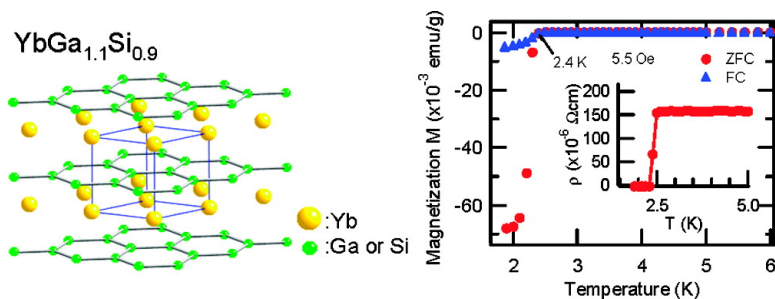Communication

Superconductivity in the AlB-Type Ternary Rare-Earth Silicide YbGaSi

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Superconductivity in the AlB$_2$-Type Ternary Rare-Earth Silicide YbGa$_{1.1}$Si$_{0.9}$

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Superconductivity with a critical temperature (T_C) of 39 K, the highest T_C among intermetallics, was reported in MgB$_2$.[1] MgB$_2$ crystallizes in a layered structure, that is, the AlB$_2$-type (space group $P6/mmm$, No. 191, $Z = 1$), in which B atoms form honeycomb layers and Mg atoms are intercalated between the B layers. Because the layered structure plays a significant role in the superconductivity in MgB$_2$,[2] a search for new layered superconducting materials was conducted. In this search, ternary silicides M$_{AE}$M$_{TRx}$Si$_{2-x}$ (M$_{AE}$ = Ca, Sr, and Ba, M$_{TR}$ = Al and Ga) were found to be superconducting materials with AlB$_2$-type or its derivative structures.[3–9] Figure 1 illustrates the crystal structure of the AlB$_2$-type M$_{AE}$M$_{TRx}$-Si$_{2-x}$, in which M$_{TR}$ and Si atoms form honeycomb layers and M$_{AE}$ atoms are intercalated between the honeycomb layers. The formation of Si–M$_{TR}$ honeycomb layers is interesting because Si atoms energetically tend to form puckered hexagonal layers instead of honeycomb layers.[10] Recently, superconductivity was reported in other layered materials, such as the graphite intercalation compounds (GICs) CaC$_6$ (T_C = 11.5 K) and YbC$_6$ (T_C = 6.5 K).[11] Since these two GICs have higher T_C's than those of other GICs, various origins of superconductivity have been proposed.[11–13] In these GICs, C atoms form honeycomb layers and Ca or Yb atoms are inserted between the honeycomb layers as intercalants. Interestingly, M$_{AE}$M$_{TRx}$Si$_{2-x}$ and the GICs have structural similarities: honeycomb structured layers and metal atoms intercalated between the honeycomb layers, which suggests a possibility that ternary Yb–M$_{TR}$–Si systems have the superconducting AlB$_2$-type intermetallic, as in the case of Ca–M$_{TR}$–Si systems.[4,5] It is thus of great interest to examine whether superconductivity appears in the layered materials with the honeycomb layers that consist of different elements, that is, the C honeycomb layers and the Si–M$_{TR}$ honeycomb layers, with the same intercalant such as Ca or Yb, for the further understanding of the superconductivity in layered materials. To the best of the authors' knowledge, there are no published reports on the ternary intermetallics YbM$_{TRx}$Si$_{2-x}$ or on superconducting AlB$_2$-type ternary rare-earth silicides. In particular, the new material search in the Yb–Ga–Si system is intriguing because no work has focused on the Yb–Ga–Si ternary intermetallics. Furthermore, the discovery of the AlB$_2$-type YbM$_{TRx}$Si$_{2-x}$ could provide a way of understanding the origin of superconductivity in YbC$_6$ and CaC$_6$, which is a controversial issue.[12,13]

In this paper, we report the synthesis of a novel ternary rare-earth silicide, YbGa$_{1.1}$Si$_{0.9}$, with the AlB$_2$-type structure and show that YbGa$_{1.1}$Si$_{0.9}$ is a type-II superconducting material with a T_C of 2.4 K.

Samples were synthesized in two stages: Ar-arc melting of a 1:1.15:0.85 molar mixture of Yb (nominal purity 99.9%), Ga (nominal purity 99.999%), and Si (nominal purity 99.9999%), followed by annealing of the samples. The samples were typically annealed at 1273 K for 1 h and then cooled down to 1073 K at 0.1 K/min.

The chemical compositions were determined to be 32.7(2) atom % Yb, 38.4(3) atom % Ga, and 28.9(3) atom % Si using electron
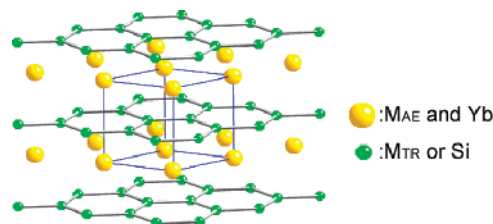

Figure 1. Crystal structure of M$_{AE}$M$_{TRx}$Si$_{2-x}$ (M$_{AE}$ = Ca, Sr, and Ba; M$_{TR}$ = Al and Ga) and YbGa$_{1.1}$Si$_{0.9}$. The yellow spheres represent M$_{AE}$ and Yb atoms and the green ones Si and M$_{TR}$ atoms, respectively. In the case of YbGa$_{1.1}$Si$_{0.9}$, Si and Ga atoms form chemically disordered honeycomb layers and Yb atoms are intercalated between the layers.

probe microanalysis (EPMA); the corresponding chemical formula is Yb$_{0.98}$Ga$_{1.15}$Si$_{0.87}$ (hereafter denoted as YbGa$_{1.1}$Si$_{0.9}$). The Cu concentration in the sample was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) to be lower than 0.003 wt %, which indicates that the sample is free of Cu contamination from the Cu hearth of the arc furnace.

The crystal structure of the single-crystalline samples at room temperature was determined using X-ray diffractometry with a three-circle goniometer combined with a CCD area detector (graphite-monochromatized Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å). We refined the diffraction data on the basis of three structure models, the AlB$_2$-type, the CeCd$_2$-type (space group $P\bar{3}m1$, No. 164, $Z = 1$),[14] and the BaPtSb-type (space group $P\bar{6}m2$, No. 187, $Z = 1$).[15] Si and Ga atoms form chemically disordered honeycomb layeres in the AlB$_2$-type (Figure 1), chemically disordered puckered hexagonal layers in the CeCd$_2$-type, and chemically ordered honeycomb layers in the BaPtSb-type. The R and wR indexes are 2.49 and 5.89% for the AlB$_2$-model, 2.45 and 5.94% for the CeCd$_2$-model, and 2.69 and 6.53% for the BaPtSb-model, respectively. In the CeCd$_2$-model, the atomic coordinate z was refined to be 0.5003-(5), which means that the hexagonal layers are flat; in this case, the CeCd$_2$-model is presumed to be identical with the AlB$_2$-model. Since adding parameters to the AlB$_2$-type does not show significant improvement in both R and wR indexes and the symmetry of the AlB$_2$-type is the highest among the three, we concluded that YbGa$_{1.1}$Si$_{0.9}$ has the AlB$_2$-type structure with lattice parameters $a = 4.1275(3)$ Å and $c = 4.2357(4)$ Å. The chemical formula deduced from this refinement is YbGa$_{1.13}$Si$_{0.87}$, which is consistent with that determined using EPMA (see Supporting Information for detail of the crystal structure and the powder X-ray diffraction pattern). YbGa$_{1.1}$Si$_{0.9}$ is isostructural with another ternary rare-earth silicide EuGa$_x$Si$_{2-x}$ (0.276 ≤ x ≤ 1.67), which does not superconduct down to 2 K.[16]

Figure 2 gives a plot of the electrical resistivity ρ as a function of temperature, where the value of ρ is 2.19×10^{-4} Ω cm at 300 K. The ρ value decreases with decreasing temperature, which indicates that YbGa$_{1.1}$Si$_{0.9}$ is a metal. The inset of Figure 2 is ρ for temperatures ranging from 1.9 to 3.5 K in field cooling at various
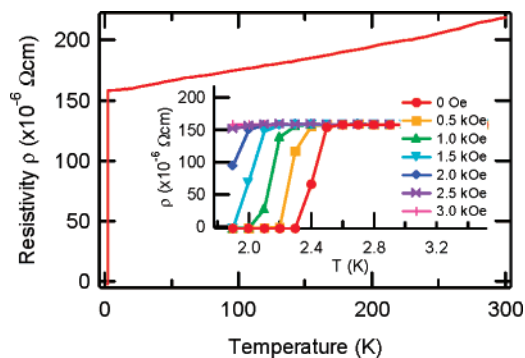
Figure 2. Electrical resistivity ρ as a function of temperature. The inset is ρ in various magnetic fields from 0 to 3.0 kOe in steps of 0.5 kOe (right to left) as a function of the temperature.
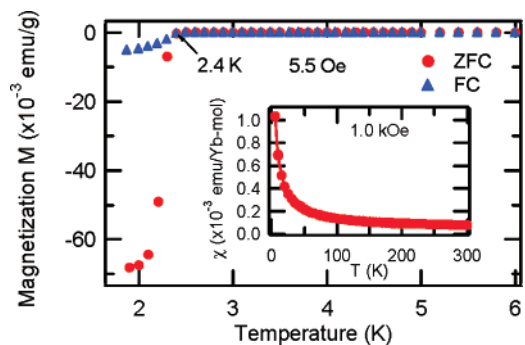

Figure 3. Magnetization (M) in zero field cooling (ZFC) and field cooling (FC) at an applied magnetic field (H) of 5.5 Oe as a function of temperature. The inset is the magnetic susceptibility χ measured after ZFC at H of 1.0 kOe as a function of temperature. The solid line is a fitting to the Curie–Weiss law: $\chi = C/(T - \theta) + \chi_0$.

magnetic fields. At 0 Oe, ρ starts to decrease significantly at 2.5 K and is found to become negligibly small at 2.3 K. The width of the transition ΔT (90%-10%) is small, approximately 0.2 K. These results suggest that YbGa$_{1.1}$Si$_{0.9}$ is a superconducting material with a T_C of approximately 2.4 K, as confirmed from the magnetization measurements. The residual resistivity ratio (RRR), $\rho_{300K}/\rho_{2.6K}$, is 1.38. The superconducting transition was suppressed by applying a magnetic field; no transition was observed at 3.0 kOe.

In Figure 3, the dc magnetization, M, measured in zero-field cooling (ZFC) and field cooling (FC) at an applied field, H, of 5.5 Oe is shown as a function of temperature, indicating that the Meissner effect is observed at temperatures below 2.4 K. This confirms that YbGa$_{1.1}$Si$_{0.9}$ is a superconducting material with a T_C of 2.4 K, as suggested by the electrical resistivity measurements. The magnetic shielding fraction in ZFC and the flux exclusion in FC at 1.9 K are approximately 100% and 8%, respectively, of the theoretical value of perfect dimagnetism, which suggests that the superconductivity is a bulk effect. For these evaluations, we used a density of 7.336(1) g/cm^3, which was calculated from the single-crystal diffraction data. The M–H curve measured at 1.9 K after ZFC indicates that YbGa$_{1.1}$Si$_{0.9}$ has lower and upper critical fields, which is indicative of a type II superconductor (see Supporting Information). Our preliminary study on YbGa$_x$Si$_{2-x}$ suggests that YbGa$_x$Si$_{2-x}$ with x approximately ranging from 1.1 to 1.3 is a superconducting material with an onset temperature higher than 1.9 K and that T_C decreases with x, which is one reason why we focus on YbGa$_{1.1}$Si$_{0.9}$ in this paper.

Since a Yb atom can have two kinds of valence states, Yb^{2+} and Yb^{3+}, we examined the valence state of the Yb atoms in YbGa$_{1.1}$Si$_{0.9}$ from the temperature dependence of the dc magnetic susceptibility χ (inset of Figure 3). The data can be fitted to the Curie–Weiss law, $\chi = C/(T - \theta) + \chi_0$, where C is the Curie constant, θ is the Weiss constant, and χ_0 is a temperature-independent term; the obtained values of C, θ, and χ_0 are 9.01(3) $\times$ 10^{-3} emu·K/Yb-mol, $-4.152(3)$ K, and 4.93(2) $\times$ 10^{-5} emu/Yb-mol, respectively. The molar fraction of Yb^{3+} was estimated to be approximately 0.35% from the value of C, assuming the following relation: $C = mC_{Yb^{3+}} + (1 - m)C_{Yb^{2+}}$, where m is the molar fraction of Yb^{3+} and C$_{Yb^{3+}}$ and C$_{Yb^{2+}}$ are the calculated Curie constants of Yb^{3+} (2.58 emu·K/Yb-mol) and Yb^{2+} (0 emu·K/Yb-mol), respectively.[17] The small value of the molar fraction of Yb^{3+} suggests that the Yb atoms in YbGa$_{1.1}$Si$_{0.9}$ are divalent, as in the case of YbC$_6$.[18]

In conclusion, the novel intermetallic YbGa$_{1.1}$Si$_{0.9}$ with the AlB$_2$-type structure was synthesized. The electrical resistivity and dc magnetization measurements revealed that YbGa$_{1.1}$Si$_{0.9}$ is a type II superconducting material with a T_C of 2.4 K, and that the Yb atoms in YbGa$_{1.1}$Si$_{0.9}$ are divalent. This study shows that superconductivity occurs in both the AlB$_2$-type ternary silicides and GICs with the same intercalant. Comparisons between these two material groups will contribute to the further understanding of superconductivity in the layered materials.

Supporting Information Available: Crystal structure data of YbGa$_{1.1}$Si$_{0.9}$, powder X-ray diffraction pattern, and M–H curve measured at 1.9 K after ZFC. This material is available free of charge via the Internet at http://pubs.acs.org.

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