Superconducting properties and thermal expansion of YbGa$_x$Si$_{2-x}$

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Abstract. YbGa$_x$Si$_{2-x}$ forms the hexagonal AlB$_2$-type crystal structure in the chemical composition range of $1.12 \leq x \leq 1.49$ and shows superconductivity with critical temperatures $T_C \leq 2.5$ K. In this paper, we investigate the electronic and thermal properties of the YbGa$_x$Si$_{2-x}$ compounds by means of electrical resistivity ($\rho$) and specific heat ($C$) measurements under magnetic fields, as well as by the temperature dependent x-ray diffraction study. The onset temperature of superconductivity, $T_{\text{onset}}$, decreases with the increase of the Ga content $x$, from 2.5 K for $x = 1.15$ to 1.9 K for $x = 1.31$. Estimated upper critical field at zero temperature, $H_{C2}(0)$, concomitantly decreases from 5.9 kOe for $x = 1.15$ to 3.1 kOe for $x = 1.31$. The normal-state electronic specific-heat coefficient is found to be almost independent to $x$; $\gamma = 8mJ/molK^2$ for $x = 1.18$, 1.31, and 1.41. The small value of $\gamma$ indicates electron-electron correlation is weak in this compound. An irreversible behavior is observed in $\rho(T)$. $\rho(T)$ of YbGa$_{1.2}$Si$_{0.8}$ shows a hump-like increase below about 200 K on cooling while it shows a rather monotonic increase on heating. Powder x-ray diffraction of this sample taken at 12 K shows no evidence of structural phase transition. Temperature dependence of the lattice parameters in this sample show normal behavior: both $a$ and $c$ decrease with decreasing temperature with thermal expansion coefficients similar to those in YbGaGe. Possible mechanism for the irreversible behavior in $\rho(T)$ is discussed.

1. Introduction

Superconductors with nearly two-dimensional crystal structures are extensively investigated because of their high $T_C$. A series of ternary silicides $M$(Ga,Al)Si ($M$ = Ca, Sr, Ba) have been reported to crystallize in the hexagonal AlB$_2$-type structure and show superconductivity [1, 2, 3, 4, 5, 6, 7, 8]. Since this compound is isostructural with MgB$_2$, in which $T_C = 39$ K is reported [9], similarities in the electronic structures between them are expected. It has, however, been found that the ternary silicide superconductors have quite contrasting properties with those of MgB$_2$. For MgB$_2$, holes in the honeycomb layer of boron are dominant carriers [10, 11, 12], and in-plane phonon mode of the boron layer is responsible for superconductivity [13, 14]. On the other hand, dominant carriers in the ternary silicides are electrons, as suggested from the negative Seebeck coefficient [5, 7] and the Hall effect measurements [15]. Softening of the out-of-plane phonon mode is observed for CaAlSi by inelastic x-ray or neutron scattering measurements [16, 17], in contrast to the in-plane mode for MgB$_2$. Therefore the phonon mode responsible for superconductivity is also different between MgB$_2$ and the ternary silicides. This fact suggests the presence of variety of superconducting mechanisms among the AlB$_2$-type superconductors, pointing to the importance of further studies of the physical and structural properties in this class of compounds.
Recently, a new compound YbGa$_{1.1}$Si$_{0.9}$ with the AlB$_2$-type structure has been discovered to be superconducting below $T_C = 2.4$ K [18]. Later it has been revealed that the AlB$_2$-type structure is stabilized for YbGa$_x$Si$_{2-x}$ with $1.12 \leq x \leq 1.49$ [19]. $T_C$ decreases linearly with $x$ from 2.4 K for $x = 1.15$ to less than 1.8 K for $x = 1.41$. The Yb ion was considered to be in the nonmagnetic divalent state, but the precise x-ray emission spectroscopy reveals a slight mixed-valent state Yb$^{2.3+}$, which does not depend on temperature and/or chemical composition [19]. Quite recently, it has been demonstrated that $T_C$ decreases rapidly by applying pressure. The coefficient of the decrease of $T_C$ against pressure, $dT_C/dP$, is one order of magnitude greater in YbGa$_x$Si$_{2-x}$ than in CaGaSi [20]. This can be due to the hybridization of $f$ electrons with conduction electrons, as inferred from the x-ray emission spectroscopy measured under high pressures [21].

In this Workshop 1, we report electrical resistivity and specific heat of YbGa$_x$Si$_{2-x}$ polycrystalline samples measured in magnetic fields. We observe an irreversible behavior in the temperature dependence of the electrical resistivity. We also performed the temperature dependent x-ray diffraction measurements for YbGa$_{1.2}$Si$_{0.8}$ powder sample to examine any structural phase transition at low temperature and also to investigate the temperature dependence of the lattice parameters.

**2. Experimental**

Polycrystalline samples of YbGa$_x$Si$_{2-x}$ were synthesized by argon arc melting and subsequent annealing, as described earlier [19]. The chemical composition was confirmed by the electron probe micro analysis (EPMA), for which single crystals of GaAs, Si, and YbAl$_3$ were used as the standard samples for chemical composition calculation. Here, the single crystal of YbAl$_3$ was grown by an Al-flux method in an alumina crucible [22, 23]. Electrical resistivity was measured by a four probe method using a Physical Property Measurement System (PPMS), Quantum Design Co. Specific heat measurement was carried out by a relaxation method using a PPMS. Powder x-ray diffraction patterns of YbGa$_{1.2}$Si$_{0.8}$ were taken with a Rigaku RINT2000 diffractometer using Cu K$_\alpha$ radiation operating at 40 kV and 200 mA from room temperature down to 12 K. The x-ray diffraction patterns were analyzed by the Rietveld method using the RIETAN-FP program [24]. The lattice parameters were determined with the silicon 640b used as an internal standard.

**3. Results and discussion**

In Figure 1, electrical resistivity of YbGa$_x$Si$_{2-x}$ at low temperatures measured under magnetic fields are shown. Defining $T_C^{onset}$ as the temperature at which the resistivity is 90% of the values at 3 K, $T_C^{onset}$ is estimated to be 2.5 K, 2.32 K, 2.15 K and 1.89 K for $x = 1.15$, 1.18, 1.26 and 1.31, respectively. Under magnetic fields, $T_C^{onset}$ also decreases almost linearly with fields. Field dependence of $T_C^{onset}$ is plotted in Figure 2. The upper critical field at zero temperature, $H_{C2}(0)$, is estimated using the Werthamer Helfand Hohenberg relation, $H_{C2}(0) = 0.69 \times (-dH_{C2}/dT) \times T_C$, which gives $H_{C2}(0) = 5.9$ kOe, 5.3 kOe, 4.2 kOe and 3.1 kOe, for $x = 1.15$, 1.18, 1.26 and 1.31, respectively. The value of $H_{C2}(0)$ for $x= 1.15$ is consistent with that recently obtained from the measurements of electrical resistivity down to 0.3 K under magnetic fields for YbGa$_{1.15}$Si$_{0.85}$ [25].

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Figure 1. Electrical resistivity measured under magnetic fields of YbGa$_x$Si$_{2-x}$ with $x = 1.15$, 1.18, 1.26 and 1.31.

Figure 2. Onset temperature of superconductivity, $T_{C}^{onset}$, under magnetic fields for YbGa$_x$Si$_{2-x}$.

In Figure 3, low temperature specific heat of YbGa$_x$Si$_{2-x}$ divided by temperature, $C/T$, is plotted against $T^2$. For zero magnetic field (Figure 3 (a)), a peak exists at $T \sim 2.3$ K. This peak can be attributed to the superconducting transition of the YbGa$_x$Si$_{2-x}$ phase and/or the antiferromagnetic transition of Yb$_2$O$_3$ impurity, the latter of which is sometimes observed in the low temperature specific heat for Yb-based intermetallic compounds [27, 28].
For $x = 1.18$, $T_C$ is close to $T_N$ of Yb$_2$O$_3$, 2.3 K, therefore both the effects are considered to be superimposed in the peak of $C/T$. For $x = 1.31$ and 1.41, $T_C$ is lower than 2.3 K. The peak in $C/T$ for the two compounds at $T = 2.3$ K is then attributed to the antiferromagnetic transition of Yb$_2$O$_3$ impurity. The entropy corresponding to the antiferromagnetic transition is calculated by integrating $C/T$ over $T$ down to 0 K, for which $C/T$ values at temperatures below 1.8 K were extrapolated assuming the magnon contribution, $C/T \propto T^2$. The entropy due to Yb$_2$O$_3$ thus estimated is 0.0034Rln2, where R is the gas constant. This indicates the amount of Yb$_2$O$_3$ is less than 0.4% of total Yb. Hence, the effect of Yb$_2$O$_3$ to the superconducting properties in YbGa$_x$Si$_{2-x}$ is not important. Nevertheless, the effect of antiferromagnetic transition of Yb$_2$O$_3$ makes it difficult to estimate the intrinsic electronic specific-heat coefficient, $\gamma$, of YbGa$_x$Si$_{2-x}$ at low temperatures. We then applied magnetic field of 50 kOe to suppress the effect of Yb$_2$O$_3$, and measured the specific heat. The results are shown in Figure 3 (b). In this figure, the anomaly due to Yb$_2$O$_3$ is not seen, thereby we are able to estimate the electronic specific heat coefficient by fitting using the relation $C/T = \gamma + \beta T^2$. The values of $\gamma$ are obtained to be $\gamma \approx 8$ mJ/molK$^2$ and are almost independent to chemical composition $x$.

The value of $\gamma = 8$ mJ/molK$^2$ indicates that the electron-electron correlation in this compounds is not important. This suggests the normal BCS-type superconductivity for the present compound. Nevertheless, it is notable that the value $\gamma = 8$ mJ/molK$^2$ is slightly larger than those for CaGaSi ($\gamma = 4$ mJ/molK$^2$) and SrAlSi ($\gamma = 5.4$ mJ/molK$^2$) [25]. This suggests that the 4f electrons participate to the formation of the Fermi surface to some extent. The x-ray absorption and photoelectron spectroscopy indeed showed weak mixed valence state, Yb$^{2.3+}$, for the present compound [21]. In addition, almost constant $\gamma$ over $x$ means the extent of hybridization between 4f and the conduction electrons does not change with chemical composition. Again, this is in good agreement with the results of x-ray emission spectroscopy, which showed the valence of Yb is almost constant, Yb$^{2.3+}$ over $x$, pointing to the same order of hybridization [19].

**Figure 3.** Specific heat divided by temperature, $C/T$, plotted as a function of squared temperature, $T^2$ under zero field (a), and under the field of 50 kOe (b). The dashed line in (b) represents the relation $C/T = \gamma + \beta T^2$. 
In the course of electrical resistivity measurements, we observed an irreversible behavior in the temperature dependence of the resistivity, $\rho(T)$. For some samples, $\rho(T)$ shows a hump-like increase with decreasing temperature, while it shows rather a monotonic increase with increasing temperature. Figure 4 displays $\rho(T)$ of YbGa$_{0.8}$Si$_{1.2}$, which showed the most prominent irreversible behavior among our measurements.

$\rho(T)$ of this sample shows a minimum at $T = 180$ K and increases with decreasing temperature for the first cooling process. Then the measurement on the heating process shows a broad maximum around $T = 200$ K. The measurement of $\rho(T)$ for the second time again shows similar anomaly, but those are less pronounced compared to the first time. Possible mechanisms for these anomalous temperature dependence of $\rho(T)$ include electronic phase transition, such as valence transition of Yb, charge density wave (CDW) formation, or structural deformation, etc. Here, valence transition of Yb is ruled out since x-ray spectroscopic measurements revealed that the valence of Yb is independent to temperature [21].

To clarify if there is a structural phase transition at low temperature, powder x-ray diffraction has been taken for YbGa$_{1.2}$Si$_{0.8}$ at low temperatures. The diffraction patterns at 300 K and 12 K are shown in Figure 5, with the results of Rietveld fittings, analyzed by the RIETAN-FP program [24]. No extra peaks other than those of the AlB$_2$-type structure and the standard Si have been observed. This rules out the possibility of a structural phase transition. In the AlB$_2$-type structure, atomic positions are not allowed to move from the symmetric positions. In case of slight structural deformation from the AlB$_2$-type structure, however, one can expect an enhancement of the isotropic atomic displacement parameter, $B$. We found that the values of $B$ shows monotonic decreases for both Yb and Ga/Si sites with decreasing temperature, without any anomalous behavior at low temperature. Thus the possibility of structural deformations at low temperature is unlikely, though we should mention that the reliability of this $B$ analysis is not sufficient because of the low signal-to-noise ratio due to the in-house powder x-ray diffraction equipment. It is desired to perform neutron diffraction and/or synchrotron x-ray diffraction experiments to discuss the thermal effect in more detail.
Figure 5. Powder x-ray diffraction patterns and the results of the Rietveld fittings for YbGa$_{1.2}$Si$_{0.8}$ at $T = 12$ K and 300 K. Reliable factors are $R_{WP} = 9.2\%$ and $S = 2.4$ for 12 K and $R_{WP} = 10.4\%$ and $S = 2.6$ for 300K.

Figure 6 shows temperature dependence of the lattice parameter, $a$ and $c$, the unit cell volume $V$, and the ratio $c/a$, between 12 and 300 K for YbGa$_{1.2}$Si$_{0.8}$. These values were determined by the Rietveld fitting of the powder XRD data with Si 640b used as internal standard. Both $a$ and $c$ show monotonic decreases with the decrease of temperature [26]. As a result, the lattice volume $V$ also decreases monotonically.

The lattice parameter $a$ decreases approximately by 0.2% from 300 to 100 K, giving the thermal expansion coefficient $\alpha_a = 1.0 \times 10^{-5}$K$^{-1}$. Similarly, $c$ decreases by 0.54% from 300 to 100 K, yielding $\alpha_c = 2.7 \times 10^{-5}$K$^{-1}$. These values of $\alpha_a$ and $\alpha_c$ are very close to those of the related compound YbGaGe and YbGa$_x$Ge$_{2-x}$, reported previously [27, 29, 30].

Up to now no structural properties appear to suggest the correlation with the irreversible behavior in the temperature dependence of the electrical resistivity. One possible explanation would be the temperature dependent $c/a$ ratio shown in Fig. 6 (D), which decreases by 0.5% with decreasing temperature from 300 K to 12 K. The monotonic decrease in the $c/a$ ratio can lead increasing lattice strain in the polycrystalline samples, possibly resulting in the large hysteresis behavior in $\rho(T)$. If this is the case, the irreversible $\rho(T)$ would only appear for polycrystalline samples and is not expected to occur for single crystals. Another possible mechanism would be the formation of CDW transition below 100 K. For this case, the temperature at which CDW transition takes place would be sensitive to the carrier density. In our case, the temperature
Figure 6. Temperature dependence of the lattice parameters $a$ and $c$, the unit cell volume $V$, and the ratio $c/a$, for YbGa$_{1.2}$Si$_{0.8}$ annealed sample.

where the irreversible behavior in $\rho(T)$ occurs is found to shift to lower temperatures for larger $x$ samples, which corresponds to the decrease of valence electron number. Therefore, more detailed studies of the electronic structure and the lattice dynamics are desired for this YbGa$_x$Si$_{2-x}$ system.

4. Summary

Electrical resistivity, specific heat and thermal expansion have been investigated for the new superconductor YbGa$_x$Si$_{2-x}$. $T_C$ shows a linear decrease with increase of $x$. The estimated upper critical field at zero temperature decreases accordingly from 5.9 kOe for $x = 1.15$ to 3.1 kOe for $x = 1.31$. The results of specific heat measurements show that the electronic specific heat coefficients are almost independent to chemical composition $x$, with $\gamma \simeq 8$ mJ/molK$^2$ for all $x$. This small value of $\gamma$ indicates that electronic correlation in YbGa$_x$Si$_{2-x}$ is not enhanced, and is consistent with the nearly divalent Yb valence, Yb$^{2.3+}$, observed by the x-ray spectroscopic measurements. Temperature dependence of the electrical resistivity reveals an irreversible behavior. This $\rho(T)$ behavior suggests some structural deformation occurs at low temperature. On the other hand, no structural phase transition is observed by powder x-ray diffraction for YbGa$_{1.2}$Si$_{0.8}$. Temperature dependence of the lattice parameters shows a monotonic decrease with decreasing temperature, both for $a$ and $c$. Further detailed studies are needed to address the electronic properties of the YbGa$_x$Si$_{2-x}$ system, including the possibility of the CDW formation at low temperature.
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