Physical properties of EuPd$_2$As$_2$ single crystals

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Abstract

The physical properties of self-flux grown EuPd$_2$As$_2$ single crystals have been investigated by means of magnetization $M$, magnetic susceptibility $\chi$, specific heat $C_p$, and electrical resistivity $\rho$ measurements versus temperature $T$ and magnetic field $H$. The crystal structure was determined using powder x-ray diffraction measurements, which confirmed the ThCr$_2$Si$_2$-type body-centered tetragonal structure (space group $I4/mmm$) reported previously. The $\rho(T)$ data indicate that EuPd$_2$As$_2$ is metallic. The $\chi(T)$ data indicate that the Eu$^{2+}$ moments have spin $S = 7/2$ with $g = 2$. Long-range antiferromagnetic (AFM) ordering is apparent from the $\chi(T)$, $C_p(T)$, and $\rho(T)$ measurements. For $H \parallel c$ the $\chi(T)$ indicates two transitions at $T_{N1} = 11.0$ K and $T_{N2} = 5.5$ K, whereas for $H \perp c$ only one transition is observed at $T_{N1} = 11.0$ K. Between $T_{N1}$ and $T_{N2}$ the anisotropic $\chi(T)$ data suggest a planar noncollinear AFM structure, whereas at $T < T_{N2}$ the $\chi(T)$ and $M(H, T)$ data suggest a spin reorientation transition in which equal numbers of spins cant in opposite directions out of the $ab$ plane. We estimate the critical field at 2 K at which all Eu moments become aligned with the field to be about 22 T. An upturn in $\rho$ at $T < T_{N1}$ suggests superzone energy gap formation below $T_{N1}$. This behavior of $\rho(T < T_{N1})$ is not sensitive to applied magnetic fields up to $H = 12$ T.

Keywords: antiferromagnetism, superzone gap, pnictides

(Some figures may appear in colour only in the online journal)
moments aligned ferromagnetically in the \( ab \) plane, forming an incommensurate AFM spiral structure along the \( c \) axis [25]. In EuCo\(_2\)P\(_2\), the magnetic ordering of Eu\(^{2+}\) is suppressed under pressure with a simultaneous magnetic ordering of itinerant carriers at \( T_N = 260 \) K with the ordered moments centered on the Co sites at a critical pressure \( p_c = 3.1 \) GPa, where a pressure-induced isostructural phase transition from a tetragonal (T) phase to a collapsed-tetragonal (cT) phase also occurs [26, 27]. EuCo\(_2\)As\(_2\) is reported to exhibit AFM ordering below 39 K for which an A-type AFM structure is proposed [28]. EuCo\(_2\)As\(_2\) also exhibits a pressure-induced isostructural phase transition from the T phase to the cT phase at 4.7 GPa [29]. EuCu\(_2\)As\(_2\) is found to order antiferromagnetically below \( N_2 = 15 \) K [30]. A strong increase is observed in the ordering temperature of EuCu\(_2\)As\(_2\) below 15 K at ambient pressure to 49 K at 10.7 GPa with a possible crossover from AFM structure to a ferromagnetic (FM) structure above 7 T [31].

Our investigations on single-crystal EuCu\(_2\)As\(_2\) with the ThCr\(_2\)Si\(_2\)-type structure and EuCu\(_2\)Sb\(_2\) with a different primitive tetragonal CaBe\(_2\)Ge\(_2\)-type structure revealed AFM ordering of the Eu\(^{2+}\) moments in both compounds below \( T_N = 17.5 \) K and 5.1 K, respectively [32]. While the \( \chi(T) \) data suggest that EuCu\(_2\)Sb\(_2\) has an A-type AFM structure, the AFM structure of EuCu\(_2\)As\(_2\) is unclear as yet [32].

We previously investigated the physical properties of EuPd\(_2\)Sb\(_2\) with the primitive tetragonal CaBe\(_2\)Ge\(_2\)-type structure, which is closely related to the ThCr\(_2\)Si\(_2\)-type structure [33]. This compound shows AFM ordering of the Eu spins at \( T_N = 6.0 \) K with another AFM transition at \( T_{N2} = 4.5 \) K that may be a spin reorientation transition. From single-crystal \( \chi(T) \) measurements, the compound appears to have a noncollinear AFM structure. We also studied APd\(_2\)As\(_2\) (A = Ca, Sr, and Ba) with the ThCr\(_2\)Si\(_2\)-type structure and discovered bulk superconductivity in CaPd\(_2\)As\(_2\) and SrPd\(_2\)As\(_2\) below \( T_c \) = 1.27 and 0.92 K, respectively [34].

EuPd\(_2\)As\(_2\) also crystallizes in the ThCr\(_2\)Si\(_2\)-type structure [35]. A preliminary investigation of the magnetic properties of EuPd\(_2\)As\(_2\) using \( \chi(T) \) and Mössbauer measurements revealed AFM ordering of the Eu moments in a polycrystalline sample below \( T_N = 11 \) K [36]. We have grown single crystals of EuPd\(_2\)As\(_2\) by the self-flux method and present herein their physical properties obtained from the magnetic susceptibility \( \chi \), isothermal magnetization \( M \), heat capacity \( C_p \), and electrical resistivity \( \rho \) measurements as a function of temperature \( T \) and magnetic field \( H \).

We confirm the presence of Eu\(^{2+}\) magnetic moments with \( S = 7/2 \) and spectroscopic splitting factor \( g = 2 \), and AFM ordering of these spins below \( T_N = 11 \) K as found in [36]. We report an additional transition at 5.5 K that is likely due to an AFM spin reorientation transition. The \( \chi(T) \) measured at low \( H \) exhibits two transitions at \( T_{N1} = 11.0 \) K and \( T_{N2} = 5.5 \) K for \( H\|c \), and one transition at \( T_{N1} = 11.0 \) K for \( H\perp c \). The \( M(H) \) at 2 K up to \( H = 14 \) T shows a weak upward curvature, consistent with an AFM structure. The \( C_p(T) \) data show a sharp \( \lambda \)-type anomaly at \( T_{N1} \), whereas the anomaly at \( T_{N2} \) is weaker. The \( \rho(T) \) data demonstrate that EuPd\(_2\)As\(_2\) is metallic and the data show anomalies at both \( T_{N1} \) and \( T_{N2} \). The \( \rho(T) \) exhibits a sharp upturn below \( T_{N1} \), possibly due to the formation of a superzone energy gap over part of the Brillouin zone at \( T_{N1} \). No change in the upturn in the \( \rho(T) \) is evident under applied magnetic fields up to \( H = 12 \) T.

For the paramagnetic state above 16 K the \( C_p(T) \) data are well represented by the Debye model of the lattice heat capacity and the \( \rho(T) \) data by the Bloch-Grüneisen model for the contribution to \( \rho(T) \) from electron-phonon scattering.

2. Experimental details

Single crystals of EuPd\(_2\)As\(_2\) were grown by the high-temperature solution growth method using self-flux. High-purity Eu (Ames Laboratory) and prereacted PdAs [Pd (99.998%) and As (99.99999%), Alfa Aesar] taken in a 1:5 molar ratio were placed in an alumina crucible and sealed inside an evacuated quartz tube. The sealed sample was heated to 1100 °C at a rate of 60 °C/h and held there for 15 h; this was followed by cooling at a rate of 2.5 °C/h to 800 °C, at which point the flux was decanted with a centrifuge, yielding shiny plate-like crystals of typical size \( 2 \times 1.5 \times 0.4 \) mm\(^3\).

The chemical composition and quality of the crystals were checked using a JEOL scanning electron microscope (SEM) equipped with an energy dispersive x-ray (EDX) analyzer. The SEM images indicated, from the uniformity of the (001) plane faces, that the crystals contain only a single phase. The EDX composition analysis indicated that the stoichiometry of the crystals with Eu:Pd:As in a 1:2:2 molar ratio. The crystal structure was determined by means of powder x-ray diffraction (XRD) using Cu K\(_\alpha\) radiation on a Rigaku Geigerflex x-ray diffractometer. The XRD data were refined by Rietveld refinement using the FullProf software package [37].

The \( \chi(T) \equiv M(T)/H \) and \( M(H) \) isotherms were measured using a Quantum Design, Inc., superconducting quantum interference device (SQUID) magnetic properties measurement system (MPMS). \( M(H) \) isotherms at high magnetic field were measured using the vibrating sample magnetometer (VSM) option of a Quantum Design, Inc., physical properties measurement system (PPMS). The sample holder contributions to the measured magnetic moments were subtracted to obtain the sample contributions. The magnetic properties are expressed exclusively in Gaussian cgs units, where the tesla (T) is a common unit of convenience for the magnetic field \( H \) defined as 1 T = 10\(^4\) Oe. The \( C_p(T) \) was measured by a relaxation method using the heat capacity option of the PPMS. The \( \rho(T) \) was measured by the standard four-probe ac technique using the ac transport option of the PPMS.

3. Results and discussion

3.1. Crystallography

Powder x-ray diffraction data collected on crushed EuPd\(_2\)As\(_2\) single crystals at room temperature are shown in figure 1.
obtained from Curie-Weiss fits to the high-temperature paramagnetic susceptibility. The short vertical bars mark the Bragg peak positions. The lowermost curve represents the difference between the experimental and calculated intensities.

Table 1. Crystallographic and Rietveld refinement parameters obtained from powder XRD data for crushed EuPd$_2$As$_2$ crystals with the body-centered tetragonal ThCr$_2$Si$_2$-type structure with space group $I4/mmm$. The atomic coordinates of the Eu, Pd and As atoms are (0, 0, 0), (0, 1/2, 1/4) and (0, 0, $z_{\text{As}}$), respectively.

| Lattice parameters | $a$ (Å) | $c$ (Å) | $V_{\text{cell}}$ (Å$^3$) | $\chi_{\text{good}}$ (Å$^3$ K mol$^{-1}$) |
|--------------------|---------|---------|--------------------------|----------------------------------|
| EuPd$_2$As$_2$     | 4.3298(2) | 10.1700(3) | 190.66(1) | 3.09 |
| Refinement quality | $R_p$ (%) | 5.33 | $R_p$ (%) | 7.46 |
|                   | 7.46    | 5.33   | 7.46        |                                  |

Table 2. Magnetic ordering temperatures $T_{\text{N1}}$ and $T_{\text{N2}}$ measured from the low-field susceptibility data in figures 3(a) and the Curie constants $C$, the Weiss temperatures $\theta_p$ and the effective moments per Eu $\mu_{\text{eff}} = \sqrt{\gamma C}$ obtained from Curie-Weiss fits to the high-temperature susceptibility data for EuPd$_2$As$_2$ in figures 2(b) and 2(c).

| Field direction | $T_{\text{N1}}$ (K) | $T_{\text{N2}}$ (K) | $C$ (cm$^3$ K mol$^{-1}$) | $\theta_p$ (K) | $\mu_{\text{eff}}$ (µB Eu$^{-1}$) |
|-----------------|---------------------|---------------------|--------------------------|----------------|----------------------------------|
| $H||c$          | 11.0                | 5.5                 | 7.73(3)                  | $-32.8(9)$     | 7.86(2)                          |
| $H_{\perp}c$    | 11.0                | 7.71(2)             | 28.1(3)                  | $-28.1(3)$     | 7.85(1)                          |

3.2. Magnetization and magnetic susceptibility

3.2.1. High-temperature paramagnetic susceptibility. The $\chi(T)$ data measured for EuPd$_2$As$_2$ in $H = 3$ T for $H||c$ and $H_{\perp}c$ up to 350 K are shown in figure 2(a). The data are nearly isotropic on the scale of the figure. The AFM transition is seen at low temperatures ≤10 K (see also figure 3(a) below and table 2). The data in the paramagnetic state follow the Curie-Weiss law $\chi(T) = \chi/[(T-\theta_p)]$, where $\chi$ is the Curie constant and $\theta_p$ is the Weiss temperature. The $\chi$ versus $T$ data for $H_{\perp}c$ and $H||c$ are shown in figures 2(b) and 2(c), respectively. Linear fits of these two sets of data by the inverse Curie-Weiss law for 50 K ≤ $T$ ≤ 350 K are shown as straight lines in the respective figures. The fits yield $C = 7.71(2)$ cm$^3$ K mol$^{-1}$ and $\theta_p = -28.1(3)$ K for $H_{\perp}c$ and $C = 7.73(2)$ cm$^3$ K mol$^{-1}$ and $\theta_p = -32.8(9)$ K for $H||c$. The negative $\theta_p$ values indicate that the dominant magnetic interactions in EuPd$_2$As$_2$ are AFM. The Curie constant calculated for Eu$^{2+}$ cations with $S = 7/2$ and spectroscopic splitting factor $g = 2$ is $C^{\text{calc}} = 7.88$ cm$^3$ K (mol Eu)$^{-1}$, which is very close to the measured values. We conclude that the Eu in EuPd$_2$As$_2$ is in the +2 oxidation state with $S = 7/2$ and $g = 2$. The parameters obtained from the Curie-Weiss fits of the $\chi^{-1}(T)$ data are summarized in table 2.

3.2.2. Low-temperature magnetic susceptibility. The zero-field-cooled (ZFC) and field-cooled (FC) $\chi(T)$ data measured in $H = 0.01$ T aligned along the $c$ axis ($\chi||c$) and in the $ab$ plane ($\chi_{\perp}ab, H_{\perp}c$) are shown in figure 3(a). No thermal hysteresis between the ZFC and FC data is observed. For $H||c$, well-defined cusps are seen in the low-field $\chi(T)$ data at 11.0 K and 5.5 K, whereas for $H_{\perp}c$ only one cusp is observed at 11.0 K. Furthermore, the $\chi(T)$ data measured at different $H$ in figures 3(b) and 3(c) show that an increase in $H$ shifts these anomalies towards lower temperatures, suggesting that the $\chi(T)$ cusps are due to AFM ordering. We infer that two zero-field AFM transitions occur at $T_{\text{N1}} = 11.0$ K and $T_{\text{N2}} = 5.5$ K. While $T_{\text{N1}}$ is due to a transition from a paramagnetic phase to an AFM phase, $T_{\text{N2}}$ may be associated with an AFM spin reorientation transition.

For $H||c$ only a barely detectable change in slope is observed near $T_{\text{N2}} = 5.5$ K in the $\chi_{\perp}ab$ data at $H = 0.01$ T in figure 3(a). However, as shown in figure 3(b), as $H$ increases, the slope change becomes clearly observable, and at $H = 5.5$ K a well-defined anomaly can be seen in $\chi(T)$ at the same temperature, 5.5 K. Thus $T_{\text{N2}}$ shows no detectable field dependence within our field range for $H_{\perp}c$. In contrast, $T_{\text{N1}}$ for $H_{\perp}c$ decreases significantly from 11.0 K at $H = 0.01$ T to <9.0 K at $H = 5.0$ T.

From the $\chi(T)$ data in figure 3(c) with $H||c$, both $T_{\text{N1}} and $T_{\text{N2}} decrease with increasing $H$. $T_{\text{N1}}$ decreases from 11.0 K at $H = 0.01$ T to 10.5 K at $H = 5.0$ T and $T_{\text{N2}}$ decreases from 5.5 K at $H = 0.01$ T to 2.2 K at $H = 5.0$ T. Thus the change in $T_{\text{N2}}$ with increasing $H$ for $H||c$ is much larger than the change in $T_{\text{N2}}$ discussed in the previous paragraph for $H_{\perp}c$. 

Figure 1. Powder x-ray diffraction pattern of EuPd$_2$As$_2$ recorded at room temperature. The solid line through the experimental points is the Rietveld refinement profile calculated for the ThCr$_2$Si$_2$-type body-centered tetragonal structure (space group $I4/mmm$). The short vertical bars mark the Bragg peak positions. The lowermost curve represents the difference between the experimental and calculated intensities.
The low-field $\chi_c(T)$ data in figure 3(a) are temperature independent between $T_{N1}$ and $T_{N2}$, whereas the $\chi_{ab}(T)$ data decrease rapidly below $T_{N1}$. Within the Weiss molecular field theory (MFT), this difference indicates that the AFM ordered moments lie in the tetragonal $ab$ plane [39]. The observation that $\chi_c < \chi_{ab}$ at $T > T_{N1}$ and $\chi_c > \chi_{ab}$ at $T < 8.5$ K suggests the presence of a small anisotropy field parallel to the $ab$ plane both above and below $T_{N1}$. On the other hand, for a collinear AFM structure with the ordered moments in the $ab$ plane and equal numbers of AFM domains with their collinear axes at 90° to each other, one expects $\chi_{ab}(T \to 0)/\chi_{ab}(T_{N1}) = 1/2$, which is not realized in the data, which show $\chi_{ab}(T \to 0)/\chi_{ab}(T_{N1}) \approx 0.80$. This large deviation from expectation for collinear AFM ordering suggests that the AFM structure of EuPd$_2$As$_2$ between $T_{N1}$ and $T_{N2}$ is a noncollinear planar helical or...
cycloidal structure with the ordered moments aligned in the $ab$ plane. The turn angle in MFT is a two-valued function of $\chi_{ab}(T \rightarrow 0)/\chi_{ab}(T_N)$ if $1/2 < \chi_{ab}(T \rightarrow 0)/\chi_{ab}(T_N) < 1$. With the observed value $\chi_{ab}(T \rightarrow 0)/\chi_{ab}(T_N) = 0.80$, one obtains a turn angle of either $\sim 104^\circ$ or $139^\circ$ along the helix/cycloid axis between ferromagnetically aligned planes perpendicular to this axis [40]. Our measurements cannot distinguish between the helical and cycloidal types of noncollinear AFM $ab$ plane ordering. In helical ordering, the spin rotation (helix) axis is along the $c$ axis, whereas for cycloidal ordering, the spin rotation (cycloid) axis is in the $ab$ plane.

The decrease in $\chi_c$ at $T < T_{N2}$ in figure 3(a) suggests that the in-plane moments become canted towards the $c$ axis in such a way as to retain the overall AFM structure, such as in a sequence of canted-up/canted-down spins out of the $ab$ plane. Furthermore, the ordered-state $M(H)$ data presented in the following section exhibit upward curvature for both $H \perp c$ and $H \parallel c$, consistent with this canted AFM structure below $T_{N2}$.

3.2.3. Magnetization versus applied magnetic field isotherms. Isothermal $M(H)$ data for a EuPd$_2$As$_2$ crystal at eight temperatures between 1.8 and 300 K for $H$ applied both along the $c$ axis ($M_c$, $H \parallel c$) and in the $ab$ plane ($M_{ab}$, $H \perp c$) are shown in figure 4 and data at 1.8 K for both increasing and decreasing $H$ are shown in figure 5, where $H \leq 5.5$ T in both figures. The magnetization does not show saturation behavior up to $H = 5.5$ T for either field direction. It is seen from figure 5 that at 1.8 K, initially the $M$ resembles a weak $S$-shaped metamagnetic behavior. The derivative $dM/dH$ versus $H$, shown in the inset of figure 5, clearly reflects this behavior, where a pronounced peak is observed at $H = 4.75$ T for $H \perp c$. The weak change in slope for $H \parallel c$ is also evident from a broad peak near 4.5 T in $dM/dH$ versus $H$. The observed magnetizations $M_{ab} = 1.80 \mu_B$ Eu$^{-1}$ and $M_c = 1.74 \mu_B$ Eu$^{-1}$ at $H = 5.5$ T for $H \perp c$ and $H \parallel c$, respectively, are much smaller than the theoretical value $M_{sat} = 7 \mu_B$ Eu$^{-1}$ for $S = 7/2$ and $g = 2$. Figure 4 shows that the $M(H)$ behaviors observed for $M_{ab}$ and $M_c$ at $T = 5$ K are similar to those at 1.8 K. For $T > T_{N1}$, $M$ is almost proportional to $H$ at fixed $T$.

Within MFT, the critical field $H^c$ of an AFM at $T = 0$, which is the field at which $M$ reaches $M_{sat}$ with increasing $H$, is given by

$$H^c = \frac{M_{sat}}{\chi(T_N)}. \quad (1)$$

From figure 3(a), for $H \perp c$ one has $\chi_{ab}(T_N) = 0.18$ cm$^3$ mol$^{-1}$ $3.2 \times 10^{-3} \mu_B$ Oe$^{-1}$ Eu$^{-1}$. Then using $M_{sat} = 7 \mu_B$ Eu$^{-1}$, equation (1) gives the calculated critical field as

$$H^c_{sat} \approx 22 \text{ T.} \quad (2)$$

This value is a factor of four larger than our maximum measurement field of 5.5 T in figures 4 and 5.

Because $M$ at $H = 5.5$ T is much smaller than the theoretical $M_{sat}$, we measured $M$ up to the higher field $H = 13.8$ T as shown at $T = 2$ K in figure 6(a). These $M(H)$ data demonstrate that $M$ does not reach $M_{sat}$ up to fields of 13.8 T, as expected from equation (2). At $T = 2$ K and $H = 13.8$ T, we find $M_{ab} = 4.58 \mu_B$ Eu$^{-1}$ for $H \perp c$ and $M_c = 4.41 \mu_B$ Eu$^{-1}$ for $H \parallel c$, which are $< 65\%$ of the theoretical $M_{sat}$ value. The $M(H)$ data for both field directions show metamagnetic transitions at $H \sim 5$ T, confirming the data in figure 5. The derivatives $dM_{ab}/dH$ and $dM_c/dH$ versus $H$ are shown in

Figure 4. Magnetization $M$ versus applied magnetic field $H$ isotherms of a EuPd$_2$As$_2$ single crystal measured at the indicated temperatures for $H$ applied (a) in the $ab$ plane ($M_{ab}$, $H \perp c$) and (b) along the $c$ axis ($M_c$, $H \parallel c$).

Figure 5. Isothermal magnetization $M$ of a EuPd$_2$As$_2$ single crystal as a function of the applied magnetic field $H$ measured at 1.8 K for $H$ applied in the $ab$ plane ($M_{ab}$, $H \perp c$) and along the $c$ axis ($M_c$, $H \parallel c$). Inset: the field derivatives $dM_{ab}/dH$ and $dM_c/dH$ versus $H$.
Figure 6. (a) Isothermal magnetization $M$ of a EuPd$_2$As$_2$ single crystal as a function of the applied magnetic field $H$ measured at 1.8 K for $H$ applied in the $ab$ plane ($M_{ab}$, $H_{lc}$) and along the $c$ axis ($M_c$, $H||c$). (b) The field derivatives $dM_{ab}/dH$ and $dM_c/dH$ versus $H$ obtained from the data in (a), more clearly revealing the metamagnetic transitions at 4.5 T and 4.6 T for $M_{ab}$ and $M_c$, respectively.

The high-field slopes of $M_{ab} \propto H$ and $M_c \propto H$ in figure 6 obtained from proportional fits of $M$ versus $H$ for the field range $6.0 \, T < H < 13.8 \, T$ are $0.335 \, \mu_B \, T^{-1}$/Eu and $0.318 \, \mu_B \, T^{-1}$/Eu, respectively. By extrapolating the proportional dependence of $M_{ab}(H)$ to the value $M_{ab} = 7 \, \mu_B \, Eu^{-1}$, one obtains the extrapolated value of the critical field as $H_{ab}^c \approx 21 \, T$ for $H_{lc}$. This value is nearly the same as the above value of $H_{ab}^c$ in equation (2) estimated from $\kappa_{ab}(T_N)$ using MFT.

3.3. Heat capacity

An overview of the $C_p(T)$ data for a EuPd$_2$As$_2$ crystal is shown in figure 7(a). The low-$T$ $C_p(T)$ data obtained in $H = 0$ are shown on an expanded scale in figure 7(b) and exhibit two clear anomalies near 5.5 K and 11 K, confirming the intrinsic nature of the AFM transitions at $T_{N1}$ and $T_{N2}$ revealed in the above $\chi(T)$ data. The $C_p(T)$ data measured at $H = 3.0 \, T$ ($H||c$) are compared with the data for $H = 0$ in figure 7(c). While no noticeable change is observed at $T_{N1}$ between the $C_p(T)$ at these two fields, the $T_{N2}$ anomaly appears to broaden slightly with increasing field and to decrease slightly in temperature at $H = 3 \, T$ compared to the zero-field data. The weak field dependence in this field range is expected, due to the much larger calculated and extrapolated critical fields in equations (2) and (3), respectively.

The zero-field $C_p(T = 300 \, K) = 123 \, J \, mol^{-1} \, K^{-1}$ is close to the expected classical Dulong–Petit value $C_V = 3nR = 15R = 124.7 \, J \, mol^{-1} \, K^{-1}$ at constant volume [41, 42] where $n = 5$ is the number of electrons per formula unit ($e_u$) and $R$ is the molar gas constant. The $C_p(T)$ data in the paramagnetic regime from 16 to 300 K were initially fitted by

$$C_p(T) = \gamma T + nC_VDebye(T),$$

where $\gamma T$ represents the electronic contribution to the heat capacity and $C_V Debye(T)$ represents the Debye lattice heat capacity due to acoustic phonons at constant volume given by [42]

$$C_V Debye(T) = 9R \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^2e^x}{(e^x-1)^2} \, dx.$$  \hspace{1cm} (5)

Here we used the recently developed analytic Padé approximant fitting function for $C_V Debye(T)$ [43]. While fitting the data we first set $\gamma$ as an adjustable parameter, which yielded $\gamma = 2(3) \, mJ \, mol^{-1} \, K^{-2}$, so in the final fit we fixed $\gamma = 0$. Thus in the final fit, the $C_p(T)$ data were fitted with only one adjustable parameter, $\Theta_D$. The fit with 16K $\leq T \leq 300$ K gives $\Theta_D = 216(2)$ K. From a comparison of the data and the fit in figure 7(a) shown by the solid red curve, the $C_p(T)$ data in the paramagnetic state from 16 K up to 300 K are described reasonably well overall by the Debye model for the lattice heat capacity.

The magnetic contribution to the heat capacity $C_{mag}(T)$ is estimated from the zero-field $C_p(T)$ data for EuPd$_2$As$_2$ by subtracting the lattice contribution. We used as the lattice contribution the $C_p(T)$ data for isostructural nonmagnetic SrPd$_2$As$_2$ [34]. The difference in formula weights of EuPd$_2$As$_2$ and SrPd$_2$As$_2$ was taken into account to estimate the lattice contribution to the heat capacity of EuPd$_2$As$_2$. Since the lattice heat capacity is a function of $T/\Theta_D$ and $\Theta_D$ depends on the formula mass $M$ ($\Theta_D \sim 1/M^{1/2}$), the mass-corrected lattice contribution can be obtained by changing the temperature scale of $C_p(T)$ to $T^*$, where

$$T^* = \left( \frac{T}{M_{EuPdAs2}/M_{SrPdAs2}} \right)^{1/2}. $$  \hspace{1cm} (6)
The nonzero anomalies in as shown in the plot of $C_T$ indicates the presence of short-range AFM correlations above $T_{N1}$. The MFT prediction of $C_{\text{mag}}(T)/T$ for spin $S = 7/2$ and $T_N = 11.0$ K is shown as the solid red curve in figure 8(a) [39]. The magnetic entropy is the area under a $C_{\text{mag}}(T)/T$ versus $T$ plot. It is seen that the missing experimental magnetic entropy at $T_{N1}$ compared with the MFT prediction is largely recovered at $T > T_{N1}$, where AFM correlations in the paramagnetic state contribute to the change in magnetic entropy.

In order to estimate the magnetic contribution to the entropy $S_{\text{mag}}(T)$ for $0 < T < 1.8$ K, which is below our measurement temperature range, we extrapolated the $C_{\text{mag}}(T)/T$ data to $T = 0$ in accordance with the MFT prediction, as shown by the dotted curve in figure 8(a). The $S_{\text{mag}}(T)$ below 25 K was then determined by integrating the $C_{\text{mag}}(T)/T$ versus $T$ data in figure 8(a) according to

$$S_{\text{mag}}(T) = \int_0^T \frac{C_{\text{mag}}(T')}{T'} \, dT',$$

as shown in figure 8(b). It is seen from figure 8(b) that $S_{\text{mag}}$ attains a value of 14.7 J mol$^{-1}$ K$^{-1}$ at $T_{N1}$ which is 85% of the expected high-$T$ limit $R\ln(2S + 1) = R\ln 8 = 17.3$ J mol$^{-1}$ K$^{-1}$ for $S = 7/2$. The estimated experimental high-$T$ limit of $S_{\text{mag}}$ is 89% of $R\ln 8$. In view of the magnetization data, which indicated that the Eu is in the Eu$^{2+}$ oxidation state with $S = 7/2$ to high accuracy, the reduced value of $S_{\text{mag}}$ compared with $R\ln(8)$ likely results from an inaccurate estimate of the lattice contribution used to obtain $C_{\text{mag}}(T)$ from the measured $C_p(T)$ data.

### 3.4. Electrical resistivity

The $\rho(T)$ data in the $ab$ plane for a EuPd$_2$As$_2$ crystal measured in zero magnetic field are shown in figure 9. The low value of the residual resistivity $\rho_0 = 12.2$ $\mu\Omega$ cm at $T = 1.8$ K and the value of the residual resistivity ratio $\text{RRR} \equiv \rho(300 \text{ K})/\rho(1.8 \text{ K}) = 4.5$ indicate a good quality of our single crystals. Metallic behavior is indicated from both the magnitude and the $T$ dependence of $\rho$.

We fitted our paramagnetic-state zero-field $\rho(T)$ data using the Bloch-Grüneisen (BG) model. The BG resistivity $\rho_{BG}$ due to the scattering of conduction electrons by acoustic lattice vibration is given by [44]

$$\rho_{BG}(T/\Theta_R) = 4\pi R \left(\frac{T}{\Theta_R}\right)^5 \int_0^{\Theta_R/T} x^5 \left(1 - e^{-x}\right) dx,$$

where $R$ is a material-dependent prefactor and $\Theta_R$ is the Debye temperature determined from resistivity data. One obtains

$$\rho_{BG}(T/\Theta_R = 1) = 0.9464635R.$$

The experimental $\rho(T)$ data were fitted by

$$\rho(T) = \rho_0 + \rho(\Theta_R) \rho_{sd}(T/\Theta_R),$$

where $\rho_0 = \rho_d + \rho_{sd}$ is the sum of $\rho_0$ and the spin-disorder resistivity $\rho_{sd}$ due to the presence of disordered magnetic moments, and the normalized dimensionless BG resistivity $\rho_{sd}(T/\Theta_R)$ can be obtained from equations (8) and (9) as

![Figure 7.](image)

(a) Heat capacity $C_p$ of a EuPd$_2$As$_2$ crystal versus temperature $T$ from 1.8 to 300 K measured in $H = 0$. The solid curve is a fit of the data from 16 to 300 K by the Debye lattice heat capacity $C_V\text{Debye}(T)$ in equation (5). (b) Expanded view of low-$T$ $C_p(T)$ data in the temperature range 1.8 K $\leq T \leq 50$ K. The $C_p(T)$ data for SrPd$_2$As$_2$ [34] and the lattice contribution to $C_p$ of EuPd$_2$As$_2$, after correcting for the difference in formula weights of EuPd$_2$As$_2$ and SrPd$_2$As$_2$, are also shown. (c) Comparison of $C_p(T)$ in magnetic fields $H = 0$ and 3.0 T applied along the $c$ axis.

The mass-corrected lattice contribution for EuPd$_2$As$_2$ is shown in figure 7(b).

The magnetic contribution to the heat capacity $C_{\text{mag}}(T)$ of EuPd$_2$As$_2$ is obtained by subtracting the $C_p(T)$ lattice contribution of SrPd$_2$As$_2$ from the measured $C_p(T)$ data for EuPd$_2$As$_2$, as shown in the plot of $C_{\text{mag}}(T)/T$ versus $T$ in figure 8(a). Clear anomalies in $C_{\text{mag}}(T)/T$ near $T_{N1} = 11$ K and $T_{N2} = 5.5$ K are apparent. The nonzero $C_{\text{mag}}(T)/T$ at $T > T_{N1}$ in figure 8(a)
We fitted the \( \rho(T) \) data by equations (10) and (11) using the three independent fitting parameters \( \rho_1, \rho(\Theta_R) \) and \( \Theta_R \) for 12 K \( \leq T \leq 300 \) K, where we used the analytic Padé approximant fitting function from [43] for \( \rho_0(T/\Theta_R) \) in equation (11). A good fit of the \( \rho(T) \) data was obtained with the fitting parameters \( \rho_1 = 13.95(5) \) \( \mu \Omega \) cm, \( \rho(\Theta_R) = 24.1(4) \) \( \mu \Omega \) cm, and \( \Theta_R = 182(3) \) K, as shown by the solid blue curve in figure 9(a). The value \( \mathcal{R} = 25.5 \) \( \mu \Omega \) cm is obtained from the value of \( \rho(\Theta_R) \) using equation (9) and \( \rho_{sd} = 1.8 \) \( \mu \Omega \) cm is obtained from the value of \( \rho_1 \) using value \( \rho_0(T = 1.8 \) K) = 12.2 \( \mu \Omega \) cm. The value \( \Theta_R = 182(3) \) K is somewhat smaller than \( \Theta_D = 216(2) \) K obtained from the above analysis of the heat capacity data in the paramagnetic state in terms of the Debye model. The values of \( \Theta_R \) and \( \Theta_D \) are not expected to be identical, because of the different assumptions and approximations made in the Debye model of the lattice heat capacity and the Bloch-Grüneisen model of the resistivity as outlined in [42–44].

From figure 9(b), \( \rho \) decreases with decreasing temperature in the paramagnetic state at \( T > T_{N1} \), but then sharply increases at \( T = T_{N1} \), reaches a maximum at \( T = 9.0 \) K and again starts decreasing with decreasing \( T < 9.0 \) K with a rapid decrease below \( T_{N2} \). We define the quantity \( \Delta \rho \) to be the difference in \( \rho \) between its value at the maximum of the peak and the value at \( T_{N1} \). Below about 4 K the resistivity is lower than the value extrapolated from above \( T_{N1} \). No thermal hysteresis is observed between the heating and cooling cycles of the \( \rho \) measurements. The increase in \( \rho \) on decreasing \( T \) below an AFM transition temperature has been observed in many systems and is usually attributed to the formation of superzone energy gaps within the Brillouin zone [45–52].

The \( \rho(T) \) data measured at different \( H \) are shown in figure 10(a). We do not see any significant effect of magnetic field on \( \Delta \rho \) below \( T_{N1} \), even at \( H = 12 \) T. However, this field is still much smaller than the critical field estimated in equations (2).
and (3). As expected for an AFM system, $T_{N2}$ decreases with increasing $H$ and, in the paramagnetic state, $\rho$ in the vicinity of $T_{N1}$ decreases with increasing $H$, which shows a negative magnetoresistance (MR) behavior. For $T_{N2} < T < T_{N1}$, initially the $\rho$ increases weakly and then decreases with increasing $H$, although the change $\Delta \rho$ upon entering the antiferromagnetic state remains nearly unchanged. Thus there is no signature of suppression of the effect of magnetic superzone formation up to the maximum measurement field of 12 T. For $T < T_{N2}$, $\rho$ increases with increasing $H$ and thus a positive MR is observed.

The $H$ dependence of $\rho$ is shown in figure 10(b) for 1.8 K and 8 K. The $\rho$ data are normalized as $\Delta \rho(H)/\rho(0) = [\rho(H)-\rho(0)]/\rho(0)$ to show the magnetoresistance behavior. The MR data are noisy but the basic trend of data can be inferred. At 1.8 K, initially the MR increases with increasing $H$ up to $\approx 5.5$ T above which the rate of increase decreases and eventually the MR approaches a constant value. The MR is positive throughout and is $\approx 12\%$ at 10 T at 1.8 K. At 8 K the MR is weakly positive for $H \lesssim 8$ T, above which it becomes negative, as was also inferred from the $\rho(T)$ data measured at different $H$ shown in figure 10(a). Because of the noise in the data, it is not possible to determine the precise field at which this crossover from positive MR to negative MR takes place.

Usually superzone boundaries collapse with the application of a magnetic field and the effect of a superzone energy gap is suppressed. Contrary to this expectation, for the present compound the effect of the superzone energy gap persists up to the maximum field investigated of 12 T without any sign of a collapse of the superzone boundaries. A similar insensitivity of the superzone gap to an external field has been observed in GdPd$_2$B$_{0.5}$C$_{0.5}$, where no change in the resistivity upturn behavior was noticed at 7 T [49]. For the case of GdPd$_2$B$_{0.5}$C$_{0.5}$ it was argued that the strength of the magnetic coupling between the moments is strong enough to prevent an effect of the external field. A similar situation may hold for the present compound, because our maximum measurement field is roughly a factor of two smaller than the critical field.

4. Summary and conclusions

The physical properties of EuPd$_2$As$_2$ single crystals were investigated using $\chi(T)$, $M(H, T)$, $C_p(H, T)$ and $\rho(H, T)$ measurements. The $\rho(T)$ data indicate metallic behavior. The high-$T$ $\chi(T)$ data follow the Curie-Weiss law with a Curie constant consistent with Eu$^{3+}$ spins $S = 7/2$ with $g = 2$ and Weiss temperature $\theta_\parallel = \approx -30$ K, indicative of dominant AFM interactions. The $C_p(T)$ data from 16 to 300 K are fitted well by the Debye theory of lattice heat capacity, yielding a Debye temperature $\Theta_D = 216(2)$ K. The $\rho(T)$ data from 12 to 300 K agree with the Bloch-Grüneisen model of the resistivity arising from electron-phonon scattering, where the fitted Debye temperature is $\Theta_R = 182(3)$ K, somewhat smaller than the value obtained from analyzing the $C_p(T)$ data.

At lower $T$, the $\rho(T)$ data indicate long-range AFM ordering at $T_{N1} = 11.0$ K with another transition at $T_{N2} = 5.5$ K that is likely a spin reorientation transition. The anisotropic $\chi(T)$ data for $T_{N2} < T < T_{N1}$ suggest a planar noncollinear AFM structure with the ordered moments aligned within the $ab$ plane, consistent with a helical or cycloidal magnetic structure with a turn angle of $\sim 104^\circ$ or $\sim 139^\circ$ between adjacent layers of ferromagnetically aligned spins. The anisotropic $\chi(T)$ and $M(H)$ isotherm data suggest that the AFM structure at $T < T_{N2}$ becomes noncoplanar, with equal numbers of spins canting in opposite directions out of the $ab$ plane, thus preserving an overall AFM structure. The $M(H)$ isotherm measurements for $H_\parallel$ and $H_{\perp}$ up to $H = 14$ T at $T = 2$ K both show weak metamagnetic transitions at $H \approx 5$ T. Two estimates indicate that the critical field at which all Eu spins become aligned with the field with increasing field at 2 K is $H_C = 22$ T, which is about 60% larger than our maximum measurement field of 14 T.

The $C_p(T)$ and $\rho(T)$ measurements show anomalies at both $T_{N1}$ and $T_{N2}$. Although $\rho$ decreases monotonically on cooling from 300 K to 10 K, it increases with decreasing $T$ below $T_{N1}$, suggesting that part of the Fermi surface becomes gapped due to the AFM ordering, and then decreases again below 9.0 K. The $\rho(T)$ shows a 12% positive magnetoresistance at
\[ T = 1.8 \text{ K} \text{ and } H = 10 \text{ T}, \text{ but the size of the upturn below } T_{N1} \text{ is not affected by fields up to 12 T.} \]

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