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High Pressure Synthesis and Superconductivity of the Ternary Compounds $Mg(Mg_{1-x}Al_x)Si$ with the Anticotunnite Structure

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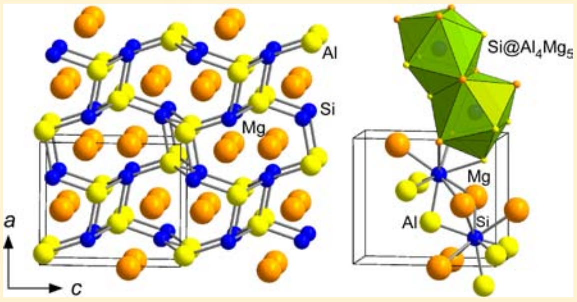
Supporting Information

ABSTRACT: Ternary compounds $Mg(Mg_{1-x}Al_x)Si$ ($0.3 < x < 0.8$) have been prepared under high pressure and high temperature conditions of 5 GPa at 800−1100 °C. The single crystal study revealed that the compound ($x = 0.45$) is isomorphous with the anticotunnite, or the TiNiSi structure, and crystallizes with space group *Pnma*, with lattice parameters $a = 6.9242(2)$, $b = 4.1380(1)$, $c = 7.9618(2)$ Å, and $Z = 4$. The compound with $x > 0.5$ shows superconductivity with a transition temperature (T_c) ∼ 6 K. The compound is a peritectic solid solution associated with other phases such as Mg_9Si_5, Al, and Si, depending on cooling protocols in the preparation. The band structure calculation on the composition MgAlSi suggests that the Al and Mg orbitals mainly contribute to the density of states near the Fermi level, and the substitution of Mg with Al favors the superconductivity.



INTRODUCTION

Since the discovery of high transition temperature ($T_c = 39$ K) superconductivity of MgB_2 with the AlB_2 structure,[1] much attention has been paid to isomorphous compounds to develop another high-T_c superconductor as well as to understand the superconducting mechanism. Alkaline earth (AE) alumino silicides AEAlSi (AE = Ca, Sr, Ba) adopt the AlB_2 structure, and have been found to become superconductors with relatively low T_cs of 7.8, 5.1, and 2.8 K,[2−8] respectively. In case of BaAlSi, the stoichiometric compound does not show superconductivity, but the nonstoichiometric compounds with excess silicon, $BaAl_{1-x}Si_{1+x}$ ($x \geq 0.05$), become superconductors.[8] Although AEAlSi are not high-T_c superconductors, the compounds are composed of only ubiquitous elements, and would be useful in application if superconductors with higher-T_cs are developed. The T_c of the AEAlSi increases as the size of AE atoms decreases; it is interesting to synthesize MgAlSi containing the smallest AE atoms. There are a number of ternary compounds in AE−Al−Si systems, including typical Zintl compounds $AEAl_2Si_2$ (AE = Ca, Sr, and Ba) besides AEAlSi.[9−13] It is strange, however, that the existence of any analog in the Mg−Al−Si system has not been reported in a bulk phase.

Recently in the study of a commercial Al alloy, it has been shown that several kinds of Mg−Al−Si ternary and Mg−Si binary compounds precipitate during low temperature hardening process.[14,15] A commercial Al alloy such as alloy 6082 contains less than 1 wt % of Mg and Si as alloying agent; very fine binary and ternary rods or needles with 10−15 nm in diameter are precipitated in Al matrix. With advanced analytical techniques using an electron microscope on thin specimens, the crystal structures, compositions, and the orientation of the fine precipitates in Al matrix have been studied. The formations of ternary compounds MgAlSi, $MgAl_2Si_2$, and $AlMg_4Si_6$ and binary compounds Mg_5Si_6 and $Mg_{1.8}Si$ have been established. For the industrial use of an Al alloy, the formation of fine coherent precipitates in the matrix without boundary is considered to play an important role for the hardening of the alloy. It is reasonable to expect that Al matrix may apply a high pressure in the formation of the precipitates, which have not been obtained under ambient pressure. In this study, an attempt has been made to prepare Mg containing ternary compounds as a bulk phase using high pressure and high temperature conditions.

EXPERIMENTAL SECTION

1. High Pressure and High Temperature (HPHT) Synthesis. Mg−Al−Si ternary metal mixtures in various nominal compositions were preheated using an h-BN crucible at 750 °C for 2 h in an RF furnace under an Ar gas stream. Reagent grade chemicals were used, Mg (98.5%, Sigma-Aldrich Chemicals), Al (99.999%, Katayama Chemicals), and Si (99.999%, Furu-uchi Chemicals). The preheated samples were ground in a glovebox (MBRAUN) and further treated under HPHT conditions using a Kawai-type multianvil press. The powder sample was filled in an h-BN cell (4.5 mm in inner diameter, 8.5 mm in depth) and placed in a graphite tube heater, which was surrounded by a calcined pyrophyllite tube for thermal insulation. The whole assembly was placed at the center of cubic anvils. Details of a similar type of assembly were given elsewhere.[16] A typical HPHT condition was 5 GPa at 1000 °C, and the sample was cooled down to room temperature using different thermal protocols. The sample can be quenched to room temperature within a few minutes when the electric power supply is turned off.

2. Characterization. X-ray single crystal analysis was carried out using a diffractometer Smart-APEX II (Bruker) equipped with a CCD

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detector and a rotary anode X-ray source (Mo Kα radiation with a mirror monochromator). The single crystal structure was refined with the program SHELX97 and WinGX software package.[17,18] X-ray powder diffraction (XRD) patterns were measured by an imaging plate Guinier diffractometer (Huber 670G) using Mo Kα1 radiation (λ = 0.710726 Å) with a glass capillary goniometer, and by a Bruker D8 diffractometer with Cu Kα radiation (λ = 1.5406 Å). The powder patterns obtained by the Guinier diffractometer were analyzed by the Rietveld refinement program TOPAS-Academic to determine the lattice parameters and the weight fractions of the coexisting phases.[19] Chemical compositions were analyzed using electron probe microanalyzers (EPMA), JCMA-733 of JEOL and Genesis XM2 of EDAX, with standards of MgO, Al_2O_3, and Si for Mg, Al, and Si, respectively; the samples were embedded in epoxy resin and polished to avoid topographic effect. Magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design SQUID-VSM) under a field of 20 Oe. Electrical resistivity was measured on a pellet sample using a 4-probe ac resistance bridge (Lake Shore, Model 370AC) and a cryostat (Niki Glass, LTS-205-TU) in a temperature range down to 2.4 K. The pellet was prepared by compression of a preshaped powder sample under a hydrostatic pressure of 1.2 kbar in an evacuated nylon bag.[20] The ab initio calculations of the band structure and the density of states were performed within the density of functional theory (DFT) framework, using the program CASTEP in the Accelrys software suite.[21,22] The calculations were carried out using the GGA-PBE (general gradient approximation, Perduw−Burke−Ernzehof) functional. Ultrasoft pseudopotentials were used within a plane wave basis with cut off energy of 310 eV.

■ RESULTS AND DISCUSSION

1. HPHT Synthesis. The ternary mixtures preheated in an RF furnace at 750 °C were found to be composed of a mixture of Mg_2Si (antifluorite structure), Al, and Si. Then, we have treated the preheated mixture with a nominal composition $Mg_{4.4}Al_{4.0}Si_{3.0}$ at 5 GPa and 950 °C for 1 h, followed by slowly cooling down to 580 °C during 2.5 h before quenching to room temperature. Figure 1 shows the XRD pattern of the product, which is very different from that obtained at ambient pressure. Figure 2 shows the compositional scanning electron microscopy (SEM) image of the same product. The compositions of large grains were analyzed and the results are shown in Table 1; it was revealed that the grains were a ternary compound with a composition $Mg_{0.52}Al_{0.15}Si_{0.33}$ (= $Mg_{1.55}Al_{0.45}Si$). Some single crystals were picked up from the product, and the structure was successfully determined as shown in Tables 2 and 3. The ternary compound was found to be isomorphous with TiNiSi, and the XRD pattern shown in Figure 1 was attributable to a mixture of the ternary compound and Al metal.

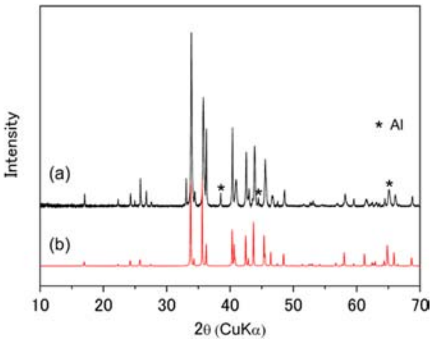

Figure 1. (a) XRD pattern for the sample obtained by HPHT treatment of a mixture with a nominal composition $Mg_{4.4}Al_{4.0}Si_{3.0}$ and (b) the simulation XRD pattern on the basis of the single crystal study for the orthorhombic phase $Mg(Mg_{0.55}Al_{0.45})Si$.

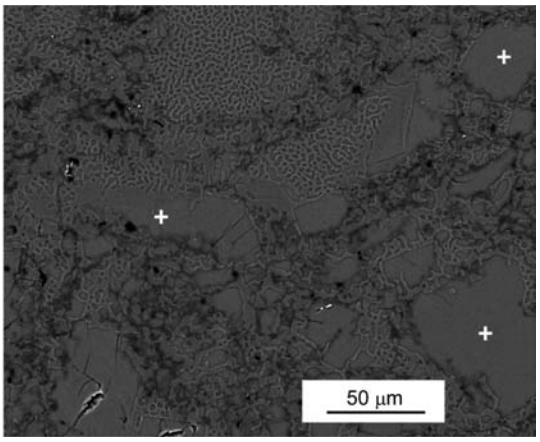

Figure 2. SEM compositional image of the sample with a nominal composition $Mg_{4.4}Al_{4.0}Si_{3.0}$. The compositions of the marked grains were analyzed by EPMA.

Table 1. Compositions of the Ternary Compounds Determined by EPMA and EDX on the Samples Obtained from Various Nominal Compositions after HPHT Treatment

nominal composition	Found			
	atomic %			formula
formula	Mg	Al	Si	$Mg(Mg_{1-x}Al_x)Si$
$Mg_{4.4}Al_{4.0}Si_{3.0}$	51.53	15.34	33.13	x = 0.45
$Mg(Mg_{1-x}Al_x)Si$				
x = 0.3	54.22	12.16	33.62	x = 0.37
x = 0.4	53.54	13.15	33.31	x = 0.4
x = 0.5	48.91	17.83	33.26	x = 0.54
x = 0.8	48.14	18.2	33.67	x = 0.55
x = 1.0	41.81	24.49	33.69	x = 0.74
x = 1.0	42.17	21.62	33.70	x = 0.71
x = 1.0	40.23	26.33	33.43	x = 0.80

2. Single Crystal Analysis. The ternary compound $Mg_{1.55}Al_{0.45}Si$ crystallizes space group *Pnma* with the lattice parameters a = 6.9242(2), b = 4.1388(1), and c = 7.9618(2) Å. The unit cell contains 4 formula units. Since there are three 4c sites in the unit cell, the formula should be $Mg(Mg_{0.55}Al_{0.45})Si$. As will be shown later, this ternary compound is one of the solid solutions with a general formula $Mg(Mg_{1-x}Al_x)Si$, where the Si content is always 33.3 atomic %, and the Al site is partially substituted with Mg. The coordinates and equivalent displacement parameters for the ternary compound are listed in Table 3. Figure 3 shows a schematic structural model of $Mg(Mg_{0.55}Al_{0.45})Si$. The structure is isomorphous with TiNiSi, a very popular versatile structure identified for hundreds of compounds composed of transition metal (T) and main group (X) elements MTX. The structure and bonding of the TiNiSi family of compounds have been studied and discussed by Landrun et al.[23] In the TiNiSi family, the compounds containing only ubiquitous elements without transition metals are very rare. The structure can be viewed as being composed of two-dimensional sheets of edge-sharing half-chair six-membered rings,[6] which are linked along the a direction, and Mg atoms sitting in the large channels. The Al sites are partially replaced with Mg atoms. The structure can also be viewed as

Table 2. Details of the Crystal Structure Investigations for $Mg(Mg_{0.55}Al_{0.45})Si$

	$Mg(Mg_{0.55}Al_{0.45})Si$
formula weight	267.9
crystal size (mm)	0.1 × 0.1 × 0.1
space group	*Pnma* (no. 62)
R_{int}	0.034
a (Å)	6.9242(2)
b (Å)	4.1380(1)
c (Å)	7.9618(2)
V (Å^3), Z	228.12(1), 4
d_{calc} (g/cm^3)	2.269
temperature (K)	293
λ Mo Kα (Å)	0.71073
μ mm^{-1}	1.173
absorption correction	empirical
$F(000)$	154
θ_{max} (deg)	28.17
index ranges	$-9 < h < 9$, $-5 < k < 5$, $-10 < l < 9$
reflection numbers	7800
total reflections	318
observed $[I \geq 2\sigma(I)]$	281
no. of variables	19
GOF on F_o^2	1.092
$R1/wR2$ $[I \geq 2\sigma(I)]$	0.0162/0.0297
$R1/wR2$ (all data)	0.0214/0.0329
largest diff. peak and hole (e$^-$/Å^3)	0.294, −0.312

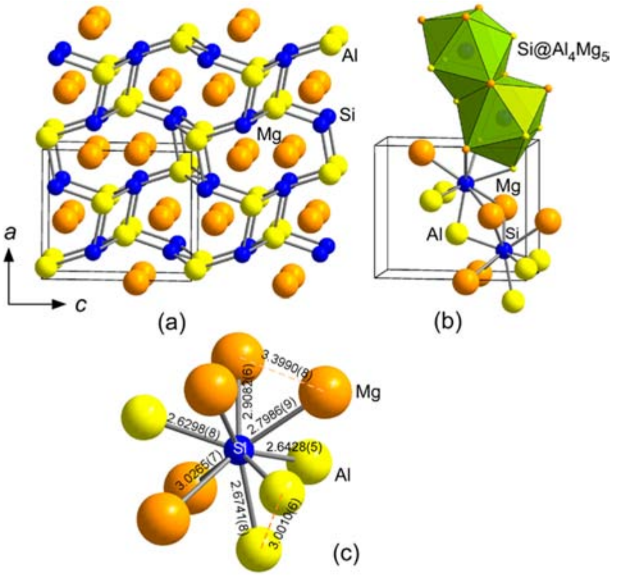

Figure 3. Schematic illustration of the crystal structure of MgAlSi: (a) a structural view isomorphous with TiNiSi with two-dimensional [AlSi] hexagonal sheets linked along the *a* direction, (b) a structural view emphasizing the structure isomorphous with the anticotunnite structure, (c) (Mg, Al) coordination polyhedron surrounding a Si atom, and some atomic distances.

the anticotunnite ($PbCl_2$) structure, where the electronegative Si atoms are surrounded by electropositive (Mg, Al) atoms as shown in Figure 3b. Each Si atom is coordinated by 9 (Mg, Al) atoms. The (Mg, Al) coordination polyhedra are linked by sharing triangles.

Recently Mg_2Si with the antifluorite structure (ambient pressure phase) was compressed under high pressure using a diamond anvil cell (DAC).[24,25] It was found that Mg_2Si was transformed to the anticotunnite structure at 7.5−10.4 GPa, and then to the $InNi_2$ structure at 22.2 GPa. In the anticotunnite structure, hereafter called $(Mg_2Si)_{HP}$, the Si atom is coordinated by 9 Mg. This coordination number is larger than 8 of the Mg in Mg_2Si of the antifluorite structure (ambient pressure phase). Although it is difficult to distinguish Al and Si sites by XRD study, it is evident that the present compound has the anticotunnite structure with the electronegative Si atoms being surrounded by electropositive Mg and Al atoms as shown in Figure 3b. The atomic distances of the polyhedron with a Si atom at the center are shown in Figure 3c. Note that the atomic distances between Al−Al (3.001 Å) and Mg−Mg (3.399 Å) sites are close to those of the corresponding metals, 2.86 and 3.22 Å, respectively, implying that the compound is composed of metallic packing of Al and Mg atoms with Si atoms occupying the nine coordination sites in the packing.

As mentioned in the foregoing paragraph, it has been reported that the ternary compound MgAlSi with the TiNiSi structure precipitates from Al alloy matrix during isothermal aging at moderate temperatures.[14] The study by an electron microscope showed that the precipitate had a stoichiometric composition MgAlSi with the lattice parameters (a = 6.75, b = 4.05, c = 7.94 Å) slightly smaller than those found in this study. It is evident that the precipitate has a very similar structure with that obtained under high pressure in this study. The ternary compound is a high pressure phase, which cannot be obtained under ambient pressure; it is reasonable to assume that the ternary precipitates are formed under high pressure from Al alloy matrix during the hardening process.

3. FORMATION OF SOLID SOLUTIONS

The ternary mixtures with various nominal compositions $Mg(Mg_{1-x}Al_x)Si$ ($0.3 \leq x \leq 1.0$) were treated under HPHT conditions of 5 GPa and 1000 °C, followed by slowly cooling down to 500 °C and quenching to room temperature. Some mixtures were directly cooled down from 1000 °C to room temperature by quenching under pressure. The content of the orthorhombic anticotunnite phase varies depending on the cooling protocols; the content decreased and was associated with a larger amount of Mg_9Si_5, Al, and Si when the product was cooled down by quenching under pressure. Mg_9Si_5, a binary compound found in an Al alloy matrix during precipitation hardening, adopts a hexagonal unit cell (space group $P63/m$, a = 7.15 and c = 12.15 Å).[15] This finding suggests that the orthorhombic phase is a peritectic compound, the decomposition temperature being estimated to be around

Table 3. Atomic Coordinates and Equivalent Displacement Parameters for $Mg(Mg_{0.55}Al_{0.45})Si$

atom	position	x	y	z	U_{eq}, Å^2
Si	4c	0.25919(8)	3/4	0.37658(7)	0.0159(1)
Mg	4c	0.46833(10)	1/4	0.16710(9)	0.0182(2)
$Mg_{0.55}Al_{0.45}$	4c	0.13913(9)	3/4	0.06321(8)	0.0145(2)

700–800 °C. Figure 4 shows the Rietveld refinement of the product obtained from a ternary mixture with a nominal composition $Mg(Mg_{0.5}Al_{0.5})Si$. The product can be refined as a mixture of two phases, 90 wt % of the orthorhombic phase and 10 wt % of Mg_9Si_5.

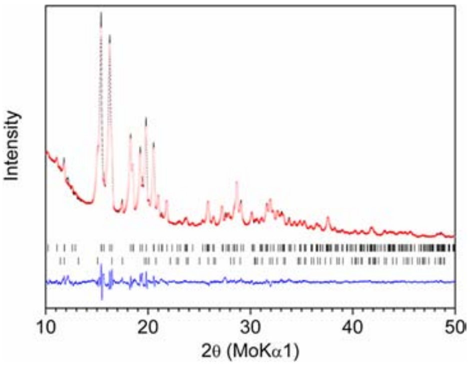

Figure 4. Rietveld refinement of the XRD pattern of the sample obtained from a mixture with a composition $Mg(Mg_{0.5}Al_{0.5})Si$ by slow cooling after HPHT treatment. Open circles show the observed data points, and the solid line represents the calculated diffraction pattern. The pattern can be refined as a mixture of two phases, 90% of the ternary compound (top tick marks) and 10% of Mg_9Si_5 (bottom tick marks).

The compositions of the products obtained from different nominal compositions by slow cooling were analyzed by EPMA, and the results are shown in Table 1. Note that the contents of Si in the solid solutions are always unchanged at ~33.3 atomic %, suggesting that the composition should be $Mg(Mg_{1-x}Al_x)Si$ as found in the single crystal analysis. As the Al content in the nominal composition increases, the Al content in the solid solution tends to increase. However, the product has a distribution in composition even from the same batch as shown for the case of the nominal composition $x = 1.0$ in Table 1.

The relationship between the compositions of the solid solutions and the lattice parameters is shown in Figure 5. Although there is a distribution in the composition, the lattice parameters vary with the composition, following Vegard's law for solid solutions. It is likely that the compositional distribution of the products observed even in the same batch sample would be caused by temperature distribution and cooling rate of reaction mixtures.

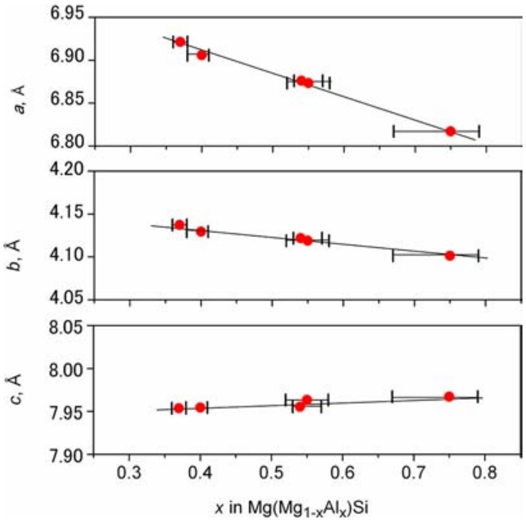

Figure 5. Lattice parameters of the ternary compounds $Mg(Mg_{1-x}Al_x)Si$ as a function of x. The compositional distribution for each sample is shown by error bars.

4. SUPERCONDUCTIVITY

Figure 6 shows the magnetic susceptibility of the sample obtained from a mixture with a nominal composition MgAlSi, which contains the orthorhombic compound $Mg(Mg_{0.25}Al_{0.75})Si$ as a major phase, and a small amount of a mixture of the hexagonal phase Mg_9Si_5 + Al + Si. The compounds with $x > 0.5$ for $Mg(Mg_{1-x}Al_x)Si$ show superconductivity with T_c 5.5–6.0 K, and a large superconducting shielding volume fraction >80%. The highest T_c was observed at $x \approx 0.75$. The resistivity of the same sample is shown in Figure 7. The temperature dependence of the resistivity also showed a sharp superconducting transition at 5.7 K, corresponding to the temperature found in the magnetic susceptibility measurement. The solid solutions with $x < 0.5$ also showed a weak diamagnetic transition due to superconductivity; however, the superconducting volume fraction was smaller than a few percent. When the compositional distribution of the solid solution is taken into account, it is reasonable that the solid solutions with superconducting volume fraction <5% should be excluded from superconductors.

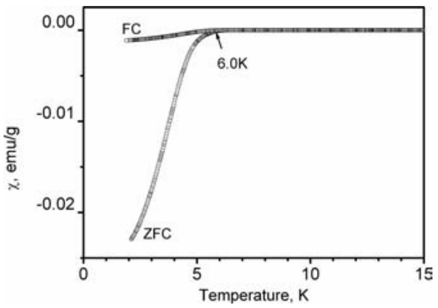

Figure 6. Magnetic susceptibility of the ternary sample obtained from a mixture with a nominal composition MgAlSi as a function of temperature measured under a field of 20 Oe using zero-field-cooling (ZFC) and field-cooling (FC) mode. A superconducting transition was observed at 6.0 K. The shielding volume fraction was estimated to be 80%.

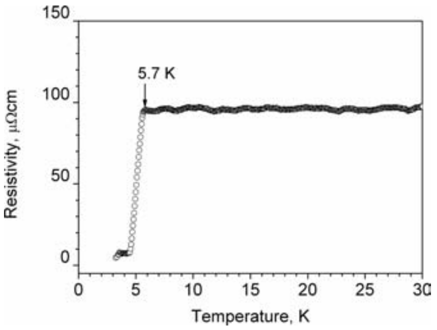

Figure 7. Temperature dependence of the resistivity of the ternary compound obtained from a mixture with a nominal composition of MgAlSi.

5. ELECTRONIC BAND STRUCTURE

The band structure of the orthorhombic compound with a stoichiometric composition MgAlSi was calculated after the structural optimization using CASTEP. $(Mg_2Si)_{HP}$ was also optimized to a structure with $a = 7.0581$, $b = 4.2230$, $c = 8.0642$ Å, and the band structure was calculated to compare with that of MgAlSi. The results are compared in Figure 8. The nonzero DOS (density of states) at the Fermi levels confirm that both compounds have metallic character. In the band structure of MgAlSi, the Mg and Al orbitals mainly contribute to the DOS at the Fermi level, and the Si and Al 3s and 3p orbitals form valence bands. The Mulliken population analysis has been done on the two compounds, and the Mulliken charges are compared in Table 4. As can be seen from the table, $(Mg_2Si)_{HP}$ is an ionic compound like a Zintl phase with a formal charge $(Mg^{2+})_2Si^{4-}$. The Fermi level of $(Mg_2Si)_{HP}$ is located at the DOS valley, supporting that the compound has a Zintl character.

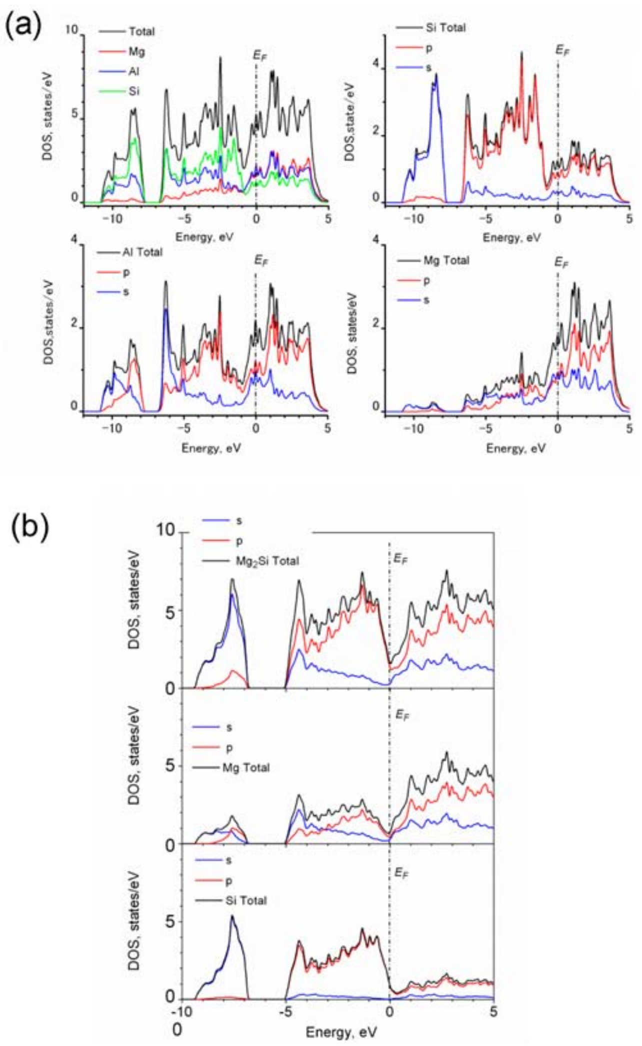

Figure 8. Electronic density of states (DOS) for the stoichiometric MgAlSi (a) and $(Mg_2Si)_{HP}$ (b) calculated using CASTEP software.

The DOS profiles of the two kinds of compounds can be compared within the rigid-band framework. The two kinds of profiles are very similar, and the Fermi energy on the DOS of $(Mg_2Si)_{HP}$ is shifted toward a higher energy by about 1.5 eV upon the substitution of divalent Mg with trivalent Al atoms in MgAlSi. The shift of the Fermi level from the DOS valley increases the DOS near the Fermi level, which will be beneficial for superconductivity. The T_c dependence on the composition may be interpreted in relation with the Fermi level shift upon the substitution.

Table 4. Mulliken Charge Distribution Calculated by CASTEP for MgAlSi and Mg_2Si with the Anticotunnite Structure

	$(Mg_2Si)_{HP}$		MgAlSi	
position	atom	charge	atom	charge
4*c* (channel)	Mg	0.58	Mg	0.76
4*c*	Mg	0.45	Al	−0.41
4*c*	Si	−1.03	Si	−0.35

■ CONCLUSIONS

The ternary solid solutions $Mg(Mg_{1-x}Al_x)Si$ $(0.3 < x < 0.8)$ isomorphous with the anticotunnite structure have been prepared in a bulk phase using HPHT conditions. The compound showed superconductivity with $T_c = 6.0$ K when $x > 0.5$. A similar ternary compound has been reported as fine precipitates in Al alloy containing Mg and Si during age hardening. It is reasonable to expect that the Al alloy matrix acts as high pressure media for the precipitation of the high pressure phase compound.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF file for $Mg(Mg_{0.55}Al_{0.45})Si$. This is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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