Highly anisotropic strain dependencies in PrIr$_2$Zn$_{20}$

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We investigated thermal expansion and magnetostriction of the quadrupolar Kondo lattice PrIr$_2$Zn$_{20}$ for which antiferroquadrupolar order at $T_Q = 0.11$ K and signatures of orbital Kondo effect were reported. Linear thermal expansion and magnetostriction, measured along and perpendicular to magnetic fields $B \parallel [001]$, provide evidence of a highly anisotropic tetragonal distortion which reflects the fundamental symmetry of the non-Kramers $\Gamma_3$ ground state doublet, formed by the cubic $T_d$ point group of the Pr-ions. The resulting volume change is vanishingly small, indicating weak hybridization between $4f^2$ and conduction electrons. Our results clarify that the enhancement of Seebeck coefficient and other physical quantities in vicinity of the critical field of antiferroquadrupolar order at $B \approx 5$ T applied along the $[001]$ direction cannot be explained by a strongly hybridized state as seen in the Ce- and Yb-based heavy fermion systems.

In recent years, comprehensive studies on heavy fermion (HF) materials imparted fundamental understanding on their competing ground states which are classified as strongly hybridized, magnetically ordered and in special cases quantum critical. As proposed by Doniach in 1977, the ground state depends on the interaction strength $J$ between localized magnetic moments and conduction electrons which can be tuned by the variation of an external control parameter, e.g. magnetic field, pressure or chemical substitution. Extensive research on materials with quadrupolar degrees of freedom followed, motivated by the aim of verifying the applicability of the Doniach picture. Even though generic behavior could not be found yet, a variety of novel quadruple driven states of matter were detected, such as exotic antiferroquadrupolar (AFQ) order in PrPb, HF superconductivity in PrOs$_4$Sb$_{12}$ and PrV$_2$Al$_2$ and signatures of orbital Kondo effect in PrIr$_2$Zn$_{20}$.

In particular, the material class of cubic Pr-based 1-2-20 systems, with the non-Kramers $\Gamma_3$ ground state doublet, provides key prerequisites to explore purely orbital driven physics. Considerable efforts have been expended on characterizing the materials PrIr$_2$Zn$_{20}$, PrRh$_2$Zn$_{20}$, PrV$_2$Al$_2$ and PrTi$_2$Al$_{20}$, which share the coexistence of quadrupolar order and superconductivity. The high coordination number and the local $T_d$ symmetry of the Pr-ions facilitate the hybridization of electric quadrupole moments and conduction electrons, whereby thermopower measurements suggest enhanced hybridization effects for the Al-based system as compared to the Zn-based system.

Up to now it remains elusive, whether a quadrupolar critical state driven by strong correlations between the fluctuating order parameter and conduction electrons can evolve in those systems. First indications could be found for PrTi$_2$Al$_{20}$, where the application of hydrostatic pressure significantly enhances the superconducting transition temperature from $T_c = 0.2$ K ($p = 0$) to 1.1 K ($p = 8.7$ GPa) as well as the effective mass from $m^* / m \approx 16$ to around 11. Further hydrostatic pressure suppresses the ferroquadrupolar phase transition. To reveal universal behavior of the quadrupolar Kondo lattice materials, systematic studies in magnetic field and under pressure are essential.

In this letter we focus on the quadrupolar Kondo lattice PrIr$_2$Zn$_{20}$, which crystallizes in the cubic CeCr$_2$Al$_{20}$-type structure with $F\bar{d}3m$ space group. The crystalline electric field ground state is the non-Kramers $\Gamma_3$ doublet, which is separated by $\Delta_{CEF} = 28$ K from the first excited $T_4$ triplet state. The material undergoes AFQ ordering at $T_Q = 0.11$ K, which is suppressed by magnetic fields of $B \approx 5$ T applied along the $[001]$ direction. In vicinity of the critical magnetic field, pronounced anomalies in Seebeck coefficient, specific heat and elastic constants as well as anomalous enhancement of the $T^2$ coefficient of electrical resistivity were observed, which prompted speculations about a field-induced strongly hybridized electronic state. For temperatures $T > T_Q$, non-Fermi liquid behavior in specific heat and electrical resistivity is a distinct signature of orbital Kondo effect. If $4f^2$ and conduction electrons hybridize, $4f^2$ moments become itinerant which results in a valence change of the Pr-ions. Since the valence of a Pr-ion is directly connected to its occupied volume, volume thermal expansion and magnetostriction are important parameters to be investigated.

To perform the thermal expansion and magnetostriction measurements, we utilized a dilution refrigerator equipped with a 13 T superconducting magnet. Linear thermal expansion $\alpha = 1/L (dL/LdT)$ and magnetostriction $\lambda = 1/L (dL/LdB)$ parallel to magnetic fields, where $\Delta L$ denotes the relative length change and $L$ the sample length at room temperature, were measured by use of a high-resolution capacitance dilatometer made of silver. In addition, a miniaturized dilatometer made of copper beryllium with a size of just 3 cm$^3$ was utilized. The small dimensions allowed to rotate the dilatometer in the bore of the superconducting magnet and enabled the measurement of $\alpha$ and $\lambda$ perpendicular to magnetic field. A calibration measurement revealed a scaling factor of $(\Delta L/L)_{Ag}/(\Delta L/L)_{CuBe} = 1.18$ between the two capacitance cells. Therefore, the data obtained by the silver dilatometer was scaled accordingly.
To deduce the relative length change from the measured capacitance value, we applied the Pott and Schefczyk principle which takes account of the shortcut capacitance of the dilatometer. Linear thermal expansion coefficient $\alpha$ and magnetostriction coefficient $\lambda$ were determined by numerical differentiation of the relative length change with respect to magnetic field or temperature. For the calculation of $\alpha$ a differentiation window of $\Delta B = 0.05$ T was used. To determine $\alpha$, the differentiation window was set to $\Delta T = 0.015$ K at the lowest temperatures and gradually increased to 0.08 K at the highest measured temperature of $T = 5$ K. The investigated single crystalline sample was grown by a Zn self-flux technique, as described in Ref.\cite{ref1}, with a length of $L = 1.295$ mm along the $[001]$ direction and a residual resistivity ratio of $RRR = 54$.

First, we present and discuss the results of the thermal expansion measurements. Fig. 1(a) shows the temperature dependence of the linear thermal expansion coefficient measured parallel $\alpha_\parallel$ and perpendicular $\alpha_\perp$ to magnetic fields $B \parallel [001]$. The volume thermal expansion coefficient is calculated as $\beta = \alpha_\parallel + 2\alpha_\perp$. For $B \leq 4$ T, the discontinuity in $\alpha$ at $T_Q \approx 0.11$ K indicates the second order phase transition into the AFQ ordered state which was reported by Onimaru et al.\cite{ref2} The uniaxial stress dependence of $T_Q$ is estimated by the Ehrenfest relation for second order phase transitions

$$
\left( \frac{\partial T_Q}{\partial p} \right)_{p\rightarrow0} = \frac{V_m T_Q \Delta \alpha_i}{\Delta C},
$$

where $V_m = 2.1887 \cdot 10^{-4}$ m$^3$/mol is the molar volume, $\Delta \alpha_i$ and $\Delta C$ assign to the jump heights in thermal expansion and specific heat and $i$ denotes the respective crystal direction. The opposite signs of $\Delta \alpha_i$ and $\Delta C$ imply that $T_Q$ is suppressed by the application of uniaxial stress, whereby the sensitivity increases continuously with increasing magnetic field from $\partial T_Q/\partial p = 0.01 \approx 10^{-3}$ K/GPa at zero field to $10^{-1}$ K/GPa at $B = 4$ T. The determination of $\Delta \alpha_{[001]}$ and $\Delta C$ by means of an equal area construction is accompanied by a non-negligible uncertainty. Therefore, only an estimation of order of magnitude is given.

At $B \approx 5$ T, the sharp anomaly at $T_Q$ vanishes and instead, a broader maximum, with a strongly enhanced value of $\alpha_\parallel \approx 43 \cdot 10^{-6} \text{K}^{-1}$, emerges. The inset highlights the evolution of the phase transition signature at $T_Q$ for $B \leq 5$ T and the gradual enhancement of $\alpha$ with magnetic field. With further increase of magnetic field, the maximum at $B = 5$ T shifts to higher temperatures and its value decreases notably. At low temperatures $T < T_Q$ and weak magnetic fields $B \leq 4$ T, the divergent behavior of $\alpha$ is a striking feature. A nuclear Schottky contribution is excluded as its cause, since the divergent behavior disappears for magnetic fields $B \geq 5$ T, which is at odds with the monotonic increase of a nuclear contribution as a function of magnetic field.

In order to clarify the origin of the divergent behavior and maxima in $\alpha$, we performed a mean-field calculation based on a two sub-lattice model with the hamiltonian

$$
\mathcal{H}_{A(B)} = \mathcal{H}_{CEF} - g_J \mu_B J H - g_I \left[ O_2^0 \epsilon_u + O_2^0 \epsilon_v \right] - K \left[ O_2^0 \langle O_2^0 \rangle_{B(A)} + O_2^0 \langle O_2^0 \rangle_{B(A)} \right] - K J \langle J \rangle_{B(A)} \right),
$$

where $g_J$ is the Landé factor, $\mu_B$ the Bohr magneton,
The quadrupole-strain coupling constant, \( g_{T_3} \), the interaction coefficient between \( T_3 \)-type quadrupoles and \( K \) the magnetic interaction coefficient. \( \epsilon_u = (2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy})/\sqrt{3} \) and \( \epsilon_v = \epsilon_{xx} - \epsilon_{yy} \) denote the \( T_3 \) symmetry strains. The relative length change \( \Delta L/L \) is proportional to the strain

\[
\epsilon_{T_3} = \frac{N g_{T_3}}{C_{T_3}^0} \langle O_{T_3} \rangle ,
\]

where \( N = 2.751 \times 10^{-27} \text{ m}^3 \) is the number of Pr-ions per unit volume, \( C_{T_3}^0 \) is the elastic modulus and \( \langle O_{T_3} \rangle \) the thermal average of the respective Stevens operator\(^{[18]}\). The crystalline electric field effect is described by the Hamiltonian

\[
\mathcal{H}_{CEF} = W \left[ \frac{x O_{T_3}^0 + 5O_4^4}{60} + (1 - |x|) \frac{O_{T_3}^0 - 21O_4^4}{1260} \right],
\]

where \( W = -1.22 \text{ K} \) and \( x = 0.53 \).\(^{[20,21]}\)

The relative length changes along and perpendicular to magnetic fields \( B \parallel [001] \) are estimated by

\[
\frac{\Delta L}{L} \bigg|_{[001]} = \frac{1}{3} \epsilon_B + \frac{1}{\sqrt{3}} \epsilon_u ,
\]

\[
\frac{\Delta L}{L} \bigg|_{[100]} = \frac{1}{3} \epsilon_B - \frac{1}{2\sqrt{3}} \epsilon_u + \frac{1}{2} \epsilon_v ,
\]

where \( \epsilon_B = \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} \) is the isotropic volume expansion of the \( I_1 \) symmetry. In zero magnetic field, a tetragonal distortion does not exist and the linear thermal expansion corresponds to \( \epsilon_B/3 \). The inset of Fig. 1 (a) illustrates that zero field thermal expansion is vanishingly small as compared to the thermal expansion in magnetic fields \( B \geq 4 \text{ T} \). Consequently, \( \epsilon_B \) is not taken into account in subsequent analysis, just like \( \epsilon_u \), which is insignificantly small as compared to \( \epsilon_v \). The quadrupole interaction is set to \( K_{T_3} = -0.0067 \text{ K} \) in order to reproduce the experimentally observed AFQ ordering temperature of \( T_Q = 0.11 \text{ K} \) in zero magnetic field. The magnetoelastic constant \( g_{T_3} = -36 \text{ K} \) and magnetic interaction \( K = -0.22 \text{ K} \) are determined by fitting the experimental data at high magnetic fields \( B \geq 10 \text{ T} \). Those values are comparable to the ones which were determined by the elastic constants measurement \((|g_{T_3}| = 30.9 \text{ K})\) and by the paramagnetic Curie temperature \((K = -0.35 \text{ K})\).

The mean-field calculation for thermal expansion at various magnetic fields is presented in Fig. 1 (b). The opposite sign of \( \alpha || \) and \( \alpha \perp \) consistent with the experimental results and at high magnetic fields \( B \geq 10 \text{ T} \), the temperature dependencies of \( \alpha \) could be well reproduced, as shown in the inset. By contrast, the experimentally observed maxima for magnetic fields \( B \leq 7 \text{ T} \) appear at much lower temperatures than in the calculation. Also the divergent behavior of \( \alpha \) within the AFQ ordered state cannot be explained by the mean-field calculation.

Next, we focus on the magnetostriction measurements. Fig. 2 (a) shows the magnetic field dependence of the linear magnetostriction coefficient \( \lambda \) measured parallel \( \lambda || \) and perpendicular \( \lambda \perp \) to magnetic fields \( B \parallel [001] \) at various temperatures. The volume magnetostriction is determined as \( \lambda_V = \lambda || + 2\lambda \perp \). Additionally, linear and volume magnetostriction of \( \text{YbIr}_2\text{Zn}_{20} \), which were extracted from\(^{[22]}\), are shown. (b) Calculation results for \( \lambda || \) and \( \lambda \perp \) at various temperatures.

**FIG. 2.** (a) Magnetic field dependence of the linear magnetostriction coefficient \( \lambda \) measured along \( \lambda || \) and perpendicular \( \lambda \perp \) to magnetic fields \( B \parallel [001] \) at various temperatures. The volume magnetostriction is determined as \( \lambda_V = \lambda || + 2\lambda \perp \). Additionally, linear and volume magnetostriction of \( \text{YbIr}_2\text{Zn}_{20} \), which were extracted from\(^{[22]}\), are shown. (b) Calculation results for \( \lambda || \) and \( \lambda \perp \) at various temperatures.
In PrIr$_2$Zn$_{20}$, $\lambda_{\parallel}$ and $\lambda_{\perp}$ exhibit a distinct maximum at $B \approx 4.9$ T and $T \leq 0.11$ K, which broadens and shifts to higher magnetic fields with increasing temperature, whereas $\lambda_{\parallel}$ is negative and $\lambda_{\perp}$ positive. The opposite signs of linear thermal expansion and magnetostriction coefficients result from the magnetic field and temperature dependencies of $\langle O^2 \rangle$. The calculated curves for $\lambda_{\parallel}$ and $\lambda_{\perp}$ are shown in Fig 2 (b), whereby the same parameters as for the calculation of the linear thermal expansion are used. At $T \geq 1.5$ K, simulated and experimental data match well, however, for $T \leq 0.9$ K the peak position obtained from the experiment is significantly higher than the calculation. This discrepancy points to an additional contribution at low temperatures and magnetic fields $B < 10$ T which cannot be explained by the simple mean-field calculation.

The deviations between experiment and calculation in vicinity of the critical magnetic field of $B \approx 5$ T might be caused by the formation of novel exotic phases, which serve as a mechanism to release the residual entropy, related to the orbital Kondo effect. A possible scenario is composite order which breaks the symmetry of the two equivalent channels of orbital Kondo effects. Alternatively, a “spin”-wave like gap with $q \neq 0$ might be cause for the enhancements around $B = 5$ T.

Notable result of our investigation is the vanishingly small volume thermal expansion and magnetostriction in the whole magnetic field and temperature range. Consequently, the anomalous enhancement of the Seebeck coefficient at $B \approx 5$ T does not simply result from the formation of a strongly c-f hybridized state as found in the Ce- and Yb-based HF systems. Another peculiarity is the divergent behavior of $\alpha_{\parallel}$ and $\alpha_{\perp}$ for $B < 5$ T within the AFQ ordered phase which cannot be explained by the mean-field calculation. In the zero temperature limit entropy goes to zero based on the third law of thermodynamics. Therefore, the linear thermal expansion coefficient $\alpha$, which is proportional to the uniaxial stress derivative of entropy $\alpha = -1/L \langle \partial S/\partial p \rangle_{T,B}$, should vanish as well. Only if the system shows a finite residual entropy even at the lowest temperatures, $\alpha$ can remain finite. Specific heat measurements give indication of a finite residual magnetic entropy for magnetic fields $1 T \leq B \leq 5$ T, as well.

To conclude, thermal expansion and magnetostriction of PrIr$_2$Zn$_{20}$ display huge uniaxial anisotropies, although volume effects are significantly small. The findings indicate that the valence of the Pr-ions shows only little alterations due to variation of temperature and magnetic field which is a fundamental difference to the Kondo lattice YbIr$_2$Zn$_{20}$ with a magnetic Kramers ground state doublet. Therefore, the orbital Kondo effect in PrIr$_2$Zn$_{20}$, which was detected in specific heat and electrical resistivity measurement, should result from a moderately weak c-f hybridization. The divergent behavior of $\alpha$ within the AFQ ordered state might be an indication of residual entropy with a high sensitivity to uniaxial stress. Further theoretical and experimental investigations are indispensable to reveal the nature of the potential residual entropy in the AFQ ordered phase and the peculiar novel state at the edge of AFQ order.

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