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Pressure effect on critical temperature for superconductivity and lattice parameters of AlB_2-type ternary silicide $YbGa_{1.1}Si_{0.9}$

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Electrical resistivity and x-ray diffraction measurements have been carried out to investigate the pressure effect on the critical temperature for superconductivity (T_C) and lattice parameters of AlB_2-type superconducting silicide $YbGa_{1.1}Si_{0.9}$ ($T_C = 2.4$ K) and its reference material CaGaSi ($T_C = 4.5$ K). The electrical resistivity measurements up to 2.5 GPa reveal that T_C decreases with pressure for both silicides and the pressure derivative of T_C (dT_C/dP) is -0.78 K/GPa and -0.026 K/GPa for $YbGa_{1.1}Si_{0.9}$ and CaGaSi, respectively. X-ray diffraction measurements up to 3.5 GPa indicate both silicides do not exhibit structural changes in this pressure range and they have similar values for the bulk moduli: $B_0 = 40 \pm 2$ GPa for $YbGa_{1.1}Si_{0.9}$ and $B_0 = 42 \pm 1$ GPa for CaGaSi. The relative pressure derivative of T_C ($d\ln T_C/dP$) and logarithmic volume derivative of T_C ($d\ln T_C/d\ln V$) are -0.33 GPa^{-1} and 13 in $YbGa_{1.1}Si_{0.9}$. These values are about tenfold larger than those for other AlB_2-type superconductors. Additionally, the origin of $d\ln T_C/dP$ and $d\ln T_C/d\ln V$ in $YbGa_{1.1}Si_{0.9}$ relative to the pressure effect on the valence of Yb atoms is discussed.

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I. INTRODUCTION

The discovery of superconductivity in magnesium diboride (MgB_2) with a critical temperature for superconductivity T_C of 39 K has stimulated the search for new superconducting materials with honeycomb layers. MgB_2 crystallizes with an aluminum diboride (AlB_2)-type structure (hexagonal; space group $P6/mmm$) in which the B atoms form honeycomb layers and the Mg atoms are intercalated between the B layers.[1] In these efforts, ternary silicides $M_{AE}M_{TRx}Si_{2-x}$ (M_{AE} = Ca, Sr, and Ba, M_{TR} = Al and Ga) with an AlB_2-type or their derivatives have been found to be superconductors with $T_C = 3.5$–8.0 K.[2–10] Si and M_{TR} atoms in these silicides form honeycomb layers, and M_{AE} atoms are intercalated between the Si-M_{TR} layers. Additionally, graphite intercalation compounds (GICs) CaC_6 and YbC_6 were later discovered as superconductors with $T_C = 11.5$ and 6.5 K,[11] respectively. In GICs, the metal atoms are intercalated between carbon honeycomb layers. The similarities in the crystal structures of $M_{AE}M_{TRx}Si_{2-x}$ and GICs, honeycomb layers, and metal intercalant, have inspired research on superconducting materials in Yb-Al-Si and Yb-Ga-Si systems.

In the Yb-Ga-Si system, a ternary rare-earth silicide $YbGa_{1.1}Si_{0.9}$[12] crystallizes with the AlB_2-type structure where the Ga and Si atoms form chemically disordered honeycomb layers, and the Yb atoms are intercalated between the Ga-Si layers (see Fig. 1). $YbGa_{1.1}Si_{0.9}$ is a type-II superconductor with T_C of 2.4 K,[12] and is the first superconductor intercalated by a rare-earth element in AlB_2-type ternary silicides. Further studies on AlB_2-type $YbGa_xSi_{2-x}$ have revealed that the AlB_2 phase exists in $YbGa_xSi_{2-x}$ ($1.12 \leqslant x \leqslant 1.49$), T_C decreases with x,[13] Yb is in a mixed valent state of $Yb^{2.3+}$[13], and the estimated electronic specific heat coefficient γ is 12 mJ/mol K^2.[14] Compared to other ternary silicides CaGaSi and 1H-CaAlSi (3.56 mJ/mol K^2 for CaGaSi[15] and 6.10 mJ/mol K^2 for 1H-CaAlSi[7]), γ for $YbGa_{1.1}Si_{0.9}$ is slightly enhanced. The mixed valent state of the Yb atom and the value of γ in $YbGa_{1.1}Si_{0.9}$ suggest the possibility that the $4f$ states affect the density of states (DOS) at the Fermi level, which is an important factor for superconductivity.

To obtain more information on the superconductivity in $YbGa_xSi_{2-x}$, investigations on the influence of pressure on the superconductivity in $YbGa_xSi_{2-x}$ should be interesting. Additionally, comparing the results with that in AlB_2-type alkaline-earth ternary silicides should be useful because elemental Yb and many other Yb compounds exhibit a pressure-induced valence change. Namely, unlike elemental alkaline-earth metals and their compounds,[16–20] the pressure-induced valence change may affect superconductivity in $YbGa_xSi_{2-x}$.

Herein we report the pressure dependences of T_C and the lattice parameters in $YbGa_{1.1}Si_{0.9}$. Additionally, those of CaGaSi (an AlB_2-type superconductor, $T_C = 4.5$ K[4]) were investigated as a reference material possessing Ga-Si honeycomb layers. CaGaSi is a suitable reference because among alkaline-earth metals divalent Ca has the closest ionic radius to that of divalent Yb (0.99 Å for Ca^{2+}, 0.93 Å for Yb^{2+}, 1.12 Å for Sr^{2+}, and 1.34 Å for Ba^{2+}). The preliminary results on the electrical resistivity measurements have been reported in Ref. 21.

II. EXPERIMENTAL

Polycrystalline $YbGa_{1.1}Si_{0.9}$ was synthesized by Ar-arc melting and subsequent annealing as described elsewhere.[12,13] CaGaSi was synthesized in two stages. A 1.03 : 1 : 1 molar mixture of Ca, Ga, and Si was initially Ar-arc melted. Then the arc-melted sample was loaded in a BN capsule and the capsule was sealed in an Ar-filled quartz tube. The sample in the tube was remelted at 1470 K for 6 hours, and cooled to 1270 K at a rate of 4 K/h.

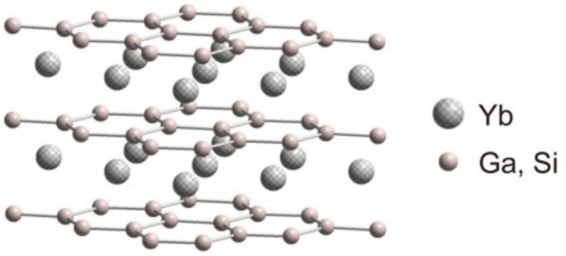

FIG. 1. (Color online) Schematic of the $YbGa_{1.1}Si_{0.9}$ crystalline structure. Ga and Si atoms (small balls) form honeycomb layers. Yb atoms (large balls) are intercalated into the space between the Ga-Si layers.

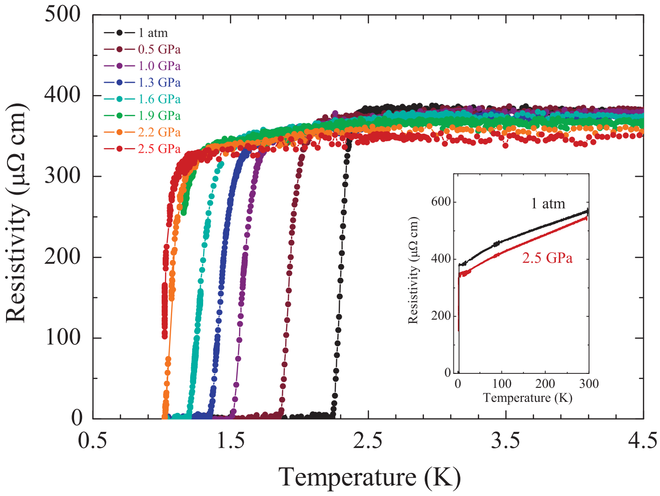

FIG. 2. (Color online) Pressure dependence of the $YbGa_{1.1}Si_{0.9}$ superconducting transition at pressures up to 2.5 GPa. Inset shows the temperature dependence of the electrical resistivity at 1 atm and 2.5 GPa between 1.0 to 300 K.

We used a piston-cylinder pressure cell for the electrical resistivity measurements under high pressure up to 2.5 GPa. A fragment of $YbGa_{1.1}Si_{0.9}$ (CaGaSi) measuring 2.5 × 0.84 × 0.60 mm^3 (2.3 × 0.80 × 0.60 mm^3) in size was placed into a Teflon capsule filled with Daphne oil 7373 as the pressure-transmitting medium for hydrostatic compression. Then the capsule was loaded into a piston-cylinder-type pressure cell. The pressure scale in the sample chamber was calibrated in advance by the pressure dependence of a T_C for lead. Each pressure cell for $YbGa_{1.1}Si_{0.9}$ and CaGaSi was cooled by a ^{3}He circulation-type 1 K cryogenic refrigerator and a 4 K Gifford-McMahon refrigerator developed by Iwatani industrial gases corporation, respectively. The temperature dependence of the electrical resistivity ρ was measured at each pressure by the four-probe method in the temperature region of 0.9−300 K for $YbGa_{1.1}Si_{0.9}$ and 3−300 K for CaGaSi at each pressure.

X-ray diffraction patterns at high pressures were measured by an energy-dispersive method using synchrotron radiation in beamline PF-AR-NE5 of High-Energy Accelerator Research Organization (KEK) in Japan.[22,23] High pressure was applied using a multianvil high-pressure apparatus MAX80. WC anvils with a 6 mm truncated edge length were used. We modified the sample assembly described in Ref. 23 for this study. The powdered sample was loaded in the h-BN capsule. Then a capsule with $YbGa_{1.1}Si_{0.9}$ and a mixture of NaCl and BN and a capsule with CaGaSi were placed in a hole at the center of a boron-epoxy pressure-transmitting medium. Both ends of the hole were sealed by pyrophyllite end plugs. Thus, we measured the diffraction patterns of $YbGa_{1.1}Si_{0.9}$ and CaGaSi in the same run. The pressure was evaluated from the lattice constant of a NaCl internal marker.[24] The typical error of pressure was 0.1 GPa.

III. RESULTS

Figure 2 shows the results of the electrical resistivity measurement of $YbGa_{1.1}Si_{0.9}$ at pressures from 1 atm to 2.5 GPa. As shown in the inset of Fig. 2, the temperature dependencies of the electrical resistivity measured at 1 atm and 2.5 GPa exhibit a metallic behavior. The temperature dependence is relatively constant regardless of pressure, indicating that there is no substantial change in the electronic states by compression. The sharp drop in electrical resistivity is associated with the superconducting transition. The width of the transition is very small, $\Delta T \sim 0.1$ K, indicating a good sample quality. The transition temperature T_C at the onset of the transition is 2.4 K at ambient pressure, which is consistent with the previous report.[12] The transition process shifts to a lower temperature as pressure increases.

Figure 3 shows the electrical resistivity of CaGaSi, which is a reference material in the ternary Ga-Si system, measured at pressures from 1 atm to 2.4 GPa. As shown in the inset of Fig. 3, the temperature dependence of the electrical resistivity shows a metallic behavior at 1 atm and 2.4 GPa. The T_C is 4.3 K at ambient pressure, which is consistent with the previous paper.[4] Similar to $YbGa_{1.1}Si_{0.9}$, the superconducting transition shifts to a lower temperature as pressure increases.

Figure 4 plots the T_C values of $YbGa_{1.1}Si_{0.9}$ and CaGaSi, which are estimated from the onset temperature of the superconducting transition as a function of pressure. In both materials, T_C decreases from 2.4 K at 1 atm to 1.1 K at 2.5 GPa for $YbGa_{1.1}Si_{0.9}$ and from 4.3 K at 1 atm to 3.9 K at 2.4 GPa

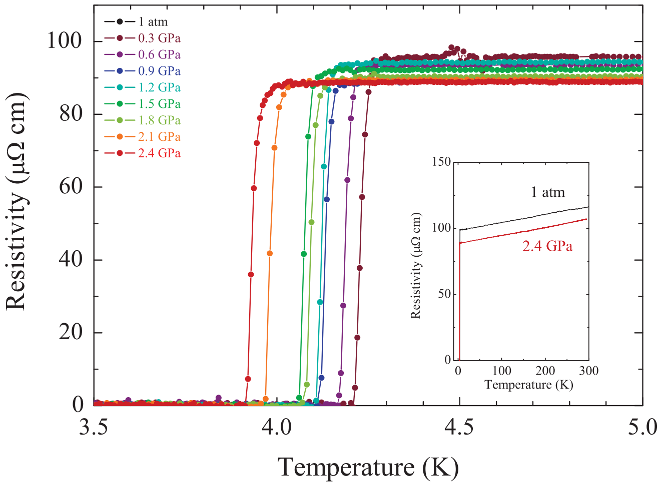

FIG. 3. (Color online) Pressure dependence of the CaGaSi superconducting transition at pressures up to 2.4 GPa. Inset shows the temperature dependence of the electrical resistivity at 1 atm and 2.4 GPa between 3.0 to 300 K.

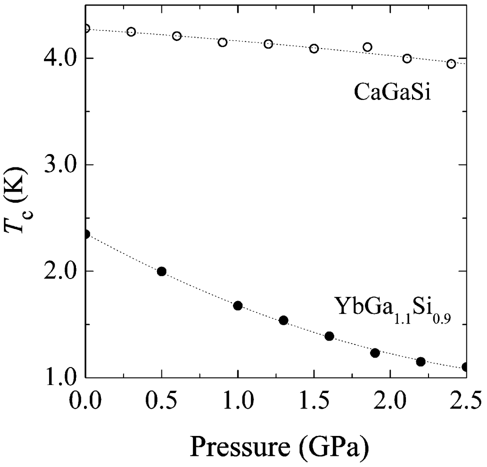

FIG. 4. Superconducting transition temperature (T_C) plotted as a function of pressure. Solid and open circles indicate T_C of $YbGa_{1.1}Si_{0.9}$ and CaGaSi, respectively. T_C is estimated at the onset of the superconducting transition.

for CaGaSi. The magnitude of the pressure derivative of T_C (dT_C/dP) of $YbGa_{1.1}Si_{0.9}$ is larger than that of CaGaSi (-0.78 K/GPa for $YbGa_{1.1}Si_{0.9}$ and -0.11 K/GPa for CaGaSi).

Figure 5(a) shows the pressure variations with normalized lattice parameters a/a_0 and c/c_0, where a_0 and c_0 are the lattice parameters at ambient pressure ($a_0 = 4.1275(3)$ Å and $c_0 = 4.2357(4)$ Å for $YbGa_{1.1}Si_{0.9}$,[12] $a_0 = 4.1200(8)$ Å and $c_0 = 4.4401(1)$ Å for CaGaSi[4]) for two different runs. The value of a_0 is almost the same between $YbGa_{1.1}Si_{0.9}$ and CaGaSi, whereas that of c_0 differs; c_0 of $YbGa_{1.1}Si_{0.9}$ is 4.6% smaller than that of CaGaSi. The difference in c_0 can be attributed to the difference in the radii of the intercalant atoms, $r_{Yb2+} = 0.93$ Å and $r_{Ca2+} = 0.99$ Å. The pressure derivatives of a/a_0 and c/c_0, $d(a/a_0)/dP$ and $d(c/c_0)/dP$, are $-0.0042(1)$ and $-0.0115(4)$ for $YbGa_{1.1}Si_{0.9}$ and $-0.0038(1)$ and $-0.0122(3)$ for CaGaSi, respectively. Thus the pressure dependencies of a/a_0 and c/c_0 of $YbGa_{1.1}Si_{0.9}$ agree with those of CaGaSi. Figure 5(b) shows the pressure dependencies of c/a for $YbGa_{1.1}Si_{0.9}$ and CaGaSi in two different runs. c/a in $YbGa_{1.1}Si_{0.9}$ is smaller than that in CaGaSi owing to the difference in c_0, but a_0 is almost the same. The pressure coefficient of c/a is almost the same between $YbGa_{1.1}Si_{0.9}$ and CaGaSi [$-0.0074(5)$ for $YbGa_{1.1}Si_{0.9}$ and $-0.0091(3)$ for CaGaSi]. The value of c/a in $YbGa_{1.1}Si_{0.9}$ is less than one at approximately 3.2 GPa.

Figure 6 shows the compression curves of $YbGa_{1.1}Si_{0.9}$ and CaGaSi, which are fitted by the Murnaghan equation of state:

$$P = B_0/B_0'[(V_0/V)^{B_0'} - 1], \qquad (1)$$

where V_0 and V are the volumes at ambient pressure and at pressure P given in GPa, B_0, and B_0' are the bulk modulus and its pressure derivative, respectively. B_0 is defined by the equation $B_0^{-1} = (1/V)(dV/dP)$. The equation of state provides $B_0 = 40 \pm 2$ GPa and $V_0 = 62.7 \pm 0.1$ Å^3 for $YbGa_{1.1}Si_{0.9}$, $B_0 = 42 \pm 1$ GPa and $V_0 = 65.4 \pm 0.1$ Å^3 for CaGaSi, assuming B_0' is 4.8.[25] These results suggest that the volume compressibility of $YbGa_{1.1}Si_{0.9}$, which is the reciprocal of the bulk modulus, is equal to that of CaGaSi within experimental error.

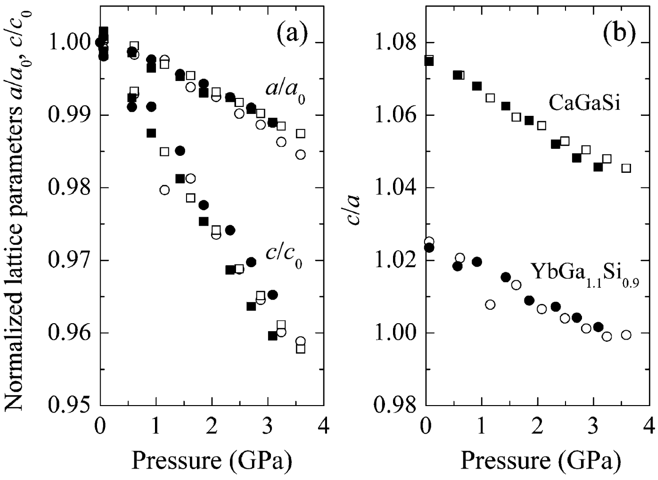

FIG. 5. (a) Pressure variations in the lattice constants a and c normalized to the values of those at 1 atm, a_0 and c_0. (b) c vs a plotted as a function of pressure. In both figures, circle and square symbols indicate the values for $YbGa_{1.1}Si_{0.9}$ and CaGaSi, respectively. Open and solid symbols indicate the data obtained from two different runs.

Table I lists T_C, dT_C/dP, relative pressure derivatives of T_C [$d\ln T_C/dP = (1/T_C)(dT_C/dP)$], bulk modulus ($B_0$), and logarithmic volume derivative of T_C ($d\ln T_C/d\ln V$) of $YbGa_{1.1}Si_{0.9}$ and CaGaSi along with those in other layered superconducting materials possessing honeycomb layers. Similar to MgB_2[26] and other AlB_2-type ternary silicides (1H-CaAlSi and SrAlSi)[27,28] the pressure derivative of T_C in $YbGa_{1.1}Si_{0.9}$ is negative. However, the values of dT_C/dP are positive for nH-CaAlSi ($n = 5$, 6),[27] YbC_6, and CaC_6.[29] The magnitude of $d\ln T_C/dP$ in $YbGa_{1.1}Si_{0.9}$ is about tenfold larger than those of other materials. The bulk modulus values in $YbGa_{1.1}Si_{0.9}$ and CaGaSi are almost the same as that of AlB_2-type ternary

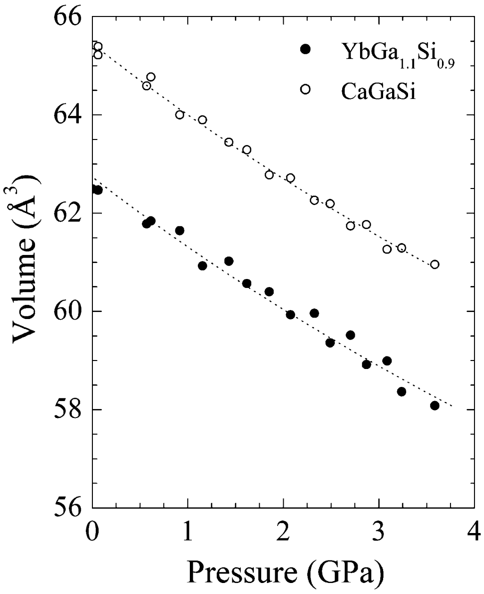

FIG. 6. Experimental unit-cell volumes plotted as a function of pressure. Solid and open circles indicate volumes of $YbGa_{1.1}Si_{0.9}$ and CaGaSi, respectively.

TABLE I. Comparison of the superconducting properties: superconducting transition temperatures (T_C), pressure dependencies of initial slope (dT_C/dP), relative pressure derivatives of T_C ($d\ln T_C/dP$), bulk moduli (B_0), and logarithmic volume derivatives of T_C ($d\ln T_C/d\ln V$), respectively. Asterisks indicate calculated bulk modulus B_0 values.

	T_C at 1 atm (K)	dT_C/dP (K/GPa)	$d\ln T_C/dP$ (GPa^{-1})	B_0 (GPa)	$d\ln T_C/d\ln V$ [$=d\ln T_C/dP*B_0$]
$YbGa_{1.1}Si_{0.9}$	2.4	−0.78	−0.33	41	13
CaGaSi	4.2	−0.11	−0.026	42	1.1
MgB_2[a]	39.6	−1.03	−0.026	172	4.4
$1H$-CaAlSi[b,c]	6.5	−0.31	−0.048	*64	3.0
nH-CaAlSi($n{\sim}6$)[b,d]	7.7	0.21	0.026	*∼50	1.3
SrAlSi[c,d]	4.9	−0.12	−0.024	*58	1.4
YbC_6[e]	6.5	0.37	0.057	...	...
CaC_6[e,f]	11.5	0.50	0.043	*103	4.4

[a] Reference 26.
[b] Reference 27.
[c] Reference 30.
[d] Reference 28.
[e] Reference 29.
[f] Reference 31

silicides, but are smaller than that of MgB_2 and CaC_6. The value of $d\ln T_C/d\ln V$ is calculated from $d\ln T_C/dP$ and B_0 as follows: $d\ln T_C/d\ln V = (1/T_C)(dT_C/dP)/(1/V)(dV/dP) = (d\ln T_C/dP)B_0$, and its magnitude for $YbGa_{1.1}Si_{0.9}$ is larger than the other values. This is a remarkable characteristic of the superconductivity in $YbGa_{1.1}Si_{0.9}$ under high pressure.

IV. DISCUSSION

First, we address the pressure dependence of T_C in CaGaSi. The electronic state near the Fermi energy in CaGaSi originates from hybridization of the Ca $3d$ and Ga/Si p states, but the Ca $3d$ character is the main component in the electronic density of states (DOS) at the Fermi level $N(E_F)$.[32] Another AlB_2-type superconductor $1H$-CaAlSi has a similar electronic structure with CaGaSi, and its superconducting mechanism has been thoroughly investigated.[27] In $1H$-CaAlSi, the electronic state near the Fermi energy originates from the hybridization of Ca $3d$ and Al/Si p states, but the Ca $3d$ character is a main component in $N(E_F)$.[27] This electronic state couples with the low-frequency mode. This low-frequency mode corresponds to the out-of-plane vibration of the Al-Si planes, which is the origin of superconductivity, but as pressure increases, this mode splits into two peaks in the phonon DOS where one peak softens and the other hardens. Furthermore, applying pressure decreases the electronic DOS at the Fermi level $N(E_F)$. Although the reason why $N(E_F)$ decreases is not described in Ref. 27, it is a plausible explanation that an increase in the interaction between Ca and Al/Si states with pressure makes the width of electronic DOS broad. Due to the peak splitting in the phonon DOS and the decrease in $N(E_F)$, the electron-phonon coupling parameter λ and logarithmic-averaged phonon frequency decrease with pressure result in the negative pressure-dependence of T_C in $1H$-CaAlSi. Because the magnitude of B_0 and the electronic structure of CaGaSi are very similar to those of $1H$-CaAlSi, the electronic DOS at the Fermi level $N(E_F)$ in CaGaSi should decrease with pressure, similar to the case of $1H$-CaAlSi. Therefore, the scenario for pressure dependence of T_C in $1H$-CaAlSi should apply to that in CaGaSi: the softening of the phonon and the decrease in $N(E_F)$ induced by pressure result in the negative pressure dependence of T_C. In fact, the sign and order of dT_C/dP and $d\ln T_C/dP$ in CaGaSi are the same as those in $1H$-CaAlSi.

Next, we discuss the pressure effect on T_C in $YbGa_{1.1}Si_{0.9}$. The main difference between $YbGa_{1.1}Si_{0.9}$ and CaGaSi is that Yb is a $4f$ metal and the external conditions can induce a change in its valence between 2+ and 3+, whereas the valence of Ca is always 2+. At high pressures, the increase in the valence of the Yb atoms has been observed in elemental Yb[16] and other Yb compounds, including $YbAl_2$, YbS, $YbInAu_2$, and YbM_2X_2 (M = transition metal, X = Si, Ge).[17–20] This trend is consistent with the fact that Yb^{3+} has a smaller ionic radius (0.85 Å) than Yb^{2+} (0.93 Å). Figure 7 shows the valence of Yb in $YbGa_{1.15}Si_{0.85}$ reported in Ref. 33 and a normalized T_C, $T_C(P)/T_C(0)$, as a function of the normalized volume V/V_0. The $T_C(P)/T_C(0)$ of CaGaSi is also plotted for comparison. The valence of Yb gradually increases with pressure from 2.2+ at ambient pressure (see Fig. 7) and is reported to increase up to 2.4+ at 5 GPa,[33] which corresponds to $V/V_0 \sim 0.91$. The variation in $T_C(P)/T_C(0)$ of $YbGa_{1.1}Si_{0.9}$ is much larger than that of CaGaSi for the same value of V/V_0. Because the bulk modulus of $YbGa_{1.1}Si_{0.9}$ is almost the same as that of CaGaSi, the difference in $T_C(P)/T_C(0)$ is most likely due to the increased valence of Yb with pressure and the different contribution of the intercalant Yb/Ca atoms to the electronic DOS at the Fermi level. The valence change can significantly alter the electronic structure around the Fermi energy, which is considered to be responsible for the rapid decrease in T_C upon pressurization in $YbGa_{1.1}Si_{0.9}$.

We discuss three possible mechanisms of the effect of $4f$ electrons on T_C in $YbGa_{1.1}Si_{0.9}$: (i) overdoping of carrier electrons due to the increased Yb valence, (ii) cooper-pair breaking by the magnetic Yb^{3+} moment, and (iii) valence fluctuations. With the overdoping mechanism, T_C of AlB_2-type ternary alkaline-earth silicides $M_{AE}M_{TRx}Si_{2-x}$ (M_{AE} = Ca,

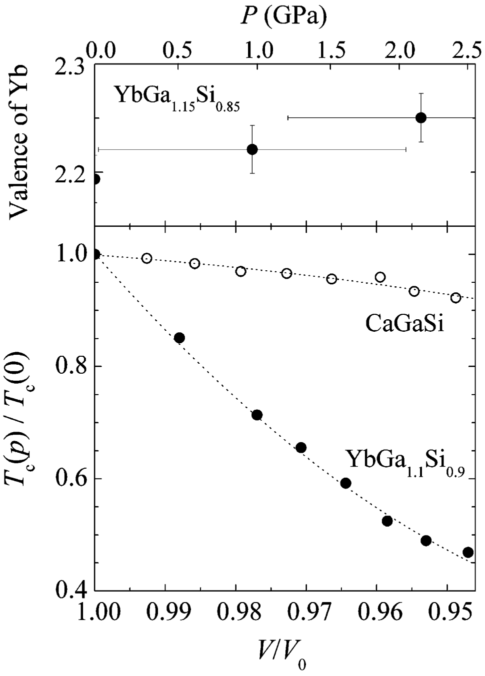

FIG. 7. Valence of Yb ions in $YbGa_{1.15}Si_{0.85}$ reported in Ref. 33 and superconducting transition temperatures T_C normalized to the values of those at 1 atm T_0 as a function of volume compressibility. Solid and open circles in the lower figure indicate normalized T_C of $YbGa_{1.1}Si_{0.9}$ and CaGaSi, respectively.

Sr, and Ba, M_{TRx} = Al and Ga) is maximized around $x = 1.0$.[5,8,9] In this case, T_C decreases with x when x is greater than one. From the analogy of $M_{AE}M_{TRx}Si_{2-x}$, Tsujii *et al.* have suggested that $YbGa_xSi_{2-x}$ ($x = 1.15-1.4$) also has an optimum carrier concentration around $x = 1$,[13] which is reflected in the x dependence of T_C in $YbGa_xSi_{2-x}$; T_C decreases monotonically as x increases from 1.1. Using this scenario, Yamaoka *et al.* have noted that overdoping of carrier electrons is a possible mechanism to reduce T_C in $YbGa_{1.1}Si_{0.9}$ by pressure.[33] As shown in Fig. 7, the valence of Yb increases from 2.2+ to 2.25+, when pressure is increased from ambient pressure to 2.5 GPa, adding 0.05 e^- to the conduction band. Therefore, if $Yb^{2.2+}Ga_{1.1}Si_{0.9}$ is assumed to have an optimum carrier concentration, T_C decrease as the valence increases from 2.2+ to 2.25+ because the carrier concentration becomes the overdoping. However, this scenario is difficult to examine because $YbGa_xSi_{2-x}$ with $x < 1.1$ has a different crystal structure and we cannot measure the x dependence of T_C in the AlB_2-type $YbGa_xSi_{2-x}$ with $x < 1.1$.

Next, the effect of the magnetic moment induced on the Yb site is considered. Superconductors with magnetic impurities have been well investigated, and magnetic impurities cause T_C to decrease.[34] When $YbGa_{1.1}Si_{0.9}$ is compressed, the valence of Yb approaches the trivalent state. Here we assume the increase of Yb valence is due to randomly-distributed Yb^{3+} ions of which concentration increases with pressure. Since the Yb^{3+} ion carries a magnetic moment of $J = 7/2$, a pair-breaking effect due to the pressure-induced Yb^{3+} ions may be a plausible explanation for the decrease of T_C in $YbGa_{1.1}Si_{0.9}$ with pressure. It is noteworthy that superconductivity is not observed in the isostructural compound EuGaSi at least above 2 K where the Eu ion has been demonstrated to be divalent with a magnetic moment of $J = 7/2$.[35] To examine quantitatively the stability of superconductivity against the magnetic moment in AlB_2-type superconductors, a systematic study such as the Eu impurity effect on T_C of $YbGa_{1.1}Si_{0.9}$ is necessary.

The third mechanism is based on the assumption that the valence of Yb shown in Fig. 7 is due to the valence fluctuation ($Yb^{2+} \longleftrightarrow Yb^{3+}$), as discussed in Ref. 13 from the results of the magnetic susceptibility and the x-ray spectroscopy. The pressure change in valence fluctuation of the Yb ions is expected to greatly influence the rapid decrease of T_C by pressure. It has been reported that superconductivity is strongly suppressed by doping with rare-earth ions whose valences can fluctuate such as Ce and Yb. For example, $YbNi_2B_2C$ does not show superconductivity although $LuNi_2B_2C$ and $TmNi_2B_2C$ are superconductors with T_C = 16 K and 11 K, respectively.[36–39] Substitution of Yb for Lu in $LuNi_2B_2C$ decreases T_C 75 times faster than the substitution of Gd for Lu,[40–42] where Gd is a magnetic impurity. Similarly, layered superconductors $La_{3-x}R_xNi_2B_2N_{3-\delta}$ strongly suppress T_C for R = Ce. The magnitude of the rate dT_C/dx is one order of magnitude larger for Ce than that for R = Pr and Nd.[43,44] These experimental data suggest that the valence fluctuation of Ce or Yb causes a more detrimental effect on superconductivity than the conventional pair-breaking mechanism of the magnetic impurities.

To date, the effect of valence fluctuations on a nonmagnetic superconductor has been discussed in terms of the theoretical results by Müller-Hartmann and Zittartz (MHZ).[42,45] They calculated the change of the value of T_C when the concentration of Kondo impurities like Ce^{3+} or Yb^{3+} increases. In our case, the Yb valence increases almost linearly with pressure (see Fig. 7). Here we consider that the increase in the Yb valence corresponds to an increase of the Yb^{3+} Kondo impurity concentration. Notably, MHZ theory predicts the decrease of T_C is less pronounced as the concentration of Kondo impurities increase when $T_C \ll T_K$ where T_K is the Kondo temperature.[45] Indeed, this behavior has been observed for Th-U alloy.[45,46] In contrast, the normal pair-breaking mechanism leads to a stronger suppression of T_C at higher impurity concentrations.[45] In $YbGa_{1.1}Si_{0.9}$, the valence of Yb is independent of temperature below room temperature, indicating that T_K is much larger than room temperature;[13,33] hence, the condition $T_C \ll T_K$ is satisfied. Figure 7 shows that the decrease of T_C is less pronounced in the high-pressure region. This is qualitatively consistent with the prediction of MHZ theory. For the reasons above, we believe that the pressure-induced increase of Kondo impurities is the most plausible reason for the rapid decrease of T_C in $YbGa_{1.1}Si_{0.9}$. However, to quantitatively compare the data to theory, a systematic study, including specific heat under high pressure, etc., is necessary.

It should also be mentioned that to date, the effect of the Kondo interaction in nonmagnetic superconductors has been investigated in doped systems, such as $Lu_{1-x}Yb_xNi_2B_2C$. In these cases, the effect of randomness can also be involved. In the present case, applying pressure to $YbGa_{1.1}Si_{0.9}$ changes the Kondo interaction, but randomness in the Yb sublattice does not occur. Hence, $YbGa_{1.1}Si_{0.9}$ is a very rare example to precisely investigate the effect of Kondo interaction on superconductivity.

V. SUMMARY

We have performed the electrical resistivity and x-ray diffraction measurements to investigate the pressure effect on superconductivity and AlB$_2$-type crystal structure of YbGa$_{1.1}$Si$_{0.9}$ with $T_C = 2.4$ K and CaGaSi with $T_C = 4.5$ K. The negative pressure derivatives of T_C are observed at pressures up to about 2.5 GPa in both materials: $dT_C/dP = -0.78$ K/GPa for YbGa$_{1.1}$Si$_{0.9}$ and -0.11 for CaGaSi. Both materials have similar bulk modulus values at pressures up to 3.5 GPa, and neither material displays a structural transition in this pressure range. $d\ln T_C/dP$ and $d\ln T_C/d\ln V$ of YbGa$_{1.1}$Si$_{0.9}$ are approximately ten times greater than those of CaGaSi. It is inferred that the large $d\ln T_C/d\ln V$ in YbGa$_{1.1}$Si$_{0.9}$ is most likely attributed to the increased Yb valence with pressure. We postulate three possible mechanisms for the suppression of superconductivity induced by the increased Yb valence: (i) overdoping of carrier electrons, (ii) cooper-pair breaking by the magnetic Yb^{3+} moment, and (iii) effect of valence fluctuation. However, we anticipate that the effect of Yb valence fluctuations should be most influential on the rapid decrease of T_C by pressure.

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