Anisotropic Thermal Expansion of $\alpha$-YbAlB$_4$

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Abstract. Thermal expansion measurements were performed for $\alpha$-YbAlB$_4$ using powder X-ray diffraction and our high resolution capacitance dilatometry. Highly anisotropic thermal expansion, which is much larger along the $c$-axis compared to the $a$- and $b$-axes, was observed. In addition, high resolution capacitance dilatometry revealed negative thermal expansion appears below 90 K only along the $a$-axis, not along the $c$-axis. The observation is consistent with anisotropic hybridization stronger in the $ab$-plane, suggesting the formation of anisotropic heavy fermion well below the valence fluctuation temperature scale of 200 – 300 K. Furthermore, linear thermal expansion coefficient along the $a$-axis starts to decrease below 115 K. The characteristic temperature scale of 90 - 115 K may correspond to the crystal electric field excited level. The in-plane negative thermal expansion can be regarded as a development of anisotropic hybridization due to $|J_z| = \pm 5/2 >$ crystal electric field ground states which becomes dominant on cooling below the excited states.

1. Introduction
In $f$-electron intermetallics, Quantum criticality (QC) is one of the subjects which has been extensively studied as a source of novel quantum phenomena, such as unconventional superconductivities and non-Fermi liquid behavior (NFL)[1, 2]. So far, the most of the studies have been restricted to magnetic QC, which arises at a magnetic quantum critical point (QCP) in the Kondo lattice systems with integer valence.

On the other hand, in the case of mixed valence compounds, local $f$ moments are expected to be screened by conduction electrons at their relatively higher Kondo temperatures. Therefore, heavy fermion (HF) and QC behavior have not been expected in this class of materials. In sharp contrast, the first Yb-based HF superconductor $\beta$-YbAlB$_4$ provides a unique example of a HF formation and a QC in the strongly mixed valence state [3, 4, 5, 6]. Furthermore, the QC cannot be described by the standard theory for the spin-density-wave instability[7, 8, 9]. The diverging magnetic susceptibility along the $c$-axis exhibits the $T/B$ scaling in the wide temperature ($T$) and magnetic field ($B$) region spanning 3 – 4 orders of magnitude[5], indicating the QC emerges without tuning any control parameter. In addition, recent resistivity measurements under pressure revealed the anomalous metallic state extends over a finite pressure range up to 0.4 GPa, suggesting a formation of an anomalous metallic phase[10].

$\beta$-YbAlB$_4$ has a locally isostructural polymorph $\alpha$-YbAlB$_4$, which is also strongly mixed valent. These have an orthorhombic crystal structure with space groups $Pbam$ and $Cmmm$ for $\alpha$- and $\beta$-YbAlB$_4$, respectively [11]. The Yb valence estimated by a hard x-ray photoemission spectroscopy is +2.73 for $\alpha$-YbAlB$_4$ and +2.75 for $\beta$-YbAlB$_4$ at 20 K [6]. The valence
fluctuation temperature scale was estimated to be $\sim 200 - 300$ K for both compounds \cite{5, 12, 13}. Nevertheless, these two systems exhibit a HF behavior with a characteristic temperature scale of $\sim 8$ K, which is far lower than the valence fluctuation scale \cite{5}. This is quite unusual because Pauli paramagnetism is usually expected in the mixed valence compounds below the valence fluctuation temperature scale. The small temperature scale of $\sim 8$ K for the anomalous HF state may indicate that $\alpha$-YbAlB$_4$ is also close to a QCP although it has a Fermi liquid (FL) ground state at zero field in contrast to $\beta$-YbAlB$_4$ \cite{12}.

Another remarkable feature for both systems is the anisotropic hybridization between conduction and $f$ electrons ($c$-$f$ hybridization). From the argument based on the local symmetry of the Yb site, the crystal field ground doublet of both $\alpha$- and $\beta$-YbAlB$_4$ is suggested to be made solely of $|J_z = \pm 5/2 >$ \cite{14}. In this case, the $c$-$f$ hybridization is expected to be highly anisotropic and have a node along the $c$-axis \cite{15}. Indeed, it was already suggested experimentally from the resistivity measurements of $\alpha$-YbAlB$_4$ \cite{12}. The resistivity is highly anisotropic and the one in the $ab$-plane is 10 times larger than the one along the $c$-axis. In addition, $A$ coefficients of $T^2$ behavior of the resistivity, which were determined below 0.24 K, are also highly anisotropic with $A_{ab}/A_c \sim 10$, suggesting anisotropic effective mass with $m_{ab}/m_c \sim 3$. Consistently, transverse magnetoresistivity also exhibits a large anisotropy \cite{16}. These are consistent with the hybridization node along the $c$-axis. Interestingly, it has been pointed out that the anisotropic $c$-$f$ hybridization plays an important role in the formation of HF state under the strong valence fluctuation and the novel QC found in $\beta$-YbAlB$_4$ \cite{15, 17}. On the other hand, a critical valence fluctuation has been also suggested as the origin of the QC \cite{18, 19}. Therefore, the role of the anisotropic $c$-$f$ hybridization is still controversial.

In order to further clarify the anisotropic nature of the system, here, we performed thermal expansion measurements using powder X-ray diffraction and capacitance dilatometry. While the temperature dependence of the lattice parameters were determined with a resolution of $\Delta L/L \sim 2 \times 10^{-4}$ by the X-ray diffraction, the measurements using the capacitance dilatometer along the $a$- and $c$-axes were performed with a high resolution of $\Delta L/L \sim 2 \times 10^{-7}$. Interestingly, we found highly anisotropic thermal expansion, which is much larger along the $c$-axis compared to the $a$- and $b$-axes. In addition, high resolution capacitance dilatometry revealed a negative thermal expansion appears below 90 K only along the $a$-axis, not along the $c$-axis. The observation is consistent with anisotropic hybridization stronger in the $ab$-plane, suggesting anisotropic heavy fermion formation well below the valence fluctuation temperature scale of 200 - 300 K. Furthermore, the linear thermal expansion coefficients start to change at 115 K on cooling. The characteristic temperature scales of 90 - 115 K may correspond to the crystal electric field (CEF) excited level, below which the anisotropic hybridization is expected to develop as $|J_z = \pm 5/2 >$ states become dominant.

2. Experimental

We used high purity single crystals of $\alpha$-YbAlB$_4$ with typical RRR (Residual Resistivity Ratio) ranging from 20 to 110 grown by a flux method \cite{11}. Powder X-ray diffraction measurements were carried out from room temperature down to 16 K. Single crystalline samples were grind into fine powder and measured using a commercial X-ray diffraction system (Rigaku RINT2100) in the angle range between $10 \leq 2\theta \leq 90^\circ$. Diffraction patterns were analyzed to determine the lattice constant using the Rietveld analysis program PDXL (Rigaku).

High resolution measurements using capacitance dilatometer \cite{20} were performed along the $a$- and $c$-axes at temperature range from 2 K to room temperature with a resolution of $\Delta L/L \sim 2 \times 10^{-7}$. The measured single crystal has a dimension of $\sim 1$ mm for both along the $a$- and $c$-axes. In order to subtract the cell background effect, we also measured a high purity Cu piece with a thickness of 1.0 mm.
Figure 1. Linear thermal expansions $\Delta L/L$ of $\alpha$-YbAlB$_4$ measured from room temperature (300 K). Open symbols are the data obtained from the X-ray diffraction measurements. Solid lines indicate the data obtained from capacitance dilatometry.

3. Results and Discussions
First we present the temperature dependence of the linear thermal expansions $\Delta L/L$ measured from room temperature in Figure 1. The data obtained from the X-ray diffraction and those from capacitance dilatometer are consistent with each other within the experimental accuracy. As it is clearly seen from the figure, $\Delta L/L$ is highly anisotropic. $\Delta L/L$ along the $c$-axis is much larger than those along the $a$- and $b$-axes. This may come from much harder covalent bond in the in-plane boron network than the $c$-axis aluminum and ytterbium chain. On the other hand, the X-ray diffraction data indicate that the in-plane anisotropy is small, i.e., $\Delta L/L$ along the $a$- and $b$-axes are roughly overlapping to each other.

Remarkably, $\Delta L/L$ along the $a$-axis, measured by capacitance dilatometer, clearly shows negative thermal expansion below 90 K, i.e., the lattice expand along the $a$-axis on cooling. In the case of Yb-based intermetallics, negative thermal expansion can be associated with a valence change due to Kondo effect. This is because the ionic radius of Yb$^{2+}$ ($4f^{14}$) is larger than that of Yb$^{3+}$ ($4f^{13}$). If the valence of the system changes through Kondo effect from Yb$^{3+}$ towards Yb$^{2+}$ on cooling, the lattice will expand correspondingly. This negative thermal expansion is observed in Yb-based Kondo lattice systems such as YbIr$_2$Zn$_{20}$ and YbCu$_2$Si$_2$ [21]. Therefore, the negative thermal expansion observed in $\alpha$-YbAlB$_4$ can also be regarded to arise from valence change from Yb$^{3+}$ towards Yb$^{2+}$ due to hybridization developing in the low temperatures.

One important feature here is that the negative thermal expansion is only observed along the $a$-axis, not along the $c$-axis. This is consistent with the anisotropic hybridization larger in the $ab$-plane and clearly suggests the formation of anisotropic heavy fermion in $\alpha$-YbAlB$_4$. Note that, although thermal expansion along the $b$-axis has not been measured using capacitance dilatometer, it is also expected to exhibit the same negative thermal expansion. This is because the in-plane resistivity does not exhibit anisotropy [12] and, furthermore, no in-plane large anisotropy has been expected in the $c$-$f$ hybridization theoretically [15]. The small in-plane anisotropy in $\Delta L/L$ by X-ray diffraction is also consistent with this expectation.

In order to discuss the anisotropic thermal expansion in detail, we present the temperature
dependence of the linear and volume thermal expansion coefficients in Figure 2. Here, the linear thermal expansion coefficient $\alpha$ is defined as $\alpha \equiv (1/L)(dL/dT)$ and estimated from the data by capacitance dilatometry. The volume thermal expansion coefficient $\alpha_V$ is given as $\alpha_V \equiv (1/V)(dV/dT) = \alpha_a + \alpha_b + \alpha_c \approx 2\alpha_a + \alpha_c$, neglecting in-plane anisotropy. $\alpha_i$ denotes $\alpha$ along the $i$-axis. While $\alpha_c$ exhibits a monotonic decrease on cooling, $\alpha_a$ exhibits almost temperature independent behavior at higher temperatures and then starts to decrease below 115 K and becomes negative below 90 K. On the other hand, $\alpha_V$ does not exhibit clearly negative value beyond experimental accuracy, while it also starts to decrease below 115 K. Interestingly, $\alpha_c$ compensates the negative contribution coming from $\alpha_a$, which results in the very small values of $\alpha_V$ close to zero below $\sim$ 60 K.

The characteristic temperature scale of 115 K (or 90 K) may correspond to the CEF excited state. As an excited state, $|J_z = \pm 1/2 > + \gamma |J_z = \mp 3/2 >$ with $\gamma \sim 0.28$ has been suggested at the excited level of 80 K for $\beta$-YbAlB$_4$ [14], which well reproduces the anisotropic magnetic susceptibility at the temperature range from 10 to 300 K. Although $\alpha$-YbAlB$_4$ was not mentioned in their work, considering the quite similar local symmetry of the Yb site and almost identical magnetic susceptibility above $T \sim 8$ K, one can expect quite similar CEF levels for both $\alpha$- and $\beta$-YbAlB$_4$. As it is already mentioned, the anisotropic hybridization is supposed to arise from CEF ground state of $|J_z = \pm 5/2 >$. If the system is cooled below the CEF excited level, the anisotropic hybridization will develop as $|J_z = \pm 5/2 >$ become dominant, which may results in anisotropic thermal expansion. If this is a case, considering that $\alpha_a$ starts to decrease already at 115 K, the CEF excited level should be a bit higher than this temperature. To confirm this, neutron inelastic scattering measurements are highly desired. Note that it is quite unusual to assume well defined CEF levels far below the valence fluctuation temperature scale. This must be closely related to one of the central issue in $\alpha$- and $\beta$-YbAlB$_4$, why HF and QC behaviors appear even under the strong valence fluctuation or why local moments survive under the strong valence fluctuation. Another point we should note is that the negative thermal expansion is expected also at the valence fluctuation temperature scale of 200 - 300 K, since the Yb valence is changing...
in this temperature range. However, this 4f electron contribution may be masked by a large lattice contribution at high temperatures. In order to discuss how the 4f electron contribution evolves on cooling, we need to subtract the lattice contribution using non-magnetic α-LuAlB₄, which is an important future issue.

Finally, the volume thermal expansion αᵥ is supposed to be proportional to the specific heat. Therefore, in the lowest temperatures, αᵥ/T in α-YbAlB₄ should be constant corresponding to its Fermi liquid ground state. Unfortunately, the resolution and the temperature range of the current measurements are not enough to see this behavior of the moderately heavy fermions with γ ~ 130 mJ/K²mol [12]. The measurements with a better resolution of ΔL/L ~ 1 x 10⁻⁸ down to much lower temperature of 0.1 K is now going to be measured.

4. Conclusion
In this work, the anisotropic nature of α-YbAlB₄ was investigated by thermal expansion measurements. Using powder X-ray diffraction and a high-resolution capacitance dilatometry, we revealed that α-YbAlB₄ exhibits highly anisotropic thermal expansion, where the one along the c-axis is much larger than those along the a- and b-axes. This is possibly due to much harder covalent bond in the in-plane boron network than the c-axis aluminum and ytterbium chain. More interestingly, high resolution capacitance dilatometry, which were done along the a- and c-axis, revealed a negative thermal expansion appears below 90 K only along the a-axis, not along the c-axis. The observation suggests anisotropic hybridization, which develops stronger in the ab-plane well below the valence fluctuation temperature scale of 200 - 300 K. One can further expect anisotropic Fermi liquid formation in the low temperature limit. On the other hand, the linear thermal expansion coefficient along the a-axis starts to decrease below 115 K. The characteristic temperature scale of 90 - 115 K may correspond to the CEF excited level. In this case, the in-plane negative thermal expansion can be regarded as a development of anisotropic hybridization due to |J₂| = ±5/2 > crystal electric field states which becomes dominant on cooling below the excited state.

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