0.4892(1)	[7]

Li\*:  $\text{Li}_2\text{B}_2\text{O}_7$ , Mg\*\*: Mg metal

The values of Vickers microhardness of the crystals are listed in Table.3. The values of Vickers microhardness are in the ranges of 20.2(0.5) to 28.6(0.4) GPa for  $\text{LiAlB}_{14}$ , and 25.5(0.5) GPa for  $\text{MgAlB}_{14}$ , respectively. The values measured on {100}, {010} and {001} faces of the  $\text{LiAlB}_{14}$  crystals are in comparatively good agreement with the values of these faces for  $\text{MgAlB}_{14}$ . Also, this anisotropic nature of hardness seems to be related to the difference in the number of  $\text{B}_{12}$  icosahedra units and B-B bonds for linkage of boron atoms in the structures.

Table 3 Vickers microhardness of  $\text{LEAlB}_{14}$  (LE = Li or Mg) crystals.

Metal salts	Compounds	Indentation planes	Hardness (GPa)	References
LiF	$\text{LiAlB}_{14}$	{100}	20.2(0.5)	This work
LiF	$\text{LiAlB}_{14}$	{010}	25.5(0.3)	This work
LiF	$\text{LiAlB}_{14}$	{001}	28.6(0.4)	This work
$\text{MgF}_2$	$\text{MgAlB}_{14}$	{010}	25.5(0.5)	This work

The oxidation process of  $\text{LiAlB}_{14}$  and  $\text{MgAlB}_{14}$  crystals were studied at temperatures below 1473 K by TG-DTA analyses, and results are shown in Fig. 4. The oxidation of  $\text{LiAlB}_{14}$  and  $\text{MgAlB}_{14}$  crystals starts at approximately 1058 and 920 K, respectively. The weight gain of the samples after TG determination are 41 mass% for  $\text{LiAlB}_{14}$  and 17 mass% for  $\text{MgAlB}_{14}$ , respectively. The final oxidation products, as analyzed by powder XRD, were  $\text{Li}_2\text{B}_2\text{O}_4$ ,  $\text{Al}_8\text{B}_2\text{O}_{15}$ ,  $\text{Al}_4\text{B}_2\text{O}_9$  and  $\text{B}_2\text{O}_3$ , and so the exothermic peaks (for  $\text{LiAlB}_{14}$ , 1229 K; for  $\text{MgAlB}_{14}$ , 1327 and 1419 K) are attributed to oxidation products.

Lately interesting magnetic behavior has been observed in  $\text{B}_{12}$  icosahedra compounds like  $\text{REB}_{50}$  (RE = rare earth) and  $\text{TbB}_{25}$ [9]. It was indicated that the magnetic interaction is mediated by the  $\text{B}_{12}$  icosahedra[9], which is a completely new phenomena in boride compounds. Although there are no atoms with large magnetic spin among the  $\text{LiAlB}_{14}$  and  $\text{MgAlB}_{14}$  samples, it is important to characterize the magnetic properties of these new  $\text{B}_{12}$  compounds, of which  $\text{LEAlB}_{14}$  has a structure similar to  $\text{TbB}_{25}$ , since the properties have been completely unknown to date. The temperature dependence of the magnetic susceptibility was measured down to 2 K, and the results of  $\text{LiAlB}_{14}$  and  $\text{MgAlB}_{14}$  are shown in Fig. 5 and 6. Neither  $\text{LiAlB}_{14}$  nor  $\text{MgAlB}_{14}$  exhibited superconductivity down to 2 K. The susceptibility measurements of  $\text{LiAlB}_{14}$  are diamagnetic ( $-4.4 \times 10^{-7} \text{ emu} \cdot \text{g}^{-1}$  at 300 K), and show an increase at

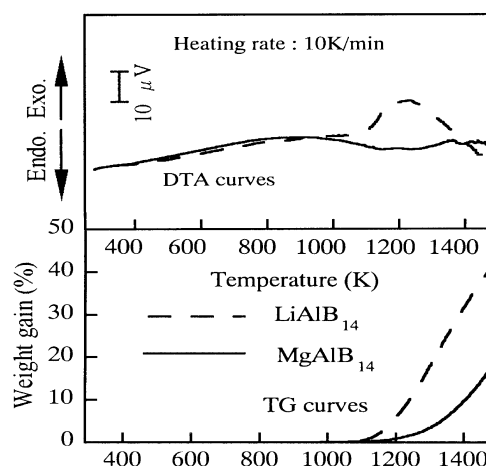


Fig.4 TG-DTA curves for  $\text{LiAlB}_{14}$  and  $\text{MgAlB}_{14}$ .

low temperatures indicative of the paramagnetic contribution. The susceptibility of the  $\text{MgAlB}_{14}$  does not show any particular features, with an increase at low temperatures indicative of a paramagnetic contribution, which is likely due to impurities or defects[10] below the detection level of our XRD measurements. We note that the paramagnetic contribution is much larger for  $\text{MgAlB}_{14}$  compared to  $\text{LiAlB}_{14}$ . Since the purity of the starting materials for both compounds is similar, this could indicate that it is easier for defects

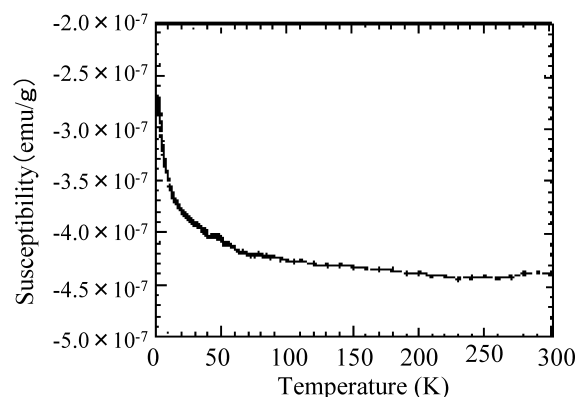


Fig.5 Temperature dependence of the magnetic susceptibility of  $\text{LiAlB}_{14}$ .

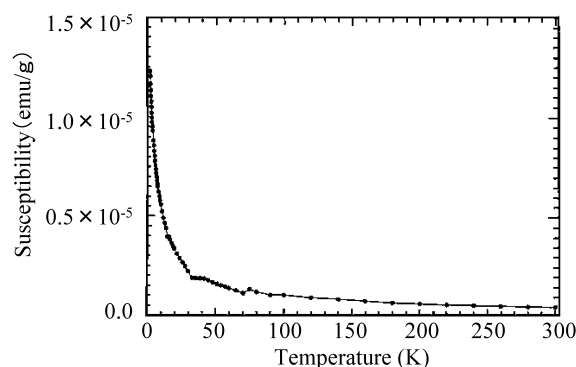


Fig.6 Temperature dependence of the magnetic susceptibility of  $\text{MgAlB}_{14}$ .

to be formed in MgAlB<sub>14</sub> which has a larger size of the alkali metal.

#### 4. Conclusions

Single crystals of LEAlB<sub>14</sub> (LE = Li, Mg) were grown from metal salts (Li<sub>2</sub>CO<sub>3</sub>, LiF, LiI, MgO, MgF<sub>2</sub>, MgI<sub>2</sub>) and crystalline boron as starting materials in Al self-flux under an Ar atmosphere. LiAlB<sub>14</sub> and MgAlB<sub>14</sub> crystals from the Al-self flux using metal salts could be obtained from all the different salts. The present study is the first to successfully utilize metal salts as starting materials for the crystal growth of higher borides. The maximum dimensions of LiAlB<sub>14</sub> and MgAlB<sub>14</sub> crystals were approximately 18 mm and 12 mm for the crystals obtained from LiF and MgF<sub>2</sub>. But the LEAlB<sub>14</sub> crystals prepared at the other metal salts (Li<sub>2</sub>CO<sub>3</sub>, LiI, MgO, MgI<sub>2</sub>) were smaller, and not always sufficiently large for some property measurements. The MgAlB<sub>14</sub> and LiAlB<sub>14</sub> crystals obtained have well-developed {001} and {010} faces, and were black (for MgAlB<sub>14</sub>) and reddish black (for LiAlB<sub>14</sub>) with metallic luster. The unit-cell parameters of these compounds are in relatively good agreement with data published previously. The values of Vickers microhardness are in the ranges of 20.2(0.5) to 28.6(0.4) GPa for LiAlB<sub>14</sub>, and 25.5(0.5) GPa for MgAlB<sub>14</sub>, respectively. The TG curves show that the oxidation of LiAlB<sub>14</sub> and MgAlB<sub>14</sub> crystals starts at approximately 1058 and 920 K, respectively. The susceptibility of LiAlB<sub>14</sub> is diamagnetic ( $-4.4 \times 10^{-7}$  emu·g<sup>-1</sup> at 300 K), and MgAlB<sub>14</sub> does not show any particular features, with the increase at low temperatures indicative of paramagnetic contributions.

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