

Low-temperature thermal expansion measurements in $\text{PrV}_2\text{Al}_{20}$

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Abstract. We have measured thermal expansion of $\text{PrV}_2\text{Al}_{20}$ and $\text{LaV}_2\text{Al}_{20}$ from room temperature down to 2 K, using a capacitance dilatometer. Linear thermal expansion $\Delta L/L$ along [111] direction decreases monotonically on cooling in both materials. The extracted $4f$ electrons contribution of the linear thermal expansion coefficient α clearly shows a broad peak at ~ 30 K which may correspond to the crystal electric field excited state at 40 K suggested in the previous specific heat study.

1. Introduction

Recently, orbital degrees of freedom have attracted much attention in condensed matter physics and a lot of interesting phenomena have been studied extensively, such as spin-orbital disordered state in $\text{Ba}_3\text{CuSb}_2\text{O}_9$ [1] and superconductivity in Iron-based compounds [2]. While spin and orbital degrees of freedom are strongly coupled in these d electron systems, f electron intermetallics can provide an interesting case, such as non-magnetic Γ_3 crystal electric field (CEF) ground doublet of f^2 configuration in a cubic site symmetry. This doublet does not have magnetic dipolar degrees of freedom but consists of quadrupolar and octupolar degrees of freedom. Therefore, in this case, we can study phenomena arising from pure orbital degrees of freedom. In particular, quadrupole Kondo effect, originally suggested as a single ion effect in the nonmagnetic cubic Γ_3 doublet [3], has attracted a lot of attention because of its non-Fermi liquid ground state. Indeed, several cubic Pr-based compounds having cubic symmetry in crystal structure, such as PrPb_3 [4, 5, 6], PrInAg_2 [7] and PrMg_3 [8], have been studied extensively in this context. However, there has been no established example with strong hybridization between f electrons and conduction electrons without structural disorders. Note that structural disorders can easily lift the degeneracy of the non-Kramers doublet and hence high quality single crystal is quite important.

On the other hand, recent studies revealed that $\text{PrTr}_2\text{Al}_{20}$ (Tr : Ti, V) are ideal systems to study quadrupolar Kondo effect. $\text{PrTr}_2\text{Al}_{20}$ are cage compounds which have cubic $\text{CeCr}_2\text{Al}_{20}$ -type structure with the space group $\text{Fd-}3\text{m}$ [9]. As it is expected from the crystal structure where Pr^{3+} ion is surrounded by 16 Al atoms, the hybridization is strong as is evident in many physical properties [10, 11]. In our previous studies, we have already succeeded in synthesizing



high-quality single crystal of $\text{PrTi}_2\text{Al}_{20}$ by Al self-flux methods [10, 11]. The both have non-magnetic Γ_3 ground doublet with the well separated excited state at $\Delta_{\text{CEF}} = 60$ K (Ti) and 40 K (V) respectively, which have been confirmed by various experiments [10, 12, 13]. $\text{PrTi}_2\text{Al}_{20}$ exhibits ferroquadrupole ordering at $T_Q = 2$ K, and $\text{PrV}_2\text{Al}_{20}$ exhibits double transitions at $T_Q = 0.75$ K and $T^* = 0.65$ K [10, 11, 14]. The origin of double transition in $\text{PrV}_2\text{Al}_{20}$ is unknown still, but should come from quadrupole and/or octupole degree of freedom. In $\text{PrV}_2\text{Al}_{20}$, c - f hybridization is expected to be stronger than that of $\text{PrTi}_2\text{Al}_{20}$ due to smallness of Al cage surrounding Pr ions. Indeed, it exhibits anomalous metallic behavior above the multipolar transitions, such as anomalous temperature dependence of electrical resistivity ($\rho \sim T^{-1/2}$ and $\rho \sim \ln T$), magnetic susceptibility ($\chi \sim -T^{1/2}$), and specific heat ($C/T \sim T^{-3/2}$) [10]. Furthermore, $\text{PrV}_2\text{Al}_{20}$ exhibits heavy fermion superconductivity at $T_C = 50$ mK in the multipole ordered state even under the ambient pressure [11], suggesting a proximity to an orbital QCP, where an orbital ordering is suppressed due to a strong hybridization and orbital fluctuation.

Here, we have performed thermal expansion measurements in $\text{PrV}_2\text{Al}_{20}$ and $\text{LaV}_2\text{Al}_{20}$ from 300 K to 2 K. Thermal expansion is a quite useful quantity to detect a lattice strain which couples to quadrupolar degrees of freedom. For example, if there is a ferroquadrupole ordering, spontaneous strain of lattice with the same symmetry as that of the quadrupole ordering emerges due to co-operative Jahn-Teller effect [15, 16]. Thermal expansion measurements are useful also for studies of heavy fermion system. One example is the recent study on EuNi_2P_2 , where it has been revealed that the heavy fermion state in this compound arises from Kondo effect for the first time in Eu-based compounds on the analogy of CeRu_2Si_2 [17, 18]. In our study, we observed obvious difference between $\text{PrV}_2\text{Al}_{20}$ and $\text{LaV}_2\text{Al}_{20}$ in linear thermal expansion coefficient α along [111] direction. The extracted $4f$ electrons contribution of the linear thermal expansion coefficient α clearly shows a broad peak at ~ 30 K, which may correspond to the crystal electric field excited state at 40 K, which was suggested from the previous specific heat measurements.

2. Experimental

Single crystals of $\text{PrV}_2\text{Al}_{20}$ and $\text{LaV}_2\text{Al}_{20}$ were prepared by Al self-flux method, using 4N (99.99%)-Pr, 4N-La, 3N-V and 5N-Al, respectively. The sample length along [111] direction is 1.2 mm and 1.1 mm for $\text{PrV}_2\text{Al}_{20}$ and $\text{LaV}_2\text{Al}_{20}$, respectively.

Thermal expansion measurements were performed at temperature range from 300 K down to 2 K, in a zero-magnetic field, by using a capacitance dilatometer installed in a commercial cryostat (PPMS, Quantum Design). Linear thermal expansion was measured with an accuracy of ~ 0.5 Å.

3. Results and discussion

The linear thermal expansion $\Delta L/L$ of $\text{PrV}_2\text{Al}_{20}$ and $\text{LaV}_2\text{Al}_{20}$ along [111] direction are shown in Figure 1. $\Delta L/L_{[111]}$ for both compounds exhibit monotonous decrease on cooling and no anomaly was observed in a temperature range from 300 K to 2 K. The magnitude of the thermal expansion $\Delta L/L \sim 0.25$ - 0.3% is close to the value for Cu $\Delta L/L \sim 0.33\%$ [19] and is relatively common value among metals. Thermal expansion consists of three contributions, namely, phonons, conduction electrons, and $4f$ electrons contributions. The length change ΔL can be written as $\Delta L = \Delta L_{\text{phonon}} + \Delta L_e + \Delta L_{4f}$. Because the former two contributions are supposed to be almost the same for both compounds, the difference between these two corresponds to the $4f$ electrons contribution.

Figure 2 shows thermal expansion coefficient α in $\text{PrV}_2\text{Al}_{20}$ and $\text{LaV}_2\text{Al}_{20}$ along [111] direction. Linear thermal expansion coefficient α is defined as the temperature derivative of normalized length change $\Delta L/L$, i.e., $\alpha \equiv \frac{d}{dT}(\Delta L/L)$. α also decreases monotonically

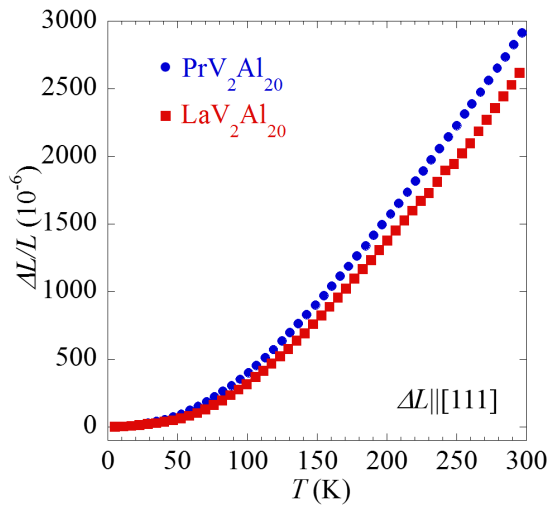


Figure 1. Linear thermal expansion along [111] direction for $\text{PrV}_2\text{Al}_{20}$ and $\text{LaV}_2\text{Al}_{20}$.

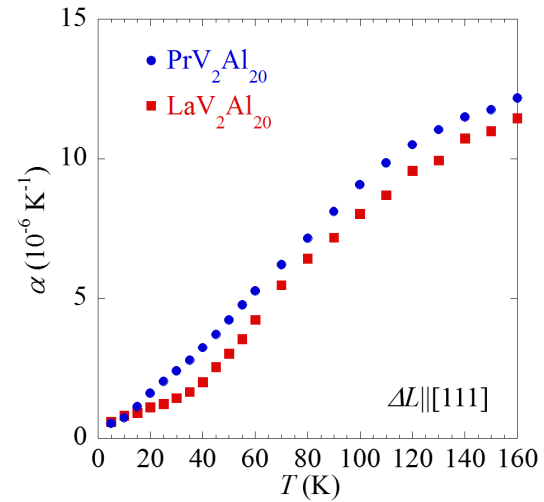


Figure 2. Linear thermal expansion coefficient α along [111] direction for $\text{PrV}_2\text{Al}_{20}$ and $\text{LaV}_2\text{Al}_{20}$.

with decreasing temperature for both samples. In general, thermal expansion coefficient α is proportional to specific heat. Therefore, in the low enough temperatures, α for $\text{LaV}_2\text{Al}_{20}$ will be expressed by a summation of T -linear and T^3 power law terms, which arise from conduction electrons and phonons, respectively. However, while the specific heat can be well expressed by a summation of T -linear and T^3 power law terms below 8.5 K [20], it is hard to see this behavior in the current thermal expansion data because of the accuracy and the temperature range of the measurements. More accurate measurements down to lower temperature are required. Note

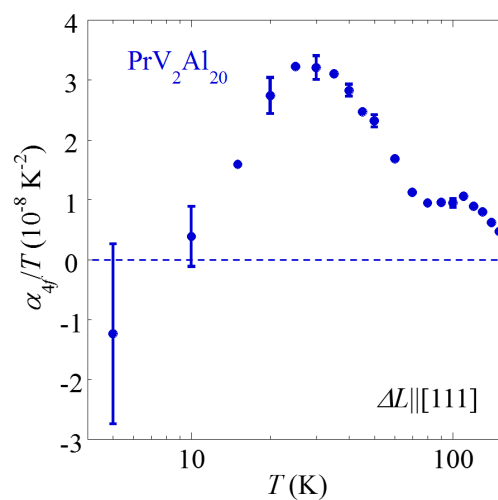


Figure 3. $4f$ electrons contribution of the linear thermal expansion coefficient α_{4f} along [111] direction divided by temperature T . For detail, see text.

that the Debye temperature θ_D of $\text{LaV}_2\text{Al}_{20}$ has been already estimated as ~ 510 K from the specific heat measurements [20].

Figure 3 shows $4f$ electrons contribution of the linear thermal expansion coefficient α_{4f} divided by temperature. α_{4f} is obtained by subtracting the α for $\text{LaV}_2\text{Al}_{20}$ from that for $\text{PrV}_2\text{Al}_{20}$, *i.e.*, $\alpha_{4f} \equiv \alpha_{\text{PrV}_2\text{Al}_{20}} - \alpha_{\text{LaV}_2\text{Al}_{20}}$. The extracted $4f$ electrons contribution of the linear thermal expansion coefficient α clearly shows a broad peak at ~ 30 K. Below ~ 30 K, it decreases rather steeply and reaches almost zero at the lowest temperature of $T \sim 5$ K. The broad peak found at ~ 30 K is supposed to arise from the CEF excited state at 40 K, which was suggested from the previous specific heat measurements. $4f$ electrons contribution of the specific heat C_{4f} exhibits broad peak at ~ 20 K [10]. In the cubic system with Γ_3 ground doublet, the excited CEF state should be either magnetic Γ_5 or Γ_4 triplet. In order to obtain further information on the excited CEF state from the thermal expansion measurements, measurements for other directions, such as [100] and [110] directions, and magnetic field angle resolved measurements will be useful, which are interesting future issues. In the lowest temperatures around 5 K, rather large experimental error makes it difficult to see if the observed negative value of α_{4f}/T is intrinsic or not. Negative thermal expansion is rather unusual behavior. Therefore, it is an interesting future issue to examine such a possibility in $\text{PrV}_2\text{Al}_{20}$. In f electron systems, there are a few examples of negative thermal expansion, such as those found in TmTe [21] and Yb-based heavy fermions [22]. In the case of TmTe , the negative thermal expansion is associated with a sign change of Grüneisen constant across the CEF level [21]. However this is unlikely in $\text{PrV}_2\text{Al}_{20}$ because the possible negative thermal expansion occurs well below the CEF excited state at 40 K. On the other hand, in Yb-based heavy fermions, negative thermal expansion occurs due to the valence change from Yb^{3+} to Yb^{2+} , which is induced by c - f hybridization (Kondo effect) [22]. Likewise, in the case of $\text{PrV}_2\text{Al}_{20}$, one interesting possibility is a negative thermal expansion arising from a valence change due to a strong hybridization between f electrons orbital degrees of freedom and conduction electrons, *i.e.*, quadrupole Kondo effect. Apparently, further experiments and theoretical inputs are required to study this.

4. Conclusion

We have measured thermal expansion of $\text{PrV}_2\text{Al}_{20}$ and $\text{LaV}_2\text{Al}_{20}$ from room temperature down to 2 K, using a capacitance dilatometer. Linear thermal expansion $\Delta L/L$ along [111] direction decreases monotonically on cooling in both materials. The extracted $4f$ electrons contribution of the linear thermal expansion coefficient α clearly shows a broad peak at ~ 30 K, which may correspond to the CEF excited state at 40 K and is consistent with the previous specific heat measurements. Further measurements are required in order to investigate the possible negative thermal expansion in the lowest temperatures and the detail of the CEF excited state at 40 K.

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