

Anomalous Schottky Specific Heat and Structural Distortion in Ferromagnetic PrAl₂

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Unique from other rare earth dialuminides, PrAl₂ undergoes a cubic to tetragonal distortion below $T = 30$ K in a zero magnetic field, but the system recovers its cubic symmetry upon the application of an external magnetic field of 10 kOe via a lifting of the 4*f* crystal field splitting. The nuclear Schottky specific heat in PrAl₂ is anomalously high compared to that of pure Pr metal. First principles calculations reveal that the 4*f* crystal field splitting in the tetragonally distorted phase of PrAl₂ underpins the observed unusual low temperature phenomena.

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Materials with structural transformations or distortions coupled to magnetic transitions show interesting magnetostrictive, magnetoresistive, and magnetocaloric behavior and are, therefore, an important subject of study in condensed matter physics [1–4]. The importance of either coupled or decoupled magnetostructural transformations has been shown for many materials starting from high temperature superconductors [5] and perovskites [6] to multifunctional intermetallics [4], just to mention a few. The anomalies close to 0 K encompass another playground for fundamental physics, and they range from the Kondo effect [7] and heavy fermion behavior [8] to quantum criticality [9] and nuclear Schottky specific heat [10]. These remarkable behaviors are ultimately related to the interplay between localized and delocalized electrons, for which lanthanides are truly the best model provided by nature. In particular, the rare earth dialuminides, which have simple cubic Laves phase structure at room temperature, have long been the system of choice to understand the fundamentals of rare earth magnetism and low temperature (LT) anomalies.

Magnetism and crystallography of $RA\text{Al}_2$ compounds (R = rare earth element) have been extensively studied over the last few decades, yet specific heat (C_p) and crystal structures of these systems at LT have not received much attention, thus creating a gap in understanding of the underlying fundamental physics of these materials. At room temperature, all of the $RA\text{Al}_2$ compounds adopt cubic MgCu_2 Laves phase-type structure with space group $Fd\bar{3}m$ [11]. These dialuminides have been employed for detailed studies of the crystal field (CF) effects that influence the physical properties such as specific heat, magnetic susceptibility, and electrical resistivity [12–16].

The cubic Laves phase structure of the dialuminides appears to be extremely stable. The LT x-ray diffraction (XRD) study of GdAl_2 suggests that this compound retains the MgCu_2 type structure down to 12 K [17]; the same is true for the pseudobinary dialuminides, such as $R'_{1-x}\text{Tb}_x\text{Al}_2$, ($R' = \text{Er}, \text{Ho}$ and Tm), that preserve the

cubic Laves phase structure down to 5 K [18,19]. To the best of our knowledge, none of the dialuminides formed by either the individual heavy lanthanides ($R = \text{Gd}–\text{Lu}$) or their mixtures have been reported to undergo a structural transformation at low temperatures. The only exception is HoAl_2 , which exhibits an orthorhombic distortion upon spin reorientation transition that occurs in the ferromagnetic state (FM) [20]. On the other hand, several of the mixed heavy lanthanide dialuminides exhibit first order—like anomalies at LT without apparent structural distortions [21]. Compared to the dialuminides formed by heavy lanthanides, much less is known about the LT crystallography of the $RA\text{Al}_2$ compounds with light lanthanides ($R = \text{La}$ and $\text{Ce}–\text{Eu}$), even though interesting phenomena have been observed, e.g., heavy fermion behavior and Kondo effect in CeAl_2 [22,23].

Another interesting feature of some of the lanthanides is high nuclear specific heat (C_N) contribution at LT, which is generally caused by the interactions of the nuclear magnetic moments with the strong magnetic field produced by the 4*f* electrons at the sites of the nuclei, the so-called hyperfine interactions [24]. Additional contributions to C_N could also result from the nuclear electric quadrupole moment interactions with the electric field gradient [25]. Since the discovery of large nuclear specific heat C_N in terbium [26], the LT C_p (from 0.4 to 4 K) for many other R metals was measured to establish the C_N [24,27]. It was reported that at sufficiently low temperature ($T \leq 2$ K) the Schottky anomaly due to the hyperfine splitting is the dominant term in the total heat capacity of several lanthanides. Despite the fact that LT C_p studies have been carried out for many rare earth systems [28], the detailed nuclear contributions to the total heat capacity of $RA\text{Al}_2$ systems have not been studied to date. Magnetic and electrical transport properties, neutron and room temperature x-ray diffraction have been reported for PrAl_2 in both the polycrystalline and single crystalline forms [29–35]. It is well established that PrAl_2 is FM with $\langle 100 \rangle$ as the easy direction of magnetization [13]. The reported values

of Curie temperature (T_C) vary from 30 to 34 K depending upon the sample [33,34,36].

In this Letter, we report a remarkable LT structural distortion and the anomalous LT heat capacity of PrAl₂ complemented with first principles electronic structure calculations indicating that a strong $4f$ CF splitting is responsible for the distorted phase of α -PrAl₂ and accounts for the unusual LT phenomena.

The polycrystalline PrAl₂ alloy was prepared by arc melting of stoichiometric amounts of the elements in an argon atmosphere. The Pr metal was obtained from the Materials Preparation Center of the Ames Laboratory and was 99.86 + at.% pure with respect to all other elements in the periodic table [37]. The Al metal of 4N purity was purchased from Alfa Aeser Inc. Powder XRD experiments were performed at temperatures ranging between 300 K and 5 K in zero and applied magnetic fields up to 30 kOe as described in Ref. [38]. The structural parameters were determined from Rietveld analysis using LHPM Rietica [39]. The dc magnetization was measured in a Quantum Design MPMS-XL7 magnetometer. The heat capacity measurements were performed using a homemade adiabatic heat-pulse calorimeter [40]. The physical property measurement system (PPMS by Quantum Design) with ³He option was used to measure the heat capacity down to 0.362 K in magnetic fields up to 140 kOe.

Heat capacity C_p measurements of PrAl₂ in various magnetic fields are shown in Figs. 1(a)–1(c). The room temperature C_p value is 72.05 J mol⁻¹ K, which is close to the classical Dulong and Petit limit of the lattice heat capacity at constant volume $C_V = 3nR = 74.83$ J mol⁻¹ K⁻¹, where $n = 3$ is the number of atoms per formula unit and R is the universal gas constant [41]. The value of C_p decreases with decreasing temperature down to the sharp peak at $T = 32.5$ K, which is due to the paramagnetic

(PM) to FM transition [16]. The anomaly in C_p is slightly suppressed upon the application of 1 kOe magnetic field, and it is significantly reduced in height and considerably broadened when applied magnetic field reaches and exceeds 10 kOe. This is the typical behavior of a ferromagnet. The magnetization measurements show that the temperature at which the anomaly observed in zero field C_p data is in an excellent agreement with the PM to FM transition temperature, $T_C = 32.5$ K [Fig. 1(a) inset]. The ZFC, FCC (or FCW) $M(T)$ curves of PrAl₂ show irreversible behavior below T_C . The irreversibility diminishes with the increasing magnetic field and it vanishes when a magnetic field approaches 10 kOe (not shown). Above T_C , magnetic susceptibility follows the Curie-Weiss law. The effective magnetic moment, p_{eff} , and the Weiss temperature, Θ_{pm} , are $3.32\mu_B$ and 32.6 K, respectively. The observed p_{eff} is slightly lower than the theoretical value $g[J(J+1)]^{1/2} = 3.58\mu_B$ of free Pr³⁺. The positive value of Θ_{pm} indicates that the FM interactions are dominant in PrAl₂. The saturation magnetization (M_S) at 2 K is $2.49\mu_B/\text{Pr}$, which is significantly lower than the theoretical gJ value of $3.2\mu_B$ for Pr in the FM state due to crystalline electric field effects.

In addition to the anomaly at 32.5 K, it is noted that C_p becomes enhanced at $T \leq 4$ K, which is clearly seen in the inset of Fig. 1(b). The LT C_p of PrAl₂ was explored down to 0.36 K in magnetic fields up to 140 kOe [Fig. 1(c)]. For comparison, LT C_p of pure Pr metal was also measured [Fig. 1(d)]. The experimentally measured C_p at $T \leq 2$ K for both Pr and PrAl₂ were fitted using the following equation

$$C_p = AT^3 + BT + C_N T^{-2}, \quad (1)$$

where the first two terms are the standard lattice and electronic contributions, respectively. The third term in Eq. (1)

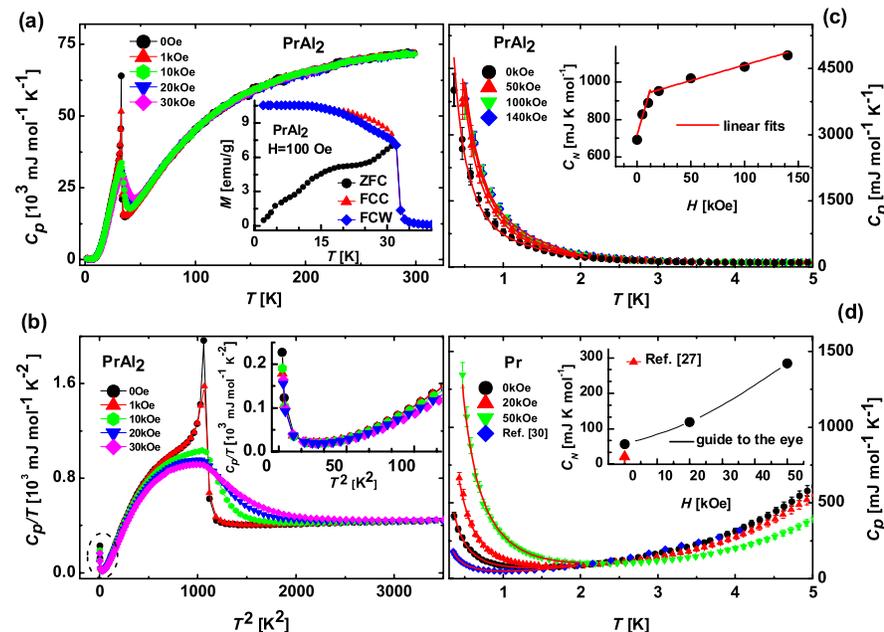


FIG. 1 (color online). (a) The heat capacity of PrAl₂ measured in different external magnetic fields. The inset shows zero field cooled (ZFC) warming, field cooled cooling (FCC), and field cooled warming (FCW) magnetization of PrAl₂ measured in $H = 100$ Oe. (b) The C_p/T as a function of T^2 . The inset shows the details at low temperature. (c) The heat capacity of α -PrAl₂ measured below 5 K in different magnetic fields. (d) The heat capacity of Pr metal measured below 5 K in different magnetic fields. The insets in (c) and (d) show nuclear specific heat coefficients C_N [from the fits of data for $0.6 \text{ K} \leq T \leq 2 \text{ K}$ to Eq. (1)] as functions of applied magnetic field. The solid triangle in the inset in (d) represents the data from Ref. [27]. The solid lines in (c) and (d) are the fits of the data to Eq. (1) for $T \leq 2$ K. The errors in C_N are about the size of the symbols.

is the contribution from the nuclear specific heat that arises due to the splitting of the nuclear hyperfine levels.

The previously reported zero field C_p of Pr metal below 4 K (see Ref. [27]) is in considerable disagreement with our data [Fig. 1(d)]. Least squares fit of the data for $0.36 \text{ K} \leq T \leq 2 \text{ K}$ from Ref. [27] using Eq. (1) gives $C_N = 20.84 \pm 0.03 \text{ mJ K mol}^{-1}$, which is significantly lower than our $C_N = 56.3 \pm 0.4 \text{ mJ K mol}^{-1}$ at $H = 0 \text{ kOe}$. This large difference is not surprising since C_N may greatly be influenced by impurities. The concentrations of major impurities in the Pr metal used in Ref. [27] [in at. %: Fe (0.0038), Ta (0.00156), Ni (0.096), C (0.176), N (0.04), and O (0.097), Na (0.0184)] are much higher than the impurity levels in Pr metal used in the present study [in at. %: Fe (0.0006), Ta (0.00006), Ni (0.000098), C (0.019), N (0.036), O (0.082), and Na (0.000031)]. C_N for pure Pr metal increases to $287 \pm 2 \text{ mJ K mol}^{-1}$ for $H = 50 \text{ kOe}$. C_p of PrAl_2 at $T = 0.364 \text{ K}$ and zero magnetic field is an order of magnitude higher than that of pure Pr metal at the same temperature and external magnetic fields. The least squares fit of C_p for $\alpha\text{-PrAl}_2$ at $H = 0 \text{ kOe}$ gives $C_N = 624 \pm 16 \text{ mJ K mol}^{-1}$, which is significantly higher than the C_N value for Pr metal. The nuclear specific heat coefficients increase with the increasing external magnetic field. Figure 1(c) inset shows that C_N exhibits two nearly linear dependencies for $H \leq 10 \text{ kOe}$, and $H > 10 \text{ kOe}$. At low external fields, C_N increases rapidly with a slope of $19.72 \text{ mJ K mol}^{-1} \text{ kOe}^{-1}$, which correlates with a rapidly increasing internal field due to the coalescence of the magnetic domain structure into a single magnetic domain at $\sim 10 \text{ kOe}$; at higher external fields the slope is reduced by an order of magnitude to $1.65 \text{ mJ K mol}^{-1} \text{ kOe}^{-1}$. The behavior of C_N as a function of external magnetic field indeed follows the behavior of $M(H)$ curve at $T = 2 \text{ K}$ where magnetization begins to saturate at $H \approx 10 \text{ kOe}$ (not shown in the manuscript). However, it should also be noted that the two linear regions of $C_N(H)$ for PrAl_2 may also be related to the CF splitting of the tetragonal phase below 10 kOe changing to the CF splitting of the cubic structure which is reintroduced by the increasing magnetic field as described below.

An x-ray powder diffraction examination of PrAl_2 was performed from room temperature down to 5 K in zero and up to 30 kOe magnetic fields. All powder XRD patterns collected above the magnetic ordering temperature ($T_C = 32.5 \text{ K}$) in zero magnetic field show that $\beta\text{-PrAl}_2$ (high temperature polymorph) crystallizes in the Laves phase (cubic MgCu_2 -type) structure adopting space group $Fd\bar{3}m$. The XRD patterns collected in a zero magnetic field below T_C reflect an unexpected structural distortion that is most noticeable as the splitting of (008) Bragg peak [Fig. 2(a)]. The crystal structure below the magnetic ordering temperature ($\alpha\text{-PrAl}_2$) becomes tetragonal with space group $I4_1/amd$. However, the splitting of the (008) peak disappears at $H = 30 \text{ kOe}$, which signals the recovery of the cubic crystal symmetry [Fig. 2(b)].

The temperature dependencies of the lattice parameters in a zero magnetic field and in 30 kOe field are presented in Fig. 2(c). While cooling, the cubic phase contracts nearly linearly with the linear thermal expansion coefficient of $\approx 1.2 \times 10^{-5} \text{ K}^{-1}$, but below T_C the lattice rapidly expands nonlinearly along the fourfold axis while it contracts in a similar fashion in the basal plane of the tetragonal structure. Despite the relatively sharp peak in C_p at 32.5 K, the unit cell volume changes continuously [Fig. 2(c) inset], suggesting that thermodynamically the magnetostructural transition at T_C is a second order transformation, which is consistent with the heat capacity data shown in Figs. 1(a) and 1(b). The increase of the unit cell volume below T_C at 30 kOe is related to the conventional magnetostriction reaching $\sim 1,000 \text{ ppm}$ for $\frac{\Delta a}{a}$ at 5 K. The field dependencies of the lattice parameters at $T = 12 \text{ K}$ show clear evidence of tetragonal distortion below 10 kOe [Fig. 2(d)]. The increasing magnetic fields drive the tetragonal phase to the parent cubic phase when $H \geq 10 \text{ kOe}$ [see Fig. 2(d)], and both the cubic and tetragonal phases coexist in 1 to 10 kOe magnetic fields [see inset b of Fig. 2(d)]. The magnetic field-induced tetragonal to cubic phase transformation that occurs below 30 K is reversible: upon removal of the magnetic field at 12 K, the cubic phase stabilized by a 30 kOe field transforms to the original tetragonal phase stable at zero field [not shown in Fig. 2(d) for clarity].

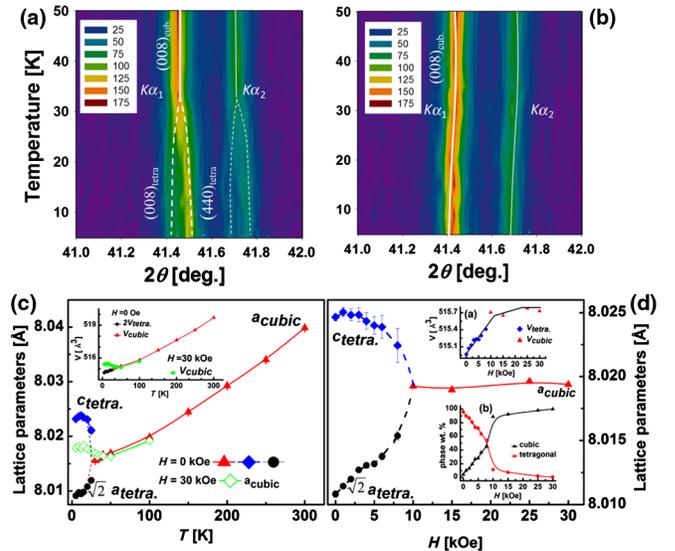


FIG. 2 (color online). The intensity contour map of the x-ray diffraction patterns of PrAl_2 measured in $H = 0 \text{ kOe}$ (a) and $H = 30 \text{ kOe}$ (b). (c) The unit-cell dimensions of PrAl_2 as a function of temperature at $H = 0$ and 30 kOe. The inset in (c) shows the phase volume as a function of temperature at $H = 0$ and 30 kOe. (d) The unit-cell dimensions of PrAl_2 as a function of field at $T = 12 \text{ K}$ measured in increasing magnetic field. The insets (a) and (b) of (d) show, respectively, the phase volumes and the concentrations of the cubic and tetragonal phases as functions of field. The solid lines are guides to the eye.

In order to clarify the structural distortion and the LT anomaly in the specific heat of PrAl_2 , we carried out density functional theory calculations using local spin density approximation with the Hubbard U correction, LSDA + U approach [42]. This approach takes into account orbital dependency of U and J and is implemented in the tight binding linear muffin tin orbital (TB-LMTO) [43] method. $U = 6.7$ eV and $J = 0.7$ eV, which are well known for Gd, were used to model the strong electron correlation for Pr in FM PrAl_2 .

The total energy of the tetragonal FM α - PrAl_2 is lower by 16.8 meV/cell compared to the cubic FM β - PrAl_2 , which confirms the tetragonal distortion in this material. The calculated magnetic moment of Pr in α - PrAl_2 for the ferromagnetic tetragonal structure is $2.36\mu_B/\text{Pr}$ ($5\mu_B/\text{Pr}$ from $4f$ orbitals, $2.49\mu_B/\text{Pr}$ from the $4f$ spins and $0.15\mu_B/\text{Pr}$ from conduction electron spins), which is in close agreement with the experimentally observed value of $2.49\mu_B/\text{Pr}$ at 2 K.

Figure 3 shows the $4f$ and $5d$ density of states (DOS) of Pr and $3p$ DOS of Al near the Fermi level in the cubic (β) and the tetragonally distorted (α) Laves phases of PrAl_2 . The unoccupied spin-up and spin-down $4f$ states located well above the Fermi level in both of the structures are not shown here. The Al $3p$ DOS are strongly hybridized with Pr $5d$ resulting in a small but non-negligible moment in Al $3p$ in both structures. The spin-up $4f$ DOS in the cubic structure is centered at two energy locations ~ 0 eV and ~ -0.5 eV. On the other hand, the spin-up $4f$ DOS in the tetragonally distorted structure is centered mainly in three energy locations ~ 0 , ~ -0.32 , and -1.7 eV. This shows that the tetragonally distorted phase exhibits CF splitting of ~ 1 eV, which apparently makes the tetragonally distorted phase the ground state as confirmed from the total energy calculations.

The $4f$ bands, located at ~ 0 , ~ -0.32 eV in the tetragonal structure, hybridize with the corresponding $5d$ bands giving rise to $5d$ DOS peaks around the Fermi level, supporting $4f$ - $5d$ exchange interactions similar to those in the cubic PrAl_2 . Because of the $4f$ band splitting in the tetragonal structure, the $4f$ bands, located at ~ -1.7 eV, also hybridize with the corresponding $5d$ bands thus providing an additional $4f$ - $5d$ contribution to exchange

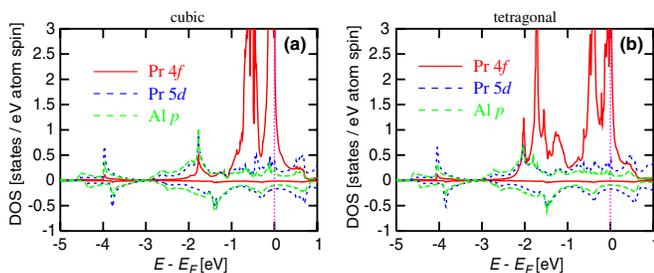


FIG. 3 (color online). The $4f$ and $5d$ density of states of Pr and $3p$ density of states of Al in the cubic (β) (a) and tetragonally distorted (α) (b) Laves phases of PrAl_2 .

interactions compared to the cubic PrAl_2 . As the $4f$ CF splitting increases, the cubic PrAl_2 orders ferromagnetically and distorts to the tetragonal structure, thus linking the FM state to the tetragonal distortion through the $4f$ CF splitting. With the application of a magnetic field, which directly interacts with the localized $4f$ spin and affects conduction electrons by inducing a polarization in the conduction band, the indirect $4f$ - $4f$ exchange interactions increase [44], and the extra $4f$ CF splitting is lifted; as a result the distorted structure changes to the original cubic structure.

The total energy of the double hexagonal structure with antiferromagnetic (AFM) configuration of elemental Pr is lower by 0.53 meV compared to the FM counterpart indicating that the AFM state here is the ground state. Interestingly, the experimentally reported antiferromagnetic transition of Pr is close to 0 K. Because degenerate occupied $4f$ bands lie well below the Fermi level (Fig. 4), it is not surprising that the aspherical $4f$ charge density having local $4f$ spin moment of $2\mu_B/\text{Pr}$ may couple to its nuclear counterpart, which is several orders of magnitude smaller than the $4f$ spin moment, via the conduction electron spins leading to modification of the energy levels of the nuclear spin system [45]. This nuclear hyperfine coupling gives rise to an anomaly in the specific heat close to 0 K in the double hexagonal Pr.

The local spin moment, $2.64\mu_B/\text{Pr}$ ($2.49\mu_B/\text{Pr}$ from the $4f$ spins and $0.15\mu_B/\text{Pr}$ from conduction electron spins), is stronger in FM α - PrAl_2 compared to the local spin moment, $2.15\mu_B/\text{Pr}$ ($2\mu_B/\text{Pr}$ from the $4f$ spins and $0.15\mu_B/\text{Pr}$ from conduction electron spins) in the elemental AFM Pr. It is well known that nuclear spins interact with one other through indirect $4f$ - $4f$ exchange interactions, commonly known as RKKY (Ruderman-Kittel-Kasuya-Yosida) interactions. Although the $5d$ spin polarizations are the same in the tetragonal PrAl_2 and hexagonal Pr, they are positive in the former and negative in the latter due to different crystallography and different Pr-Pr distances, thus resulting in the stronger nuclear hyperfine interactions in PrAl_2 compared to metallic Pr. Moreover, there is a strong $4f$ CF splitting in PrAl_2 . This should further modify the nuclear energy levels leading to a stronger nuclear hyperfine splitting.

In conclusion, we report abnormally high Schottky specific heat in PrAl_2 , an order of magnitude higher than that

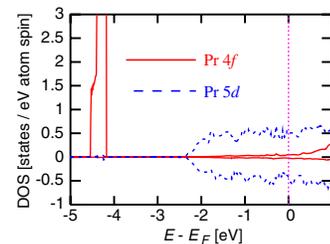


FIG. 4 (color online). The $4f$ and $5d$ density of states of the antiferromagnetic Pr in double hexagonal structure.

of pure Pr. The low temperature XRD demonstrates that the FM transition in PrAl₂ at T_C is accompanied by a structural transformation from the cubic to the tetragonal crystal structure with a continuous volume change. The cubic symmetry is fully recovered with the application of magnetic field of 10 kOe and higher by lifting the $4f$ CF splitting. The strong $4f$ splitting and the $4f$ DOS peak at the Fermi level established from the first principles calculations confirm the low temperature anomaly and the structural distortion below T_C . The modification of the energy levels of the nuclear spin system due to the $4f$ band splitting gives rise to additional nuclear hyperfine splitting resulting in higher Schottky specific heat close to 0 K in α -PrAl₂ compared to the elemental Pr.

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