Field-Orientiation Effect on Ferro-Quadrupole Order in PrTi$_2$Al$_{20}$

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Ferro-quadrupole (FQ) order in the non-Kramers $\Gamma_3$ doublet system PrTi$_2$Al$_{20}$ has been investigated via angle-resolved measurements of the specific heat, rotational magnetocaloric effect, and entropy, under a rotating magnetic field within the (110) plane. The FQ transition occurring at 2 K is robust when the magnetic field $B$ is applied precisely along the [111] direction or in low fields below 1 T. By contrast, the magnetic field of larger than 1 T tilted away from the [111] direction sensitively changes the FQ transition to a crossover. The energy gap between the ground and first-excited states in the FQ order increases remarkably with the magnetic field in $B$ || [001], but hardly depends on the magnetic-field strength, at least up to 5 T, in the field orientation between the [111] and [110] axes. These features can be reproduced by using a phenomenological model for FQ order assuming an anisotropic field-dependent interaction between quadrupoles, which has been recently proposed to explain the field-induced first-order phase transition in PrTi$_2$Al$_{20}$. The present study demonstrates the great potential of the field-angle-resolved measurements for evaluating possible scenarios for multipole orders.

Multipole degrees of freedom often play an essential role in causing a variety of ordered phases in spin-orbit coupled systems. Recently, the Pr$_2$Z$_{20}$ system ($T$=transition elements, $X$=Al or Zn) with the cubic CeCr$_2$Al$_{20}$-type structure has attracted much attention because it has a non-Kramers $\Gamma_3$ doublet ground state under the crystalline electric field (CEF). These $\Gamma_3$-doublet materials provide a significant chance to study novel phenomena caused by electric quadrupoles ($O_{20}$ and $O_{22}$) and a magnetic octupole ($T_{xyz}$) in the absence of active magnetic dipoles. Furthermore, it provides a unique opportunity to investigate the relation between exotic superconductivity and multipole fluctuations because superconductivity likely driven by multipole fluctuations has been found in PrTi$_2$Al$_{20}$, Pr$_2$V$_{20}$, Pr$_2$Z$_{20}$, and PrRh$_2$Z$_{20}$. In this letter, we focus on multipole order in PrTi$_2$Al$_{20}$ occurring at $T_{FQ}$ ~ 2 K. The ground state of the non-Kramers doublet $\Gamma_3$ and the first-excited state of the triplet $\Gamma_4$ are well separated by a substantial energy gap of 54 K. Therefore, it is expected that the low-temperature physics in this material is dominated by degrees of freedom of the non-magnetic $\Gamma_3$ doublet. On the basis of broadening of the transition under a magnetic field $B$ parallel to the [100] axis together with the absence of a magnetic superlattice reflection in the neutron scattering experiment, the multiple order can be attributed to ferroquadrupole (FQ) one. Moreover, evidence for the order of $O_{20}$ quadrupole has been provided from NMR measurements.

Recently, $^{27}$Al-NMR and magnetization measurements have revealed highly-anisotropic phase diagram of the FQ order in PrTi$_2$Al$_{20}$. A field-induced first-order phase transition was found in the FQ ordered state near 2 T for $B$ || [100] and [110], whereas it was absent in $B$ || [111]. Such a highly-anisotropic phase diagram is unexpected for the $\Gamma_3$-doublet system because the magnetic dipole is not active. As a possible origin, competition between the Zeeman effect and multipole interactions was proposed in Ref. 4, resulting in switching of the FQ order parameters under $B$. Indeed, by assuming an anisotropic field-dependent quadrupole-quadrupole interaction, which is overcome by the Zeeman effect in high fields, the phase diagrams for three field orientations, $B$ || [100], [111], and [110], have been successfully reproduced by a Landau theory based on the mean-field approximation. However, this scenario is based on a phenomenological assumption whose validity has not yet been established, e.g., from the microscopic theory. Further investigations are necessary to elucidate the FQ order parameters of PrTi$_2$Al$_{20}$, both experimentally and theoretically.

In this study, the field-orientation effect on this highly-anisotropic phase diagram of PrTi$_2$Al$_{20}$ has been investigated precisely from thermal experiments. The specific heat is particularly useful to distinguish between the low-field and field-induced FQ phases; a sharp (broad) peak in the specific heat corresponds to an occurrence of the low-field (field-induced) FQ phase because the FQ transition at $T_{FQ}$ changes into a crossover in the field-induced phase due to the predominant Zeeman effect. Our experimental results demonstrate that the broadening of the FQ transition is sensitively induced by a magnetic field of larger than 1 T applied away from the [111] axis. Furthermore, it has been clarified that, when the field angle is in the range between the [111] and [110] directions, the energy gap between the ground and first-excited states in the FQ ordered state is nearly invariant with $B$, at least up to 5 T. These experimental results can be explained...
by a phenomenological model including the field-dependent
anisotropic quadrupole interaction, which was introduced in
the previous study.\(^{11}\)

Single crystals of PrTi\(_2\)Al\(_{20}\) were grown by an Al self-flux
method.\(^{7}\) A single crystal with its mass of 1.258 mg was
used in this study, having a small, triangular facet which cor-
responds to the (111) plane. The residual resistivity ratio of
a crystal cut from the same batch is as large as 170, which
ensures high quality of the present sample. This (111) sam-
ple face was attached on a sample stage of our home-made
calorimeter,\(^{14}\) and it was placed in a dilution refrigerator so
that the [110] axis of the sample is roughly parallel to the
vertical \(z\) direction. A magnetic field was generated within
the \(xz\) plane by using a vector magnet, and the refrigerator
was rotated around the \(z\) axis by using a stepper motor which
was mounted at the top of the dewar. By using this system,
the orientation of the magnetic field can be controlled three-
dimensionally. In this study, the magnetic field was aligned
precisely parallel to the (110) plane with an accuracy of better
than 0.1°. The field angle \(\phi_B\) is defined as the angle between
the [001] axis and the magnetic field.

The specific heat \(C\) and the rotational magnetocaloric effect
\((\partial T / \partial \phi_B)_{S,B}\) were investigated by the standard semi-adiabatic
method\(^{14}\) in a rotating magnetic field within the (110) plane.
From the field-angle anisotropy in \(C\), it was found that the
[110] axis was tilted away from the rotational axis (\(\parallel z\)) by
approximately 10.6°. Therefore, in all the field-angle-resolved
measurements shown here, we took two processes to rotate
the magnetic field within the (110) plane; first, the refrigerator
was rotated to a target angle, and then, horizontal and vertical
magnetic fields were fine-tuned so that the resulting field ori-
entation is parallel to the (110) plane. During the first process,
we precisely measured the relative change in the sample tem-
perature, \(\delta T(\phi_B) = T(\phi_B) - T_0\), upon a semi-adiabatic small-
angle rotation of the magnetic field (typically 1°). Here, \(T_0\)
is the base temperature of the sample. The rotational magne-
tocaloric effect was evaluated from the initial slope of \(\delta T(\phi_B)\)
just after starting the field rotation. Then, the field-angle de-
pendence of the entropy \(S(\phi_B)\) can be obtained from the rela-
tion
\[ \frac{\partial S}{\partial \phi_B} \bigg|_{T,B} = \frac{C}{T} \frac{\partial T}{\partial \phi_B} \bigg|_{S,B}. \]  

Figures 1(a)–1(c) show the temperature dependence of \(C\) under various magnetic fields parallel to the [001] \((\phi_B = 0°)\),
[111] \((\phi_B = 54.7°)\), and [110] \((\phi_B = 90°)\) axes, respectively.
In zero field, a steep increase in \(C(T)\) is observed on cooling
at \(T_{FG} \approx 2.07\) K (midpoint). By contrast, a specific-heat
jump cannot be clearly observed at a superconducting tran-
sition temperature of 0.2 K,\(^{15}\) probably due to the residual
magnetic field in the superconducting magnet (several mT)
comparable to the upper critical field (~ 6 mT) and/or due to
small electronic contribution to \(C(T)\) in PrTi\(_2\)Al\(_{20}\). With in-
creasing a magnetic field up to 5 T, the increase in \(C(T)\) at
\(T_{FG}\) becomes gradual in \(B \parallel [001]\) and [110], whereas it re-
mains nearly unchanged in \(B \parallel [111]\). These features are
consistent with the previous reports.\(^{7,16}\) In high magnetic fields,
a prominent upturn is seen in \(C(T)\) at low temperatures below
roughly 0.4 K, which can be attributed to the nuclear contribu-
tion.\(^{15}\)

The broadening of the FQ transition can be more clearly
seen in the field dependence of \(C\). Figures 2(a) and 2(b) show \(C(B)\) measured at temperatures slightly above and be-
low \(T_{FG}\), respectively; the increase (decrease) in \(C(B)\) at 2.3
(1.8) K with increasing \(B\) corresponds to the broadening of the
FQ transition, as observed in the \(C(T)\) data. Again, no clear
change is detected in the \(C(B)\) data in \(B \parallel [111]\). By contrast,
the transition starts to broaden around 1 T for both \(B \parallel [001]\)
and [110]. This indicates that the field-induced phase appears
above roughly 1 T in these field orientations. The broadening
is more prominent in \(B \parallel [001]\) than in \(B \parallel [110]\).

A contrasting feature has been observed in \(C(B)\) at low tem-

Fig. 1. (Color online) Temperature dependence of the specific heat under a
magnetic field parallel to the (a) [001], (b) [111], and (c) [110] axes.

Fig. 2. (Color online) Field variation of the specific heat at (a) 2.3, (b) 1.8,
and (c) 0.9 K. Labels represent the field orientation.
The high-field at 0.9 and 1.8 K, as shown in Figs. 3(a) and 3(b), respectively. smoothly decreases with rotating $B$ significantly with $B^2$ and first-excited states in the FQ ordered state does not change tively in the framework of the conventional CEF model. 15) on the FQ order, the the $C$ the nently in $B$ transition into a crossover as the field strength becomes larger field orientation away from the [111] axis transforms the FQ is nearly insensitive to the magnetic field at least up to 5 T in temperatures well below $T_{\text{FO}}$. As shown in Fig. 2(c), $C(B)$ at 0.9 K is nearly insensitive to the magnetic field at least up to 5 T in $B$ || [110] as well as $B$ || [111], whereas $C(B)$ decreases prominently in $B$ || [001]. These features can also be confirmed in the $C(T)$ data (Fig. 1). This field-insensitive behavior at low temperatures implies that the energy gap between the ground and first-excited states in the FQ ordered state does not change significantly with $B$. This feature can be understood qualitatively in the framework of the conventional CEF model.15)

To provide further insight into the field-orientation effect on the FO order, the $\phi_B$ dependence of $C$ has been measured at 0.9 and 1.8 K, as shown in Figs. 3(a) and 3(b), respectively. The high-field $C(\phi_B)$ exhibits a clear cusp at $\phi_B = 54.7^\circ$, i.e., in the [111] direction. At 1.8 K, slightly below $T_{\text{FO}}$, $C(\phi_B)$ smoothly decreases with rotating $B$ from [111] to [001] or [110]. This result indicates that a small tilt of the magnetic-field orientation away from the [111] axis transforms the FQ transition into a crossover as the field strength becomes larger than 1 T. No clear signature of a phase transition by the rotation of $B$ was detected from $C(\phi_B)$ measurements.

Figures 3(c) and 3(d) present the $\phi_B$ dependence of the rotational magnetocaloric effect at 0.9 and 1.8 K, respectively. The field-rotational speed is set to $d\phi_B/dt = 5$ and 2.5 s/deg at 0.9 and 1.8 K, respectively. The data are obtained by averaging $dT/d\phi_B$ taken under clockwise and anticlockwise field rotations in order to cancel out the heat-transfer effect.14) A clear rotational magnetocaloric effect is observed in high fields for $B \geq 2$ T. It becomes zero when $B$ orients to the [001], [111], or [110] direction. This result suggests an occurrence of the temperature-independent zero-torque state ($\tau_\phi = 0$) in these field orientations because $dS/d\phi_B$ corresponds to $d\tau_\phi/dT$ according to the Maxwell relation. Here, $\tau_\phi$ represents the magnetic torque within the field-rotation plane.

The $\phi_B$ dependence of the entropy can be evaluated as $S(\phi_B) = S(\phi_B = 0^\circ) - \int_0^{\phi_B} C(T)d\phi_B$ by using the results of specific-heat and rotational magnetocaloric effect measurements. The relative entropy change defined as $\Delta S = S(\phi_B) - S(\phi_B = 54.7^\circ)$ are plotted for $T = 0.9$ and 1.8 K in Figs. 3(e) and 3(f), respectively. This definition is useful because the $C(T)$ data demonstrate that $S(\phi_B = 54.7^\circ)$ is nearly unchanged with $B$ in the present range. Whereas the entropy is strongly suppressed with increasing $B$ for $B$ || [001], it is relatively robust against $B$ for $B$ || [110].

In order to understand the observed field-angle-dependent phenomena, $C(T, B, \phi_B)$ has been calculated by using the Hamiltonian within the $J = 4$ multiplet of $\text{Pr}^{3+}$,

$$H = \mathcal{H}_{\text{CEF}} + \mathcal{H}_Z + \mathcal{H}_\Omega + \mathcal{H}_Q + \mathcal{H}_O,$$

which is the same one proposed in Ref. 11. Here, the conventional CEF potential with the $T_d$ point symmetry $\mathcal{H}_{\text{CEF}},$
the Zeeman interaction $H_Z$, an exchange interaction between magnetic dipoles $H_{\text{CEF}}$, a quadrupole-quadrupole interaction $H_Q$, and a small $T^4$ octupole-octupole interaction $H_O$ are expressed as

$$
H_{\text{CEF}} = \varepsilon_2 (Q^2 - \varepsilon_1 (Q^3 - 3Q_x^2)),
$$

$$
H_Z = - g J \mu_B \mathbf{J} \cdot \mathbf{B},
$$

$$
H_D = - \lambda (Q_x, J_x, J_y),
$$

$$
H_Q = - \lambda (Q_x, Q_y, Q_z)
+ \frac{\lambda}{2} f(B^2) h_i(Q_x, Q_y, Q_z),
$$

$$
H_O = - \lambda \phi (T^4) \cdot \mathbf{T}^4,
$$

respectively, where $h_x = 2B_x^2 - B_z^2 - B_y^2$ and $h_z = \sqrt[3]{(B_x^2 - B_z^2)}$. For convenience, two-component order parameters, i.e., $Q_x = (Q_x, Q_y, Q_z) = Q \cos \theta, \sin \theta$, are adopted, where $Q_z = \sqrt[3]{(J_x^2 - J_z^2)/2} (\propto O_{22})$ and $Q_x = (3J_x^2 - J_z^2)/8 (\propto O_{20})$. The factor $f(B^2) = 1/(1 + c_2B^2 + c_4B^4)$ is phenomenologically assumed so that the effect of $H_O (H_Z)$ becomes predominant at low (high) fields. The parameters are set to the same as those in Ref. 11: $J_x = 2 K_c, \lambda_D = -0.8 K, \lambda_T = 0.0004 K, \phi = 0.08 K/T^2, c_2 = 0.8 T^{-2}$, and $c_4 = 0.8 T^{-4}$.

The calculated results of $C(T)$ for $B \parallel [001], [111]$, and [110] are plotted in Figs. 4(a)–4(c), respectively. Note that electronic and phonon contributions to the specific heat are not included in the present calculations. The anisotropic broadening of the FQ transition as well as the low-temperature $C(T)$ insensitive to $B$ along the [110] direction are reproduced reasonably. Figures 4(d) and 4(e) present $C(\phi_B)$ calculated at 0.9 and 1.76 K ($< T_{\text{FQ}}$), respectively, in a rotating field within the (110) plane. Both the cusp structure in $C(\phi_B)$ at $\phi_B \sim 54.7^\circ$ and the gradual decrease in $C(\phi_B)$ with tilting $B$ from the [111] to [001] axes are consistent with the experimental observations.

On the basis of the present model calculations, the occurrence of a phase transition has been predicted not only in the field scan but also in the temperature and field-angle scans. For instance, a clear phase transition can be seen in $C(T)$ slightly below $T_{\text{FQ}}$ at 1 T in $B \parallel [001]$ [Fig. 4(a)] and in $C(\phi_B)$ around $\phi_B \sim 75^\circ$ at 3 T and 1.76 K [Fig. 4(e)]. Although such anomalies have not been clearly detected from our specific-heat measurements, the latter might be detected via $\Delta S(\phi_B)$, showing a small step-like change around $\phi_B \sim 75^\circ$ at 3 T and 1.8 K [Fig. 3(b)]. This is probably because we directly measured the physical quantity corresponding to the field-angle derivative of the entropy, i.e., $(\partial T / \partial \phi_B)_{T,B} = - T / C(\partial S / \partial \phi_B)_{T,B}$, for determining $\Delta S(\phi_B)$.

As already reported in Ref. 11, the FQ order parameters with $\theta = 0$ and $\pm 2\pi/3$ are stabilized in zero field or $B \parallel [111]$, when $B \parallel [001] ([110]), \pi/2 \leq |\theta| \leq 2\pi/3 (\theta = 0)$ is stabilized in the low-field FQ phase and changes to $\theta = 0$ ($2\pi/3 \leq |\theta| \leq \pi$) in the field-induced phase. Figures 5(a) and 5(b) show the order-parameter angle $\theta$ as a function of $\phi_B$ at 0.32 and 1.81 K, respectively, obtained from the present calculation. The phase transition around $\phi_B \sim 75^\circ$ at 3 T and 1.8 K can be attributed to a change in the order parameter from $2\pi/3 < |\theta| < \pi$ to $|\theta| = \pi$; in the latter phase, spontaneous symmetry breaking does not occur.

The main effect of the newly introduced $\lambda'$ term is explained in the Supplemental Material. It is noted that a finite $\lambda'$ is necessary to reproduce the low-field experimental data of $C(\phi_B)$ near $B \parallel [001]$. Thus, the recently-proposed model, phenomenologically assuming an unconventional anisotropic quadrupole-quadrupole interaction, is in good agreements with the experimental observations under a rotating $B$ for PrTi$_2$Al$_3$.

In conclusion, we have investigated the specific heat and entropy of PrTi$_2$Al$_3$ in a rotating magnetic field within the (110) plane. It was found that the FQ transition becomes a crossover in fields larger than 1 T in any direction except for $B \parallel [111]$. Our experimental results support the scenario that the competition between the anisotropic quadrupole-quadrupole interaction and the Zeeman effect causes a discontinuous change in FQ order parameters under a magnetic field. The field-angle-resolved thermal measurements can be a useful tool to test order parameters for multiple phases.

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15) (Supplemental Material) (I) Low-temperature specific heat of PrTi$_2$Al$_{20}$, and (II) Effect of the $\lambda'$ term in the calculation are provided online.
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I. Low-temperature specific heat of PrTi$_2$Al$_20$

The low-temperature part of $C(T)/T$ for $B \parallel [111]$ is shown in Fig. S1. Although the ferroquadrupole transition at $T_{FQ} \sim 2$ K is nearly unchanged in this field orientation, the low-temperature upturn in $C/T$ becomes prominent with increasing $B$. This upturn can be fitted satisfactorily by using a function $f(T) = a + b/T^3$, as represented by dashed lines in Fig. S1. The fitting parameter $b$ is plotted as a function of $B$ in the inset of Fig. S1(a). It is nearly proportional to $B^2$, which is reminiscent of the nuclear Schottky contribution.

Let us calculate the nuclear specific heat $C_N(T, B) = b_{\text{calc}}^{\text{Al}}(B)/T^2$ of PrTi$_2$Al$_20$. Here, the effect of a quadrupole splitting of nuclei is ignored; indeed, the upturn in $C/T$ in zero field is small and does not follow $T^{-3}$ dependence [Fig. S1(b)]. The observed $C_N$ is mostly caused by $^{27}$Al ($I = 5/2$ with the natural abundance of 100%) and $^{141}$Pr ($I = 5/2$ with the natural abundance of 100%) nuclei. The former contribution can be evaluated as $b_{\text{calc}}^{\text{Al}}(B) = 0.14B^2$ mJ K/mol by using a nuclear spin Hamiltonian;

$$\mathcal{H}_{\text{Al}} = -g_N^{\text{Al}}\mu_N I \cdot B,$$

where $g_N^{\text{Al}} = 1.46$ is the nuclear $g$ factor of an Al ion and $\mu_N$ is the nuclear magneton.

Because a strong hyperfine coupling arises between a Pr nucleus and 4$f$-electrons on the same ion, contribution from Pr nuclei can be calculated by using the Hamiltonian\(^1\)

$$\mathcal{H}_{\text{Pr}} = I \cdot (A_{\text{hf}}J - g_N^{\text{Pr}}\mu_N B),$$

where $A_{\text{hf}}$ is a coupling constant of hyperfine interaction of a Pr ion, $J$ is the total angular momentum of 4$f$ electrons, and $g_N^{\text{Pr}} = 1.71$ is the nuclear $g$ factor of a Pr ion.\(^2\) Then, the latter contribution $b_{\text{calc}}^{\text{Pr}}(B)$ can be expressed by

$$b_{\text{calc}}^{\text{Pr}}(B) = R[A_{\text{hf}}m_{\text{Pr}}(B)/g_J + g_N^{\text{Pr}}\mu_N B]^2I(I+1)/(3k_B^2),$$

where $R$ is the gas constant, $m_{\text{Pr}} = g_J\langle|J_z|^2\rangle^{1/2}$ is the site-averaged magnitude of the Pr magnetic moment, $g_J = 4/5$ is the Landé $g$ factor, and $k_B$ is the Boltzmann constant. In this calculation, we adopt $A_{\text{hf}}/k_B = 0.052$ K\(^3\) and $m_{\text{Pr}}(B) = 0.068B \mu_B/Pr$ for $B \leq 5$ T.\(^3\) Then, we obtain $b_{\text{calc}}^{\text{Pr}}(B) = 0.62B^2$ mJ K/mol. The sum of these nuclear contributions is $b_{\text{calc}}(B) = b_{\text{calc}}^{\text{Al}}(B) + b_{\text{calc}}^{\text{Pr}}(B) = 0.76B^2$ mJ K/mol [a solid line in the inset of Fig. S1(a)]. Good agreement between experimental and calculated results demonstrates that the observed upturn in $C/T$ can be attributed to the nuclear contribution.
Figure S1(b) shows the low-temperature $C(T)/T$ in zero field. In a previous report,$^5$ the occurrence of a superconducting transition was reported at $T_c = 0.2$ K. A slight deviation from the $T^{-3}$ behavior is seen below 0.2 K in Fig. S1(b), which might be attributed to the superconducting transition. However, it is rather broad and other possible origins, e.g., nuclear contribution, cannot be fully ruled out. Because the upper critical field is roughly 6 mT, a residual magnetic field in a superconducting magnet (typically several mT) would suppress the superconducting transition.

II. Effect of the $\lambda'$ term in the calculation

Figure S2 shows the calculated results of $C(\phi_B)$ with (a), (b) $\lambda' = 0$ and (c), (d) $\lambda' = 0.08$ K/T$^2$. The experimental results of $C(\phi_B)$ in high fields can be reproduced qualitatively from the calculation with $\lambda' = 0$ as well. The $\lambda'$ term mainly affects the low-field data in $C(\phi_B)$ around $B \parallel [001]$. For instance, at 0.9 K, the difference between $C(\phi_B)$ at 1 and 2 T becomes small with changing $\lambda'$ from 0 to 0.08 K/T$^2$. Moreover, at 1.76 K, $C(\phi_H)$ in $B \parallel [001]$ is comparable to that in $B \parallel [111]$ when $\lambda' = 0.08$ K/T$^2$, whereas $C(\phi_H)$ gradually decreases with rotating $B$ from the [111] to [001] axes for $\lambda' = 0$. Thus, the calculated results for $\lambda' = 0.08$ K/T$^2$ provide a better match with the experimental observations in $C(\phi_B)$ and $S(\phi_B)$ at low fields.
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Fig. S1. (a) Temperature dependence of $C/T$ at several magnetic fields in $B \parallel [111]$. Dashed lines represent fits to the data below 0.35 K using the function $f(T) = a + b/T^3$. The inset shows $b(B)$ obtained by the fits (circles). A solid line represents $b_{calc}(B)$ obtained from the calculation using the nuclear spin Hamiltonian (see text). (b) The low-temperature $C(T)/T$ in zero field.

Fig. S2. Calculated results of the specific heat as a function of the field angle $\phi_B$ at (a) [(c)] 0.9 and (b) [(d)] 1.76 K with $\lambda' = 0$ (0.08) K/T^2.