

Formation of a simple cubic antiferromagnet through charge ordering in a double Dirac material

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Following the topological classification of electronic phases, interest has grown in materials with unique electronic or magnetic properties driven by topology and interactions. Here we report that the topologically nontrivial mixed valent intermetallic EuPd_3S_4 undergoes long-range charge ordering at $T_{\text{CO}} = 340$ K, wherein $J = 7/2$ Eu^{2+} and Van Vleck $J = 0$ Eu^{3+} ions on a body-centered-cubic lattice separate into two interpenetrating simple cubic sublattices. The reduced symmetry transmutes eightfold double Dirac states into fourfold Dirac states and leads to a simple cubic Heisenberg antiferromagnet with G-type antiferromagnetic order for $T < T_N = 2.85(6)$ K. While time reversal symmetry is broken, its combination with nearest neighbor lattice translation can form a nonsymmorphic symmetry preserving the fourfold Dirac point. The application of a magnetic field yields a spin flop transition at the lowest temperatures but, as a consequence of the extreme isotropy of Eu, that phase transition turns into a crossover at higher temperatures. Our work demonstrates how charge order modifies topology in EuPd_3S_4 and exposes an archetypal simple cubic Heisenberg antiferromagnet.

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I. INTRODUCTION

The highest known electronic degeneracy compatible with the 32 crystallographic point groups is six, as realized in the t_{2g} state of $3d$ electrons in an octahedral crystal field system. Recently, it was recognized [1,2] that nonsymmorphic symmetries, and in particular the combination of a fractional translation and point symmetry operation, can raise the degeneracy at suitable high symmetry points of the Brillouin Zone

to twelve (without spin-orbit coupling), or eight (with spin-orbit coupling). Palladium bronzes, of the general formula LnPd_3S_4 (Ln = rare-earth), consist of a three-dimensional network of corner sharing PdS_4 polyanions with eightfold sulfur coordinated cavities where Ln ions reside on a body-centered-cubic (bcc) lattice (Fig. 1). This nonsymmorphic $Pm\bar{3}n$ space group [3,4] has recently been proposed to harbor such “double Dirac” states when the Ln cation is nonmagnetic (e.g., La^{3+}) [2,5].

In the case of magnetic rare-earth ions, EuPd_3S_4 is particularly interesting. Reported to have mixed $\text{Eu}^{2+}/\text{Eu}^{3+}$ valency [7–10], the reduced charge transfer to the $[\text{Pd}_3\text{S}_4]$ framework should move the Fermi level closer to an eightfold degenerate Dirac point. Further, the breaking of time reversal symmetry from Eu^{2+} magnetic order could produce a magnetic Weyl state, depending on the details of the magnetic order.

Previous Mössbauer measurements [7,10] suggest a 1:1 ratio of Eu^{2+} and Eu^{3+} , opening the possibility of two distinct sites for Eu^{2+} and Eu^{3+} , and the formation of a Heisenberg magnet on the Eu^{2+} lattice defined by charge ordering. While G-type antiferromagnetism has been reported in cubic perovskite EuTiO_3 below $T_N = 5$ K [11], a cubic to tetragonal

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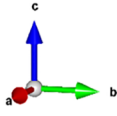
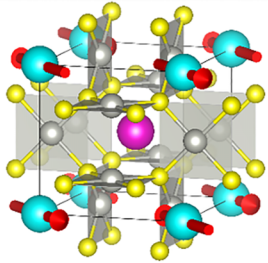
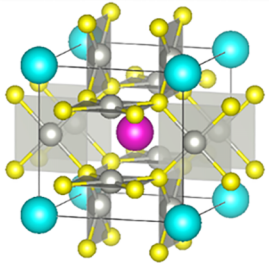
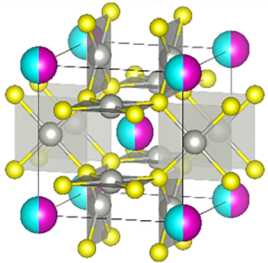
	$T \leq 2.85(6) \text{ K}$	$2.85(6) \text{ K} \leq T \leq 340 \text{ K}$	$T \geq 340 \text{ K}$
Inversion symmetry	✓	✓	✓
Time reversal symmetry	✗	✓	✓
Nonsymmorphic symmetry	✗	✗	✓
Space group	$\text{Pm}\bar{3}$	$\text{Pm}\bar{3}$	$\text{Pm}\bar{3}\text{n}$
Charge order	✓ (Eu^{2+} and Eu^{3+} , 1:1)	✓ (Eu^{2+} and Eu^{3+} , 1:1)	✗
Magnetism	$(\pi\pi\pi)$ Antiferromagnetic	Paramagnetic	Paramagnetic
Band crossing	R point (2-/4-fold)	R point (4-fold)	R point (8-fold)
Structure Eu^{2+} , Eu^{3+} , Pd and S 			

FIG. 1. Overview of phase transitions in EuPd_3S_4 . Above $T_{\text{CO}} = 340 \text{ K}$, the $\text{Eu}^{2+}/\text{Eu}^{3+}$ valence fluctuates, and EuPd_3S_4 adopts a $\text{Pm}\bar{3}\text{n}$ structure with inversion, time reversal, and a nonsymmorphic n -glide that produces double Dirac fermions at the **R** point. The emergence of charge order below $T_{\text{CO}} = 340 \text{ K}$ removes the n -glide and gaps out the double Dirac point to yield a pair of fourfold degenerate states. This charge order produces a simple cubic magnetic lattice upon which G-type AFM order forms below $T_{\text{N}} = 2.85(6) \text{ K}$. Depending on the spin direction in the ground state, the fourfold degeneracies are preserved or split into pairs of twofold degenerate states. Crystal structures were generated in VESTA [6] using a modified .cif file from [4].

distortion is observed slightly below room temperature [12]. To our knowledge, EuPd_3S_4 would be the first example of a rare-earth-based simple cubic (sc) Heisenberg antiferromagnet.

We show that such charge ordering indeed occurs and we study the resulting Eu^{2+} -based simple cubic Heisenberg antiferromagnetism as illustrated in Fig. 1. We determine how both the charge and the magnetic order modify degeneracies in the band structure.

The paper is organized as follows. Section II describes our experimental and density function theory (DFT) methods, and provides a brief overview of the sequence of measurements that have been performed. Section III describes our key experimental observations with a minimal amount of analysis, relying on few assumptions. The reader may proceed directly to this section and return to Sec. II as-needed. Section IV presents a more detailed analysis, in particular the DFT results.

II. METHODS

A. Synthesis

EuPd_3S_4 single crystals were grown by two approaches, inspired by previous related syntheses [5,13–17]. The first approach, “crystal A,” was a solid state grain growth approach. For this approach stoichiometric quantities of Eu (ingot, Yeemeida Technology Co., LTD 99.995%), Pd (J&J materials, 99.9+%), and S (Alfa Aesar, 99.999+%) were sealed in evacuated quartz ampoules with total theoretical mass of 0.5 g. The ampoules were placed in a box furnace

at a 45° angle (with the sample charge close to the interiors of the furnace) and heated to $T = 900^\circ\text{C}$ at a rate of 80°C h^{-1} for 24 hr and subsequently heated to $T = 1100^\circ\text{C}$ at a rate of 80°C h^{-1} for 14 days. The ampoules were removed at $T = 1100^\circ\text{C}$, allowed to air cool, and opened at room temperature. The obtained crystals were 1–3 mm in size. Phase purity and single crystal domain size were characterized using powder x-ray diffraction and Laue diffraction (Fig. S10 in Ref. [18], see also Refs. [19–21] therein).

In the second approach, “crystal B,” a self-flux technique using a two-step process described previously was used [13]. Elemental Eu (Ames Lab, 99.9%), Pd powder (Engelhard, 99+ % purity), and S (Alpha-Aesar, 99.99%) were weighed according to a nominal composition of $\text{Eu}_5\text{Pd}_{57}\text{S}_{38}$ and loaded into 2 mL alumina Canfield Crucible sets, or CCS [15]. The crucible sets were flame sealed inside evacuated fused silica ampoules and, prior to sealing, the ampoules were back-filled with $\sim 1/6$ atm Ar gas. The ampoules were then heated in a box furnace to 450°C over 8 h and then to 1150°C in another 8 h, held at 1150°C for 6 h, and finally cooled to 1050°C over 6 h. At this point the excess liquid was decanted by inverting the ampoules into a centrifuge. In our previous work, we found that mixtures of Ln (rare-earth), Pd, and S generally do not form a clean, single phase, liquid below 1200°C , and this first step allows us to remove unwanted secondary phases and obtain a clean solution for crystal growth [13].

After cooling to room temperature, a second CCS was assembled, using the original “catch” crucible and the material within it (that was captured during decanting) as the starting material. The second CCS was evacuated and sealed

as described above, heated to 1075 °C, and allowed to dwell for 6 h, during which the decant melted into a single-phase liquid. The furnace was finally slowly cooled to 875 °C in ~ 150 h, where the excess liquid phase was again decanted. The ampoules and crucibles were opened to reveal large (up to 5–6 mm), well-faceted crystals of EuPd_3S_4 .

B. X-ray diffraction

Single crystal x-ray diffraction data at $T = 213$ K on “crystal A” were collected on a Bruker-Nonius X8 Proteum (Mo K_α radiation) diffractometer equipped with an Oxford cryostream. Integration and scaling were performed using CRYSLISPRO (version 1.171.39.29c, Rigaku OD, 2017). A multiscan absorption correction was applied using SADABS [22]. The structure was solved by direct methods, and successive interpretations of difference Fourier maps were followed by least-squares refinement using SHELX and WINGX [23,24].

For “crystal B”, single crystal x-ray diffraction measurements were performed at $T = 370$ and 301 K. The data were collected over a full sphere of reciprocal space with 0.5° ω scans and an exposure time of 10 seconds per frame. All measurements were performed using a Bruker Apex II diffractometer with Mo radiation $K_{\alpha 1}$ ($\lambda = 0.71073$ Å). The 2θ range was from 5° to 75° . The SMART software was used for data acquisition. We corrected scattering intensities for the Lorentz factor using the SAINT program. Numerical absorption corrections were done using XPREP, which is based on face-indexed absorption. With the SHELXTL package, the crystal structures were solved through direct methods and refined by full-matrix least squares on F^2 [23,24]. The disorder refinements on Eu, Pd, and S sites show no vacancies in either EuPd_3S_4 crystal to within instrumental precision ($\sim 3\%$). To acquire the temperature dependence of the forbidden (001) peak, measurements were done with a narrow 2θ range around the peak and the temperature was controlled using a liquid nitrogen stream.

C. Magnetization and heat capacity

The magnetic and specific heat capacity measurements were performed with Quantum Design Magnetic and Physical Property Measurement Systems (MPMS-7T, PPMS-9T, and PPMS-14T) [25,26], the latter equipped with a dilution refrigerator (DR option).

$M(T)$ measurements from $T = 2$ to 300 K were performed using the MPMS-7T, with an applied field of $\mu_0 H = 0.05$ T. A 74.9(1) mg powder sample was wrapped in plastic and mounted in a plastic drinking straw [Fig. 2(c)]. A 15.5(1) mg crystal, mounted on a quartz rod using GE varnish [27], was measured under the same field (Fig. S2). Isothermal $M(H)$ measurements on a powder sample placed in a straw sample holder were performed at $T = 1.8, 2.9, 5, 10$, and 25 K, using the ACMS option for the PPMS in DC mode [Fig. 2(d)].

For heat capacity measurements under field, a thin 0.19(3) mg EuPd_3S_4 plate was aligned along (122) using Laue diffraction (Fig. S10), mounted to the Heat Capacity option puck using Apiezon N Grease [28] following the addenda measurement, and measured using the semi-adiabatic method with a 2% temperature rise. The field direction was selected based on

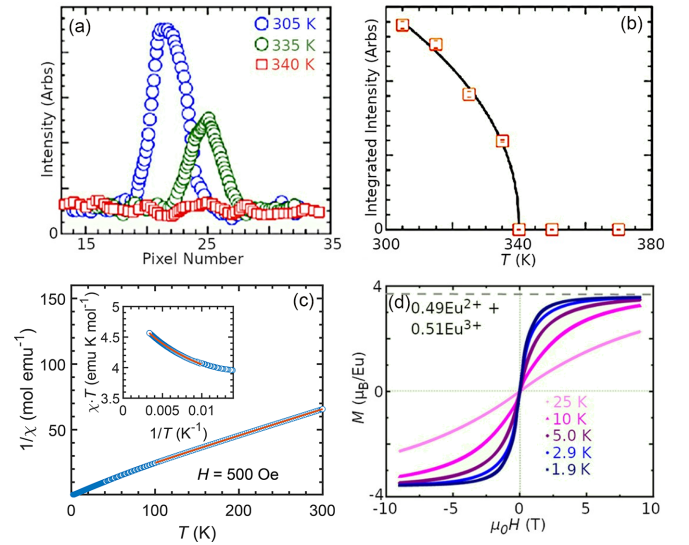


FIG. 2. Charge and magnetic order develop in different temperature regimes in EuPd_3S_4 . (a) Representative x-ray line scans of the $Pm\bar{3}n$ allowed, $Pm\bar{3}n$ forbidden (001) Bragg reflection as a function of temperature showing its complete suppression on warming beyond $T_{\text{CO}} = 340$ K. (b) Integrated intensities from fitting the line scans with a Gaussian lineshape indicate a phase transition at $T_{\text{CO}} = 340$ K. The black line is to guide the eye. (c) Temperature-dependent magnetic susceptibility of a 74.9(1) mg powder sample under a $\mu_0 H = 0.05$ T applied field upon warming. Note that uncertainty in the measured mass gives a 1.3% systematic uncertainty. The model includes the first nontrivial term of the high- T expansion for the Eu^{2+} susceptibility and the Eu^{3+} Van Vleck susceptibility with $\lambda = 480$ K [41,42]. Fitting from $T = 300$ to 100 K while taking the $\text{Eu}^{2+}:\text{Eu}^{3+}$ ratio to be 1:1 yields $\Theta_{\text{CW}} = -5.29(2)$ K and $\mu_{\text{eff}} = 7.95(1)$ μ_B for $\chi_r = 0.0004$. We note that the high- T data approach $T_{\text{CO}} = 340$ K, so that charge fluctuations may play a role in this regime. The extracted Θ_{CW} is a function of the fitting range with fits down to 125 K giving $\Theta_{\text{CW}} = -5.72(1)$ K and 75 K giving $\Theta_{\text{CW}} = -4.25(3)$ K. (d) $M(H)$ data show development of a field polarized state, saturating at a value consistent with a 1:1 mixture of Eu^{2+} and Eu^{3+} . The field derivative at $T = 1.9$ K (Fig. S11) shows the AFM to canted AFM phase line as in Fig. 6(f).

the most accessible facet of this particular sample. Field and temperature scans were performed in the range from $T = 0.3$ to 4 K and $\mu_0 H = 0$ to 4 T using the DR option (Figs. 5, 6, 13, and S7). Figure 13 shows that no latent heat was found so the phase transition appears to be of the second order. Additional measurements on a 2.34(3) mg crystal (Figs. 9–12) were performed to determine the magnetic entropy. The absolute scale (1.07) for the specific heat capacity data measured with the 0.19(3) mg sample was determined by comparison to the results for the 2.34(3) mg sample where the mass could be measured with higher relative accuracy.

D. Electrical transport

Resistivity measurements were carried out in a Physical Property Measurement System (PPMS-14T and PPMS-9T, Quantum Design) using the Resistivity option. Current was applied in the (122) plane, and magnetic fields perpendicular to that along the (122) direction. For longitudinal resistivity

(Fig. 7), linear contacts were made on the naturally grown crystals by silver paint and 25 μm platinum wires.

E. Neutron diffraction

Neutron diffraction was performed over the course of two experiments on the BT-7 triple-axis spectrometer at the NIST Center for Neutron Research (NCNR) [29] and in a third experiment using EIGER at the Paul Scherrer Institut (PSI) [30].

For the first and second experiments, a 30 mg EuPd_3S_4 single crystal was attached to an oxygen-free copper sample holder with Cd shielding and aligned with a horizontal (hhl) scattering plane by Laue diffraction [31]. For the first experiment, the sample was placed in an ILL-type cryostat. For the second experiment, the sample was placed in a 7 T cryomagnet system [with the applied field vertical along $(1\bar{1}0)$] and cooled in a ^3He insert. The field direction was selected based on the most accessible orientation of this particular sample. The impact of different choices for the applied field direction (cf. Sec. II C) is expected to be modest due to the isotropy of Eu^{2+} . In both cases the neutron energy was $E_i = E_f = 35$ meV, collimation was open $-25' - 25' - 120'$, and the monochromator and analyzer crystals were PG(002). Measurements included survey scans through the Brillouin zone (BZ) and rocking scans for accessible magnetic and nuclear Bragg points. The rocking scans were obtained at base temperature, for temperatures above T_N , and for fields of 0, 0.5, and 3 T. Temperature scans and field scans were acquired while monitoring the $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ peak intensity. Preliminary analysis was performed using DAVE [32] and MATLAB R2023A [33], with the magnetic and nuclear refinement completed in FULLPROF [34,35] (Fig. S6, Table S4, Sec. S6). Group theoretical analysis to determine magnetic structures that can arise through a second-order phase transition was carried out using SARAh [36] and the ISOTROPY tools [37–39].

For the third neutron diffraction experiment, a 2.35 mg EuPd_3S_4 single crystal was attached to an Al sample holder using the CTX-109AE grade fluoropolymer glue CYTOP [40]. The holder was wrapped in Cd shielding. The crystal was aligned for diffraction in the (hhl) scattering plane by Laue x-ray backscattering and loaded into an MA10 magnet on a dilution insert for neutron diffraction on EIGER at PSI. A field of 0.05 T was applied throughout the experiment to suppress Al superconductivity and ensure good thermal contact to the cold finger of the dilution refrigerator. $\mathbf{k}_c = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ peaks appeared below T_N , while both (001) and (002) appeared upon application of field at $T = 0.1$ K. The temperature dependence of both peaks was measured up to $T = 50$ K in a $\mu_0 H = 8$ T applied field. These results are presented in Figs. 3 and 4.

F. Band structure calculations

Density functional theory calculations for EuPd_3S_4 , including band symmetry analysis, were performed using QUANTUM ESPRESSO 7.0 [43] compiled with the Intel compiler 2020.1 on the Advanced Research Computing at Hopkins (ARCH) Rockfish cluster. Kinetic energy cutoffs and $\mathbf{k}$ -point meshes were chosen to ensure convergence with respect

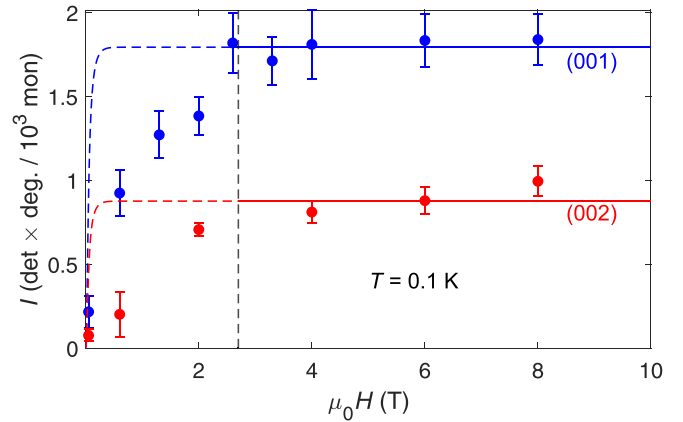


FIG. 3. Single crystal neutron diffraction field scans with field perpendicular to the (hhl) scattering plane. Integrated intensity of the (001) and (002) Bragg peaks are shown as a function of applied field measured at $T = 0.1$ K. For the $Pm\bar{3}$ simple cubic charge ordered system (Fig. 1) both peaks probe the uniform magnetization squared versus field. However, for the $Pm\bar{3}n$ space group (001) probes a staggered magnetization squared while (002) still probes the squared uniform magnetization. Up to high fields, at which we expect the moment to saturate, we find an indistinguishable field-dependent integrated intensity for the two Bragg peaks. The dashed vertical line at $\mu_0 H = 2.7$ T indicates the lower fitting limit below which we expect the sample to be antiferromagnetically ordered based on our $T = 0.3$ K field scans from BT7 [Fig. 5(d)]. The dashed line fits are to a Brillouin function squared extrapolated into the antiferromagnetic regime. Data from EIGER at PSI.

to those parameter choices. For non-spin-orbit calculations, PAW pseudopotentials with the LDA functional, nonlinear core correction, and a scalar relativistic treatment, obtained from Ref. [44], were used, with a 75 Ry kinetic energy cutoff and an $11 \times 11 \times 11$ $\mathbf{k}$ -point mesh. For non-spin-orbit,

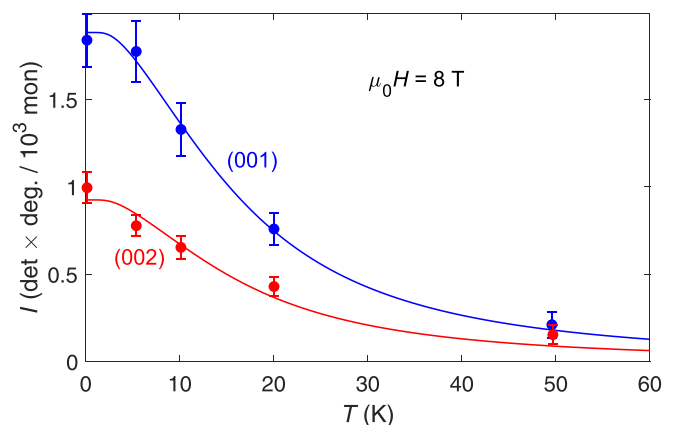


FIG. 4. Single crystal neutron diffraction temperature scans. Peaks are scanned as a function of temperature at $\mu_0 H = 8$ T, with the field perpendicular to (hhl). Up to the highest temperatures, we see no significant deviation from fits to a squared Brillouin function. In the absence of charge ordering, high field magnetic Bragg diffraction at (001) should vanish. Consistent with Fig. 2, there appears to be no changes in the charge order in the temperature regime probed here. Data from EIGER at PSI.

nonmagnetic calculations, the $4f$ electrons were in the pseudopotential core. For magnetic calculations, the Eu^{2+} ions used PAW pseudopotentials with $4f$ electrons in the valence, from the Virtual Laboratory for Earth and Planetary Materials, with $U = 10$ eV. For spin-orbit calculations in $Pm\bar{3}n$, PAW pseudopotentials with the LDA functional, nonlinear core correction, $4f$ electrons in the core, and a full relativistic treatment, obtained from Ref. [44], were used, with a 120 Ryd kinetic energy cutoff and an $11 \times 11 \times 11$ $\mathbf{k}$ -point mesh. For spin-orbit, nonmagnetic calculations in $Pm\bar{3}$, the same conditions were used, except with custom Eu PAW, LDA, nonlinear core correction, fully relativistic, pseudopotentials with $4f^6$ electrons in the core (for Eu^{3+}), and $4f^7$ electrons in the core (for Eu^{2+}), generated using the “atomic” code [45]. For spin-orbit, magnetic calculations in $Pm\bar{3}$ and $Fmmm'$, the Eu^{2+} pseudopotential was replaced with a custom PAW, LDA, nonlinear core correction, fully relativistic, pseudopotential, with $4f^7$ electrons in the valence. In magnetic calculations, moments were taken to lie along the crystallographic $\mathbf{c}$ axis. Calculations in the magnetic group $Fmmm'$ were performed with space group $Fm\bar{3}$. Band unfolding was performed using a modified version of the code available in Ref. [46].

III. EXPERIMENTAL RESULTS

A. Charge ordering

We discovered the charge order in high-resolution single crystal x-ray diffraction data acquired at $T = 213$ K. While a reasonable refinement is obtained with a mixed $\text{Eu}^{2+}/\text{Eu}^{3+}$ site in space group $Pm\bar{3}n$, inspection of precession images revealed weak forbidden reflections at $(h00)$ (h odd) with an average of 5.5σ ($\sigma =$ one standard deviation) discrepancy, and (hhl) (l odd) positions with average 6.8σ deviation, implying breaking of the n -glide symmetry. A more satisfactory refinement was obtained using $Pm\bar{3}$ (Fig. 1, Table S1). While our x-ray diffraction data are not directly sensitive to the $1e^-$ difference between Eu^{3+} and Eu^{2+} , the charge order is detectable due to the concomitant displacements of S anions, which yields distinct Eu-S bond lengths $d_{\text{short}} = 2.84604(5)$ Å and $d_{\text{long}} = 2.93528(5)$ Å. The corresponding bond valence sums, using $d_0 = 2.48$ Å are 2.8(1) and 2.2(1), implying formal valences of Eu^{3+} and Eu^{2+} , respectively.

The charge order and $Pm\bar{3}$ symmetry was confirmed by measurements at $T = 301(2)$ K on a different crystal and x-ray diffractometer. Figure 2(a) and Tables SI, SII document the presence of the $\{001\}$ -type reflections, which are forbidden in $Pm\bar{3}n$. Measurements on warming demonstrate that the (001) Bragg reflection disappears by $T_{\text{CO}} = 340$ K [Fig. 2(b)], which indicates restoration of the n -glide. The refined high- T structure [$T = 370(2)$ K] is detailed in Table S3. The critical temperature is consistent with extrapolation of the temperature of mixed valency behavior in the $\text{La}_{1-x}\text{Eu}_x\text{Pd}_3\text{S}_4$ series to $x = 1.0$ (pure EuPd_3S_4) [10].

Neutron diffraction in the presence of a magnetic field directly distinguishes Eu^{2+} and Eu^{3+} because magnetized Eu^{2+} ($L = 0$, $J = S = 7/2$) has a different scattering cross section compared to the Van Vleck ion Eu^{3+} ($J = 0$). Indeed, we did detect the (001) and (002) Bragg peaks by neutron diffraction upon magnetizing EuPd_3S_4 and the full temper-

ature and field dependence of the intensities of both these reflections are well-fit to squared Brillouin functions in the charge ordered magnetized paramagnetic phase (Figs. 3 and 4). This provides direct evidence that Eu^{2+} forms a simple cubic lattice in the charge ordered state.

B. Magnetic moments and their interactions

To isolate the $4f$ Eu contribution to the magnetic susceptibility, we measured and subtracted $\chi(T)$ for LaPd_3S_4 from the corresponding data for EuPd_3S_4 . The resulting molar susceptibility for EuPd_3S_4 is shown in Fig. 2(c). A fit to the susceptibility data must include the van Vleck contribution from $(J = 0)$ Eu^{3+} as well as the Curie-Weiss contribution from Eu^{2+} . This results in $\mu_{\text{eff}} = 7.95(1) \mu_B$, which is consistent with the spin-only Eu^{2+} $J = 7/2$ moment for which $\mu_{\text{eff}} = 2\sqrt{\frac{7}{2}(\frac{7}{2} + 1)} = 7.94 \mu_B$, and $\Theta_{\text{CW}} = -5.29(2)$ K indicating net antiferromagnetic interactions. Note that single crystalline samples can be impacted by inclusion of small quantities of EuS , which is ferromagnetic with $T_C = 16.5$ K [47]. The resulting anomaly in the magnetic susceptibility is shown in Fig. S2 [18].

Charge ordering has profound impacts on the magnetism of EuPd_3S_4 : It changes the magnetic lattice from bcc to simple cubic and eliminates magnetic bcc nearest neighbors. The eventual magnetic phase transition occurs at just 1% of the charge ordering temperature. For temperatures below 3 K, a field of $\mu_0 H = 3$ T is sufficient to fully magnetize EuPd_3S_4 [Fig. 2(d)]. The resulting saturation magnetization of $3.7 \mu_B$ is as expected for a 1:1 mixture of Eu^{2+} and Eu^{3+} .

Heat capacity measurements versus field and temperature were employed to determine the overall magnetic entropy and the magnetic phase diagram. Using the heat capacity of LaPd_3S_4 as a nonmagnetic reference (Appendix A) [5], the magnetic heat capacity and the magnetic entropy were determined and are displayed versus T in Fig. 9. The zero-field magnetic entropy integrates to $|\Delta S| = 8.0(5)$ J mol f.u. $^{-1}$ K $^{-1}$, which is close to the value expected for 50% Eu^{2+} ($J = 7/2$), $0.5R \log 8 = 8.6$ J mol f.u. $^{-1}$ K $^{-1}$. A lambda-like anomaly consistent with a second order phase transition is observed at $T_N = 2.85(6)$ K [Fig. 5(a)]. Analysis of this peak (Figs. 10–12) yields a critical exponent $\alpha = \alpha' \in [-0.3, -0.02]$ (Appendix B). For reference, the exponents for the 3D Heisenberg and mean field classes are $\alpha = \alpha' = -0.12(1)$ and $\alpha = \alpha' = 0$, respectively [48]. Upon applying a magnetic field along (122) , the peak progressively shifts to lower temperatures until for $\mu_0 H = 3$ T, there is no longer a phase transition observed. The small upturn in $C(T)$ for $T < 0.3$ K is attributed to the polarization of the Eu^{2+} nuclear spin system in the hyperfine enhanced field generated by the electronic sublattice polarization (Fig. 14 and Table II). Just above T_N , for $T = 3.15(7)$ K, the heat capacity is approximately independent of applied field for $\mu_0 H < 3$ T.

C. Magnetic order

To determine the ordered magnetic structure, we use magnetic neutron diffraction. EuPd_3S_4 poses challenges for neutron scattering as natural Eu absorbs neutrons, with an absorption coefficient $\mu_a = 2.60$ mm $^{-1}$ at the $\lambda = 1.5$ Å wavelength employed in our measurements (see Sec. S1

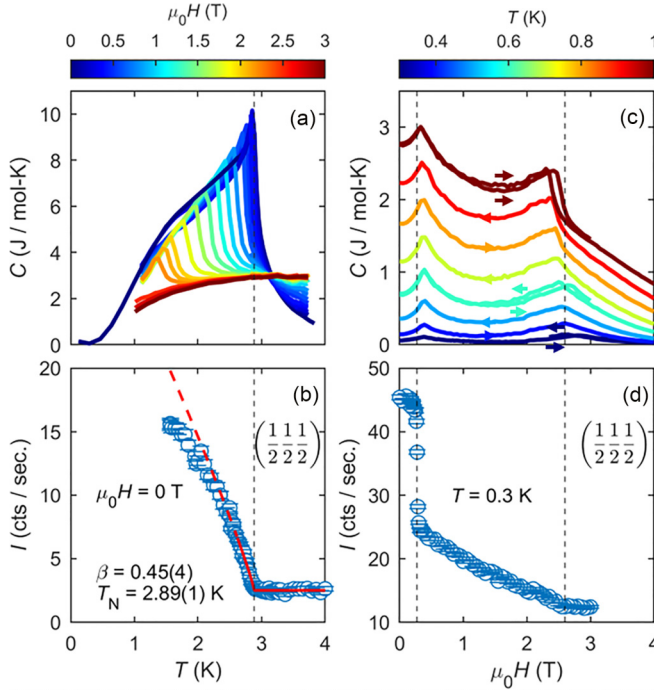


FIG. 5. Specific heat capacity and neutron diffraction measurements indicate a magnetic field tunable second order phase transition. (a) Temperature-dependent heat capacity scans at fixed fields from $\mu_0 H = 0$ T to 3 T from two experiments on the same EuPd_3S_4 single crystal with the field applied along the (122) direction. Fields include 0.0, 0.1, 0.2, 0.23, 0.3, 0.37 T, and 0.4 to 0.8 T in 0.1 T increments, 1.0 to 2.0 T in 0.2 T increments, 2.1, 2.2, 2.5, 2.75, and 3.0 T. (b) Order parameter measurement of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ peak from neutron diffraction at $\mu_0 H = 0$ T, indicating $T_N = 2.89(1)$ K. The solid line is a fit of the intensity to a power law (Fig. S5), while the dashed line shows this model's behavior well beyond the critical regime. Sample inhomogeneities can give neutron diffraction critical exponents approaching the mean field result. Alternatively, longer range interactions in this metallic system could give rise to mean field like criticality in the accessible regime of reduced temperature. (c) Field-dependent heat capacity scans at fixed temperatures from $T = 0.3$ to 1 K in 0.1 K increments. Measurements above 1 K show the peak at lower field becomes a shoulder (Fig. S6). Arrows indicate the direction of each field scan. (d) Field scan of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ peak intensity at $T = 0.3$ K. The same two transitions from (c) are observed at low and high field. The peak vanishes beyond the upper transition. The lower field step is attributable to the transition from a simple multidomain state to a smaller number of domains with staggered magnetization perpendicular to the applied field and the moments canted along the applied field. The magnetic structure becomes entirely polarized along the field beyond the upper transition.

for details) [49]. Additionally, cubic symmetry implies that magnetic neutron diffraction from a multidomain sample is independent of the moment direction within each domain. Nonetheless, we were able to establish key aspects of the magnetic order and the magnetic phase diagram through neutron diffraction from millimeter-scale EuPd_3S_4 single crystals with the natural isotopic abundance.

Contrary to expectations from theory [8] and experiments in related materials [50], scans through reciprocal space at $T = 1.6$ K and $\mu_0 H = 0$ T show that Bragg diffraction at

(001) is induced when applying a field [Fig. 6(a)]. The zero-field magnetic ordering is instead associated with magnetic Bragg diffraction at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ [Fig. 6(b)]. This indicates a doubling of the unit cell along the *a*, *b*, and *c* axes. Consistent with heat capacity and magnetization data, Figure 5(b) shows the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ peak onsets for temperatures $T < T_N = 2.89(1)$ K (see Fig. S5). As a function of field applied along (110), we find a sharp decrease in the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ peak intensity near $\mu_0 H = 0.3$ T followed by a linear decrease that culminates in the complete disappearance of this AFM diffraction for $\mu_0 H = 3$ T [Fig. 5(d)]. Both anomalies have counterparts in constant temperature field sweeps of the heat capacity [Fig. 5(c)]. We infer that the lowest field transition is associated with alignment of the staggered magnetization perpendicular to the applied field. The subsequent decreasing intensity indicates spin canting that gradually reduces the staggered magnetization until, at $\mu_0 H = 3$ T, EuPd_3S_4 is fully magnetized.

D. Electrical transport

The longitudinal and Hall resistivities were measured in four-wire and five-wire geometry respectively using a current of 3.0–5.0 mA in a temperature range from 0.45 to 300 K and magnetic fields up to 14 T. The resistivity of EuPd_3S_4 decreases monotonically upon cooling as expected for a metal (Fig. 7). We find the low-temperature residual resistivity is large, indicative of a low carrier density and little disorder. The anomaly at $T_N = 2.8$ K is associated with antiferromagnetic ordering.

IV. ANALYSIS AND DISCUSSION

A. Spin Hamiltonian

In the low-*T* regime where charge is localized on the simple cubic lattice, the magnetism of EuPd_3S_4 should be well-described by a spin Hamiltonian of the form $\hat{H} = -(1/2)\sum_{\langle \mathbf{R}, \mathbf{R}' \rangle} J(\mathbf{R} - \mathbf{R}') \mathbf{S}(\mathbf{R}) \cdot \mathbf{S}(\mathbf{R}')$, where $\sum_{\langle \mathbf{R}, \mathbf{R}' \rangle}$ indicates a summation over all unique pairs of simple cubic Bravais sites. Considering only nearest-neighbor interactions *J*, Monte Carlo simulations of the classical Heisenberg model on a simple cubic lattice [51–53] give $k_B T_N = -1.442929 J S^2$.

In the field-polarized state, the spin wave dispersion relation reads $E_{\mathbf{k}} = S[J(\mathbf{k} = \mathbf{0}) - J(\mathbf{k})] + g\mu_B \mathbf{B}$ [54]. Here $J(\mathbf{k})$ is the lattice Fourier transform of the exchange constants $J(\mathbf{R})$. From $E_{\mathbf{k}}$, again considering only nearest-neighbor interactions, we obtain a second collective energy scale $g\mu_B B_c(T = 0 \text{ K}) = -12JS$.

Combining these, we obtain $T_N = 1.5(1)$ K which is below the observed $T_N = 2.85(6)$ K transition. Although longer range, e.g., RKKY interactions may be significant, for this nearest-neighbor model we find $J = -g\mu_B B_c/(12k_B S) = -86(6)$ mK from the observed critical field and $J = -T_N/(1.442929 S^2) = -161(3)$ mK from the observed critical temperature, both favoring the $\mathbf{k}_c = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ type AFM order [Fig. 6(c)].

B. Magnetic refinements

For magnetic structure refinement, we acquired sets of neutron diffraction peaks in the PM, AFM, and canted states (Fig. S6, Table S4). Below T_N , $\mathbf{k}_c = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ AFM peaks

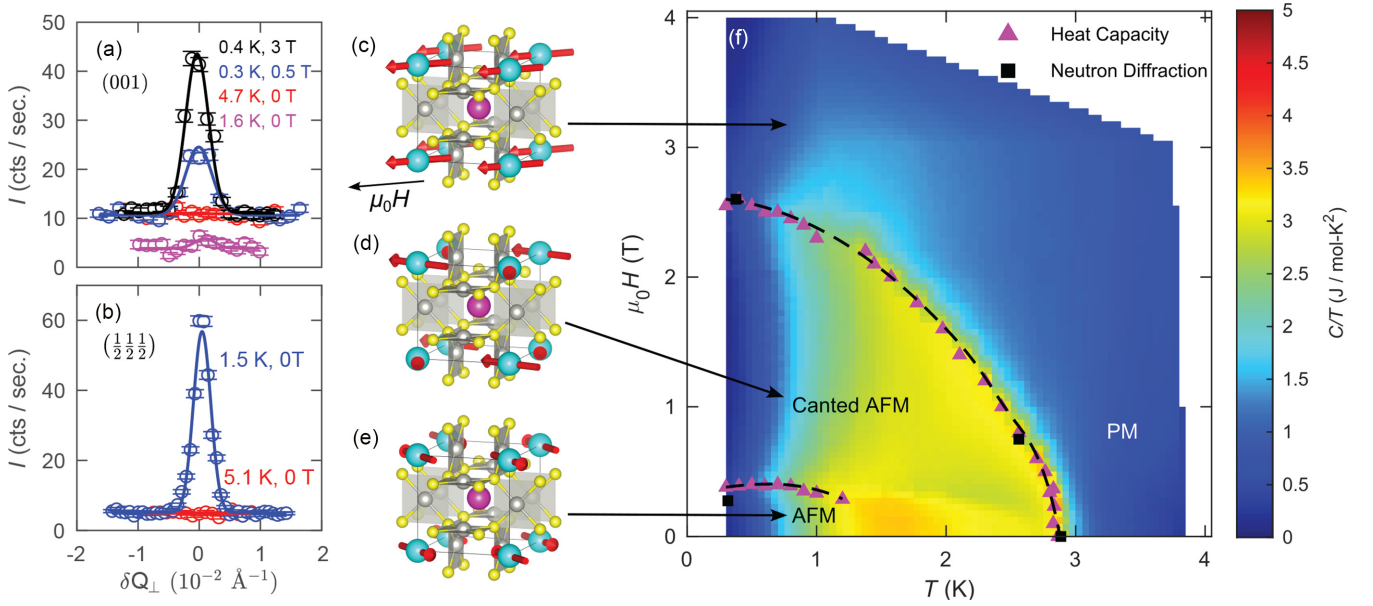


FIG. 6. Field-dependent magnetic phase diagram. (a) Rocking scans with $\delta Q_{\perp}$ perpendicular to the (001) direction of wave-vector transfer, lying in the (hhl) plane. Green points were collected without a cryomagnet so that the background is lower. The intensity has been scaled to the intensity of the (112) peak measured with a 70 mm Orange cryomagnet so peak intensity data can be directly compared for the two configurations employed. The (001) reflection has zero nuclear Bragg intensity at $T = 4.7$ K because the nuclei of Eu^{2+} and Eu^{3+} are equivalent. (001) remains absent below T_N in zero magnetic field. As the applied field along $(1\bar{1}0)$ increases and the Eu^{2+} sublattice becomes magnetized, however, the (001) peak appears. (b) Rocking scans with $\delta Q_{\perp}$ perpendicular to $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ and within the (hhl) reciprocal lattice plane, showing the development of AFM order below T_N . Gaussian fits are shown in frames (a) and (b). (c) The field polarized paramagnetic state in which all magnetic Eu^{2+} atoms are aligned along the applied $(1\bar{1}0)$ field direction. (d) The intermediate canted AFM state in which the Eu^{2+} spins cant along the applied field. (e) The multidomain $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ AFM state in the absence of an applied field. Due to domain averaging, the moment directions in the zero field state cannot be determined by neutron diffraction (Sec. S5). Because a small $(1\bar{1}0)$ field forces the staggered magnetization along (110) , we show the moments oriented along (110) . (f) Resultant magnetic phase diagram for EuPd_3S_4 . The points indicating phase transitions were determined by inspection of anomalies in the field and temperature dependence of the underlying specific heat capacity and neutron scattering data.

indicate the zero-field low temperature state [Fig. 6(e)]. Of note is the emergence of Bragg diffraction at (001) upon application of a field [Fig. 6(a)], which implies a field induced difference in the neutron scattering amplitude between the

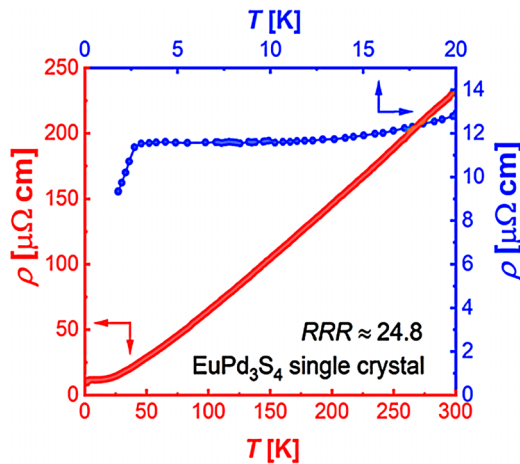


FIG. 7. Resistivity of EuPd_3S_4 single crystals as a function of temperature from $T = 1.8$ to 300 K. Measurements were taken with zero applied magnetic field and with current perpendicular to the (122) direction.

corner and center Eu sites of the bcc lattice. This is consistent with the observation of $\text{Eu}^{2+}/\text{Eu}^{3+}$ charge ordering in the x-ray data. The resolution limited nature of the field induced (001) peak yields a lower bound of $490(20)$ Å on the correlation length for the charge ordered state (Fig. S4). Refinements of the $\mathbf{k}_c = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ diffraction data acquired under a 0.5 T field applied along $(1\bar{1}0)$ with simple cubic charge order and a spherical absorption correction (Sec. S4) indicate the staggered magnetization is oriented along the $[110]$ rather than the $[001]$ direction [Fig. 6(d)]. At $\mu_0 H = 3$ T, the $\mathbf{k}_c = (\frac{1}{2}\frac{1}{2}\frac{1}{2})$ peaks disappear indicating a uniform magnetization oriented entirely along the applied field [Fig. 6(c)]. Together with additional field-dependent heat capacity sweeps (Fig. S7), these data establish the magnetic phase diagram for EuPd_3S_4 [Fig. 6(f)].

C. Electronic structure

DFT calculations (Figs. 8 and S8) including spin-orbit coupling (SOC) for the high temperature structure [Fig. 8(c)] show protected eightfold crossings at the $\mathbf{R}(1/2, 1/2, 1/2)$ point in the BZ. As there is only a single crystallographic site, DFT cannot capture distinct Eu valences, and the total charge transfer to the $[\text{Pd}_3\text{S}_4]$ framework is similar to that found for La^{3+} [5]. A symmetry analysis shows that the eightfold Fermion just above E_F transforms as the $\Gamma_6^- + \Gamma_7^- + \Gamma_6^+ +$

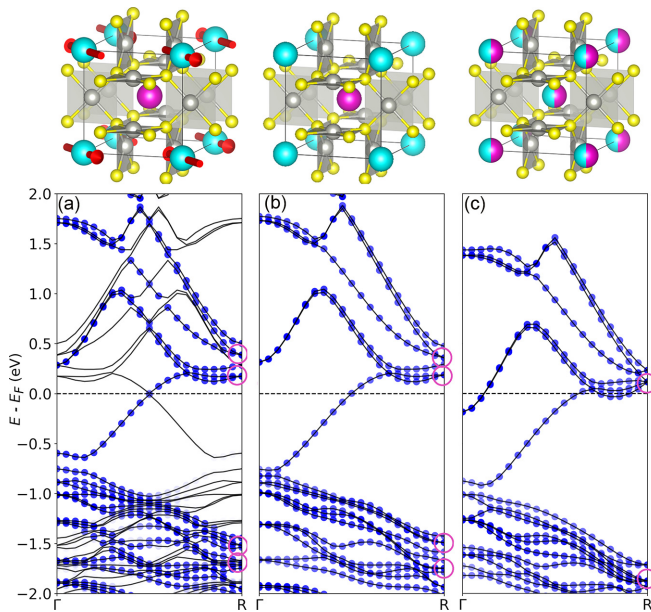


FIG. 8. Spin-orbit density functional theory band structures from $\Gamma(0,0,0)$ to $\mathbf{R}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ showing charge and magnetic order transmuting an eightfold fermion. (a) Unfolded band structure from the G-type simple cubic AFM magnetic state below $T_N = 2.85(6)$ K showing retention of the fourfold fermions when the magnetic moments lie along an axis with $Fmmm'$ magnetic symmetry. Solid lines show bands as computed, blue dots indicate band weight in the unfolded BZ. (b) Below 340 K, $\text{Eu}^{2+}/\text{Eu}^{3+}$ charge order, corresponding to $Pm\bar{3}$ crystal symmetry, splits the eightfold fermions into pairs of fourfold fermions, circled. (c) The crystal structure of EuPd_3S_4 at $T = 370(2)$ K corresponds to $Pm\bar{3}n$ crystal symmetry, with a single crystallographically unique Eu site; the n -glide plane protectseightfold degenerate states at the $\mathbf{R}$ point, circled.

Γ_7^+ irreducible representations, with the states of opposite parity constrained to be equivalent due to the nonsymmorphic n -glide. A DFT calculation including charge order [Fig. 8(b)], however, can capture distinct Eu valences since there are now two distinct Eu sites. This results in less charge transfer to the $[\text{Pd}_3\text{S}_4]$ polyanion, indicated by a lowering of E_F relative to rigid bands.

Let us now consider the interplay between the collective charge and spin order in EuPd_3S_4 on the electronic band structure. The charge order breaks the n -glide and lifts the degeneracy of states of opposite parity at $\mathbf{R}$, resulting in fourfold Fermions $\Gamma_6^- + \Gamma_7^-$ and $\Gamma_6^+ + \Gamma_7^+$. This demonstrates an alternative avenue by which eightfold degeneracies can be lifted [55,56]. The AFM order for $T < T_N = 2.85(6)$ K, however, does not necessarily further reduce the electronic degeneracy [Fig. 8(a)]. With G-type AFM and spins along a crystallographic symmetry axis, the magnetic group symmetry is $Fmmm'$. Unfolding back to the primitive BZ shows that the fourfold degeneracies at $\mathbf{R}$ remain, transforming as $2\Gamma_3^+ + 2\Gamma_4^+$ in the C_{2h} double group.

V. CONCLUSION

Given the lack of large rearrangements of the band structures, no exceptional transport anomalies are expected, and

none are observed (Fig. 7, Sec. IIID). However, considering the proximity of the eightfold fermion to E_F , future work should explore whether charge ordering might be understood as an instability of double Dirac states [57] as in Jahn-Teller distortions where the energy is lowered by breaking symmetries that protect degeneracies. More broadly, our results demonstrate an intricate interplay between charge and spin order that conspire to alter the electronic topology of EuPd_3S_4 .

Additional DFT calculations may be performed to improve our understanding of the exchange interactions. Future work should also resolve ambiguities in the magnetic structure determination, in particular the nature of the low-field crossover in the phase diagram and the moment orientation. Further research should precisely quantify the magnitude of the moment on the Eu^{3+} site and investigate the possibility for Eu^{2+} impurities on the Eu^{3+} site. Such a moment may be present while preserving the observed simple cubic symmetry of the magnetic order, so long as it is different from the Eu^{2+} site over a long length scale. Finally, the behavior of domain walls between charge ordered volumes remains an open question.

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T.B. and V.C.M. contributed equally to this work.

DATA AVAILABILITY

All data are available upon request from the authors. Data and code from V.C.M. are publicly available at [58]. Neutron data from BT-7 is also publicly available at [59] under the date range from 2020-01-13 11:13 to 2023-04-20 15:48 and from 2020-03-04 15:43 to 2020-03-08 12:05. Please contact V.C.M. regarding questions about the neutron data.

APPENDIX A: HEAT CAPACITY PHONON SUBTRACTION

The phonon contributions are subtracted (Fig. 9) from EuPd_3S_4 using the heat capacity data from LaPd_3S_4 through a normalization procedure to account for their molar mass differences [Eq. (A1)] [60].

$$\begin{aligned} & (\Theta_{L_m Y_s Z_p}^3) / (\Theta_{X_m Y_s Z_p}^3) \\ &= (mM_X^{1.5} + sM_Y^{1.5} + pM_Z^{1.5}) / (mM_L^{1.5} + sM_Y^{1.5} + pM_Z^{1.5}), \end{aligned} \quad (\text{A1})$$

where Θ is the Debye temperature, M is the mass of the atom, and $(m + s + p)$ is the number of atoms per formula unit.

APPENDIX B: HEAT CAPACITY CRITICAL EXPONENT FITS

Initially assuming $\alpha > 0$ and a divergent critical contribution $C_p \propto |\tau|^{-\alpha}$ to the specific heat capacity, a linear regression was performed on a double-logarithmic plot of C_p versus $|\tau|$ [61]. Data for $|\tau| < 0.05$ were included in the analysis. This approach however, yields different values for $\alpha > 0$ above and below T_N , which is inconsistent with the assumed power law form (Fig. 10). We therefore attempted the power-law analysis described in Refs. [62,63] to see if a reasonable fit with identical $\alpha < 0$ on both sides of the transition can be found (Fig. 11). When $\alpha < 0$, there is no longer a diverging power law contribution near T_N and additional terms in the specific heat capacity become significant. The specific form used in the analysis is

$$C(\tau) = \begin{cases} \frac{A}{\alpha} |\tau|^{-\alpha} + B + E\tau, & \tau > 0 \\ \frac{A'}{\alpha} |\tau|^{-\alpha} + B + E\tau, & \tau < 0 \end{cases} \quad (\text{B1})$$

We expect and observe some rounding near the critical temperature, so the fit was limited to the two temperature ranges $\tau_{\min} < |\tau| < \tau_{\max}$ about the fitted T_N . The error bars reported below were taken to be half the range of the parameter over which the reduced chi-squared remains within the threshold best fit reduced chi-squared. This threshold is given by $(1 + 1/\nu)\chi_r^2$ where ν is the degrees of freedom, taken to be the number of datapoints minus the number of fitted parameters. Fits for A, A', B, E, α , and T_N were initially performed using MATLAB's MultiStart and GlobalSearch algorithms, [64] while

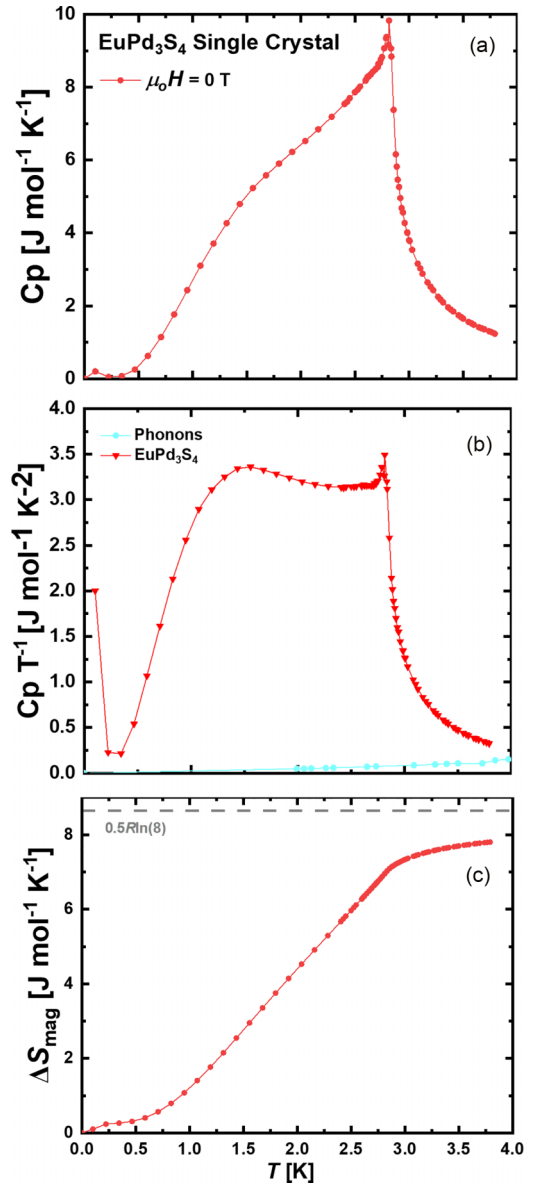


FIG. 9. Magnetic heat capacity and entropy in EuPd_3S_4 . [(a) and (b)] The magnetic heat capacity as determined by subtracting the phonon portion obtained from the reported heat capacity [5] of LaPd_3S_4 as an estimator of the phonon contribution. (c) The estimated change in magnetic entropy obtained by integration of the data in (b). A EuS impurity, an unequal distribution of Eu valences, and correlations extending to higher T may account for the entropy remaining beyond T_N .

fmincon alone was used as the local fitting function for error bar calculations. As an example, we find for $0.007 < |\tau| < 0.05$ the best fit given by Figs. 11 and 12, and Table I.

The experimental uncertainty in the critical temperature is dominated by the 20 mK calibration accuracy of the thermometer. E refined to approximately 0, hitting the lower bound set in the initial round of fitting. The fitting is rather sensitive to the selection of starting parameters and fitting range. We notice that a smaller value of T_N appears to give decent fits with $\alpha = -0.24$ and $\chi_r^2 = 4.3$, though increasing α improves the goodness of fit. For the $0.007 < |\tau| < 0.05$

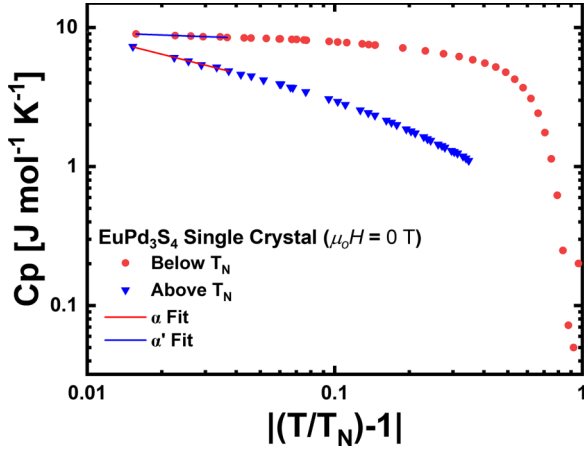


FIG. 10. Critical scaling analysis of magnetic heat capacity. Double logarithmic plot of specific heat versus reduced temperature $|\tau| = |T/T_N - 1|$ where $T_N = 2.81(1)$ K was taken to be the datapoint with the largest specific heat capacity. The approximately linear behavior near the maximum in the specific heat capacity yields exponents $\alpha = 0.448(14)$ for $T > T_N$ and $\alpha' = 0.006(7)$ for $T < T_N$. We note that the critical exponent fitting may be confounded by, for example, rounding of the peak at T_N due to disorder. Nevertheless the different values obtained here indicate that the critical exponent is negative for this phase transition and leads to the alternate analysis described in the following Figs. 11 and 12 [62]. The phonon contribution to the specific heat capacity was subtracted though it represents less than 1.53% of the specific heat capacity in this temperature range (Fig. 9).

range, the best fit with $\alpha = -0.10(3)$ and $\chi_r^2 = 3.5$ corresponds to a universal parameter $P = (1 - A/A')/\alpha = 5(1)$. This is consistent with the range of this parameter in previous experimental and theoretical work [62,63]. On the other hand, changing the fitting range to $0.01 < |\tau| < 0.05$ and allowing the model to refine gives a best fit $\alpha = -0.06(3)$ with $\chi_r^2 = 3.4$. Given the dependence of α on the choice of fitting range, we estimate $\alpha = [-0.3, -0.03]$. For reference, the exponents for the 3D Heisenberg and mean field classes are $\alpha = -0.12(1)$ and $\alpha = 0$, respectively [48]. The 3D Heisenberg class is consistent with short range isotropic magnetic interactions but does not capture longer range dipole interactions. The calculated change in the dipole-dipole energy associated with flipping a moment in the 0-field antiferromagnetic configuration, however, is vanishing [65,66]. While we do not find a precise value of α , we do find $\alpha = \alpha' < 0$ is a reasonable model to our data.

TABLE I. Parameters for the best fit of Eq. (B1) to specific heat capacity data in the reduced temperature range $0.007 < |\tau| < 0.05$. This fit is compared to the experimental data in Figs. 11 and 12.

$A(\text{J mol}^{-1} \text{K}^{-1})$	$A'(\text{J mol}^{-1} \text{K}^{-1})$	$B(\text{J mol}^{-1} \text{K}^{-1})$
2.0(3)	1.38(9)	18(3)
$E(\text{J mol}^{-1} \text{K}^{-2})$	α	T_N (K)
≈ 0	-0.10(3)	2.85(2)

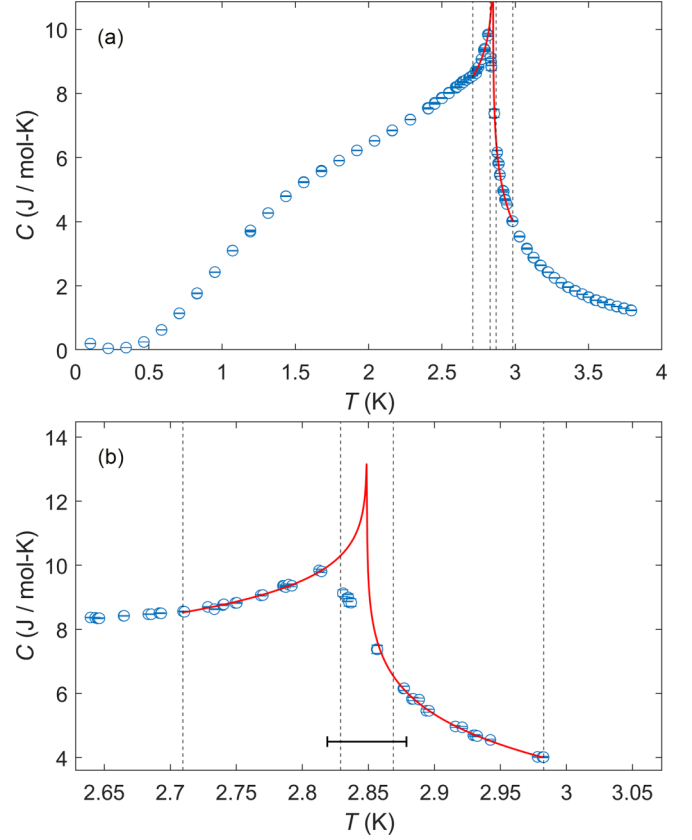


FIG. 11. Heat capacity critical exponent direct fits to Eq. (B1). [(a) and (b)] Fitting to the pure-power-law model in [62,63] with $0.007 < |\tau| < 0.05$ gives a critical exponent of $\alpha = -0.10(3)$. Dashed black lines indicate the two intermediate regions included in our fit. As described in Appendix B, the fitting is rather sensitive to the excluded range and initial parameters. But we do find good fits for $\alpha = \alpha' < 0$ (Table I). Near T_N , the adiabatic heat pulse results in a typical 0.06 K temperature rise during each measurement. The horizontal bar centered about the best fit T_N indicates this full range.

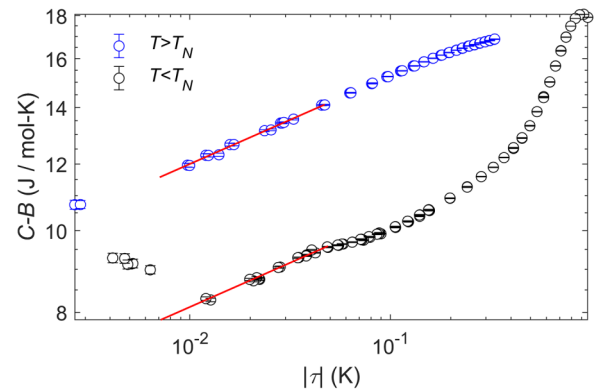


FIG. 12. Heat capacity critical exponent log-log plots. C is the overall heat capacity, B is a constant term in heat capacity, and τ is the reduced temperature. When α is negative we expect $\log(C - B)$ versus $\log(\tau)$ to be linear near T_N . The red line indicates the critical exponent fit for $0.007 < |\tau| < 0.05$ (Table I).

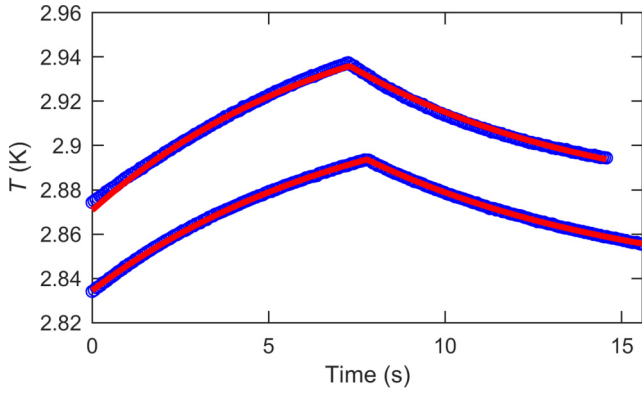


FIG. 13. Temperature versus time for EuPd_3S_4 from two conventional adiabatic heat pulse measurements obtained on a thin 0.19(3) mg platelike single crystal. Excellent fits are obtained for the pulse at lower- T . Worse fits at higher- T are likely due to large changes in heat capacity as a function of T just above T_N . There is no plateau that would indicate a latent heat (and thus first order transition).

APPENDIX C: HEAT CAPACITY HEAT PULSES

Details regarding the adiabatic heat pulses performed during heat capacity measurements are available in Fig. 13.

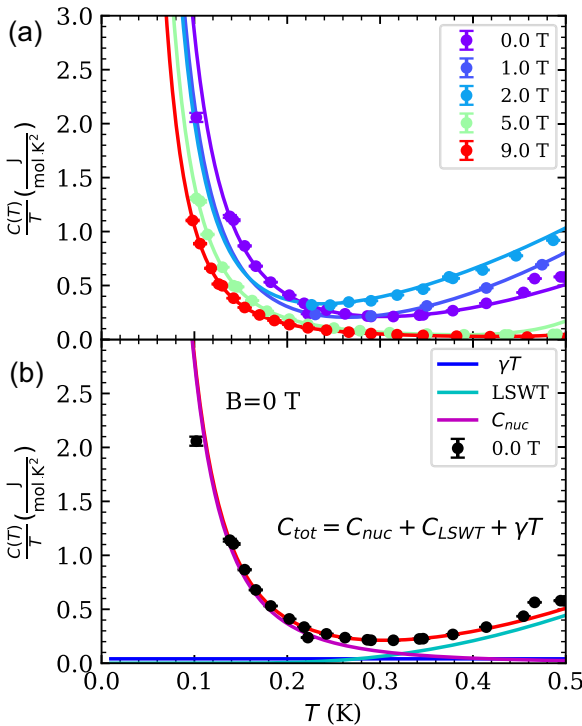


FIG. 14. Fitting of low temperature upturn to a nuclear Schottky anomaly. (a) Magnetic field dependent heat capacity. (b) Analysis of low temperature upturn as a Schottky anomaly arising from hyperfine enhanced nuclear spin polarization in the presence of Eu magnetic order.

TABLE II. Parameters from fitting of the nuclear Schottky anomaly. Analysis of low temperature upturn as a Schottky anomaly arising from nuclear spins freezing in the presence of Eu magnetic order [67,68]. Heat capacity below $T = 0.4$ K was fitted by a superposition of three contributions. $C_{\text{nuc}}(T) = 1/(Zk_B T^2) [\sum_i E_i^2 \exp((-E_i)/(k_B T))] - 1/Z(\sum_i [E_i \exp((-E_i)/(k_B T))])^2$ is the specific heat capacity associated with nuclear spin states arising from the hyperfine Hamiltonian $H = a'I_z + P(I_z^2 - 1/3I(I+1))$ where $a' = a\langle J_z \rangle$ and $\langle J_z \rangle = \mu_{\text{eff}}/g_L$. $C_{\text{elec}}(T) = \gamma T$ is associated with the electronic density of states at the Fermi level. Finally from linear spin wave theory, $C_{\text{LSWT}} \approx \partial U / \partial T$ for a generic 3D magnon is modeled by $U(T) = \int_{\Delta}^{\infty} \epsilon g(\epsilon) / (\exp(\beta\epsilon) - 1) d\epsilon$ where ϵ is the spin wave excitation energy, Δ is the excitation gap, $\beta = 1/(k_B T)$, and $g(\epsilon)$ is the magnon density of states. For a three-dimensional antiferromagnet with dispersion relation $\epsilon(q) = \sqrt{\Delta^2 + (cq)^2}$ where c is the spin wave velocity, the density of states is $g(\epsilon) = V\eta/(2c^3\pi^2)\epsilon\sqrt{\epsilon^2 - \Delta^2}$ where V is the unit cell volume and η is a constant. Without information on dispersion, we take the entire prefactor $V\eta/(2c^3\pi^2)$ to be a single constant A . The gap was found to be about 0.1 meV/1.2 K. Because our model works below the gap, we fit to data below $T = 0.4$ K. The Eu^{2+} occupancy was held fixed at 50% throughout.

$\mu_0 H$ (T)	μ_{eff}	γ (mJ/mol/K)	Δ (meV)	A (a.u.)
0	8.0(1)	40(10)	0.14(2)	77(10)
1	7.3(7)	2(8)	0.11(2)	120(20)
2	7(3)	90(20)	0.04(3)	90(5)
5	5.8(1)	12(5)	0.29(5)	38(4)
9	5.0(1)	0.0(2)	0.0(1)	6(1)

APPENDIX D: HEAT CAPACITY SCHOTTKY ANOMALY

Details regarding the nuclear Schottky fitting are available in Fig. 14 and Table II.

APPENDIX E: ELECTRICAL TRANSPORT MEASUREMENTS

The carrier concentration in Fig. S9(a) is consistent with that of a normal metal across a few temperature ranges. In Fig. S9(b), the negative magnetoresistance may be associated in part with a reduction in spin disorder scattering as the material is magnetized. The reduction in resistivity observed below the T_N in Fig. S9(a) are consistent with $R(T)$ reduction upon cooling through T_N in Fig. 7. Further, the Fig. S9(b) inset shows a monotonic decrease close to T_N . The maxima in the field-dependent resistivity were obtained by visual inspection of Fig. S9(b).

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