Crystal structure and physical properties of EuPtIn$_4$ intermetallic antiferromagnet

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We report the synthesis of EuPtIn$_4$ single crystalline platelets by the In-flux technique. This compound crystallizes in the orthorhombic Cmcm structure with lattice parameters $a = 4.542(1)$ Å, $b = 16.955(2)$ Å and $c = 7.389(1)$ Å. Measurements of magnetic susceptibility, heat capacity, electrical resistivity, and electron spin resonance (ESR) reveal that EuPtIn$_4$ is a metallic Curie-Weiss paramagnet at high temperatures and presents antiferromagnetic (AFM) ordering below $T_N = 13.3$ K. In addition, we observe a successive anomaly at $T^* = 12.6$ K and a spin-flop transition at $H_c \sim 2.5$ T applied along the $ac$-plane. In the paramagnetic state, a single Eu$^{2+}$ Dysonian ESR line with a Korringa relaxation rate of $b = 4.1(2)$ Oe/K is observed. Interestingly, even at high temperatures, both ESR linewidth and electrical resistivity reveal a similar anisotropy. We discuss a possible common microscopic origin for the observed anisotropy in these physical quantities likely associated with an anisotropic magnetic interaction between Eu$^{2+}$ 4$f$ electrons mediated by conduction electrons.

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INTRODUCTION

Low-dimensional rare-earth based intermetallic compounds exhibit a variety of interesting phenomena including Ruderman-Kittel-Kasuya-Yoshida (RKKY) magnetic interaction, heavy fermion (HF) behavior, unconventional superconductivity, crystalline electrical field (CEF) and Fermi surface (FS) effects. In order to systematically explore the interplay between such versatile physical properties in structurally related series, it is highly desirable to separate the role of the each interaction in determining the behavior of the system. For instance, the study of isostructural magnetic analogs have been often employed to elucidate the role of RKKY interactions and CEF effects in the evolution of the magnetic properties in $R_mM_nIn_{3m+2n}$ ($R =$ rare-earth; $M =$ Rh, Ir; $m = 0, 1$; $n = 1, 2$) series \cite{4, 5}. In particular, Gd$^{3+}$- and Eu$^{2+}$-based members are usually taken as reference compounds due to their $S$-state ($S = 7/2$, $L = 0$) ground state. As such, CEF effects are higher order effects and their magnetic properties purely reflect the details of RKKY interaction and FS effects.

Among the Indium-rich compounds, the series $RMI_{n}$ (114 system; $R =$ e.g. Ca, Eu, Yb, Ce; $M =$ e.g. Ni, Pd, Au) adopt the orthorhombic YNiAl$_4$-type structure which contains complex [PtIn$_4$] polyamionic networks with europium atoms filling distorted hexagonal channels (Fig. 1a) \cite{6, 7}. The clear elongation of the $b$-axis indicates the possibility of a 2D Brillouin zone with cylindrical Fermi surfaces along the $b$ direction. Although the member CeNiIn$_4$ has been reported to display most likely a three-dimensional electronic state \cite{7}, the promising features of this series of compounds have not been extensively explored yet, particularly for single crystalline samples. In order to test the above hypothesis in new members of this series, we here report the synthesis and physical properties of EuPtIn$_4$ single crystals. We have carried out electrical resistivity, magnetic susceptibility, specific heat and electron spin resonance (ESR) measurements. The field-dependent magnetic susceptibility shows an AFM ordering at $T_N = 13.3$ K followed by a successive transition at $T^* = 12.8$ K. Both electrical resistivity and ESR linewidth are found to be anisotropic even at high temperatures, suggesting the presence of an anisotropic magnetic interaction between the Eu$^{2+}$ 4$f$ electrons mediated by conduction electrons (ee).

EXPERIMENTAL DETAILS

Single crystalline samples of EuPtIn$_4$ were grown using flux technique with starting composition Eu:Pt:In=1:1:25. The mixture was placed in an alumina crucible and sealed in a quartz tube under vacuum. The sealed tube was heated up to 1100°C for 2 h, cooled down to 800°C at 20°C/h and then cooled down to 350°C at 10°C/h. The flux was then removed by centrifugation and the obtained shiny platelet crystals are stable in air and have typical dimensions of 1 mm x 1 mm x 0.1 mm, as shown in Fig. 1b. Phase purity was checked by X-ray powder diffraction using a Rigaku diffractometer (Cu-Kα radiation). Figure 1c shows the pattern of EuPtIn$_4$, which could be completely fitted with a single phase. Rietveld refinements of EuPtIn$_4$ ($R_{wp} = 13.6\%$) yields lattice parameters $a = 4.542(1)$ Å, $b = 16.955(2)$ Å and $c = 7.389(1)$ Å. Specific heat measurements were performed in a Quantum Design PPMS small-mass calorimeter that employs a quasiadiabatic thermal relaxation technique. The electrical resistivity was measured using a standard four-probe method also in the Quantum Design PPMS. The magnetization was measured using a VSM superconducting quantum
interference device (SQUID) magnetometer (Quantum Design). ESR measurements were performed in a BRUKER spectrometer equipped with a continuous He gas-flow cryostat. X-Band ($\nu \sim 9$ GHz) frequency was used in the temperature region $4.2 \ K < T < 300 \ K$.

RESULTS AND DISCUSSION

The macroscopic physical properties of our EuPtIn$_4$ single crystals are presented in Fig. 2. Panel a) displays the zero-field in-plane electrical resistivity, $\rho_{ac}$ ($T$), and a line connecting the b-axis, $\rho_b$ ($T$), as a function of temperature. A weakly anisotropic metallic behavior is observed in the paramagnetic regime followed by a clear peak at $T_N = 13.3 \ K$. Residual resistivity ($\rho_0$) and residual resistivity ratio (RRR) values of $\rho(T)$ are $0.1 - 0.5 \ \mu\Omega\cdot cm$ and $\sim 70$, respectively, indicating good crystallinity of our samples. However, the magnetoresistance (MR = $\Delta\rho/\rho = \rho(H) - \rho(H = 0)/\rho(H = 0)$) at $T = 2 \ K$ is linear with magnetic field and no quantum oscillations have been found (inset of Fig. 2a) up to $14 \ T$.

Fig. 2b shows the magnetic susceptibility as a function of temperature for a magnetic field $H = 1 \ kOe$ applied parallel and perpendicular to the ac-plane of the sample. $\chi(T)$ shows an isotropic Curie-Weiss (CW) behavior at high-$T$ followed by an AFM transition at $T_N = 13.3 \ K$. The sharp decrease of $\chi(T)$ below $T_N$ for $H \parallel$ ac-plane suggests that the ac plane is the plane of easy magnetization. From the CW magnetic susceptibility fits for $T > 10T_N$ (solid lines in Fig. 2b) we obtained for both directions a CW temperature of $\theta_{CW} \approx -15(1) \ K$ and an effective moment of $\mu_{eff} \approx 7.8(1)\mu_B$ for Eu$^{2+}$ in EuPtIn$_4$, which is in good agreement with the theo-

FIG. 1: a) Orthorhombic crystal structure of EuPtIn$_4$ (space group Cmcm). b) Scanning electron microscope (FE-SEM) image of as-grown EuPtIn$_4$ single crystal. c) X-ray powder pattern and Rietveld fit ($R_{wp} = 13.6\%$) of EuPtIn$_4$ at $300 \ K$.

FIG. 2: Temperature dependence of macroscopic physical properties of EuPtIn$_4$ single crystals. a) Electrical resistivity as a function of temperature for two current orientations. The inset shows the magnetoresistance for $H \parallel$ b-axis with applied field along the b-axis. b) Magnetic susceptibility with applied field $H= 1 \ kOe$ parallel to ac-plane and b-axis. c) Temperature dependence of specific heat. The insets show the recovered entropy (left) and the suppression of $T_N$ and $T^*$ with applied field along the b-axis.
Interestingly, even at high temperatures, the Eu-ions experience a metallic contribution of demagnetization effects on this apparent $g$-anisotropy. Furthermore, there is a weak $T$-dependence of the $g$-values, which may suggest the presence of short range magnetic correlations which yield non-trivial local fields at the Eu$^{2+}$ sites. However, we cannot rule out the contributions of ‘bottleneck’ and “dynamic” effects [13].

**FIG. 3**: a) X-Band (~9.5 GHz) ESR spectra of EuPtIn$_4$ single crystals at $T = 100$ K. b) Angle dependence of ESR linewidth $\Delta H$ and resonance field $H_{res}$. The $\Delta H$ and the $g$-value temperature dependence of the ESR line of EuPtIn$_4$ for the X-Band is presented in Figure 4a and 4b, respectively. An isotropic linear (Korringa) increase of $\Delta H$ with increasing-$T$ is observed for the Eu$^{2+}$ ESR signal in the paramagnetic state. From linear fits to $\Delta H(T)$ (solid lines) for $T > 100$ K, we extracted the value of the Korringa rate $b \equiv \Delta H/\Delta T = 4.1(2)$. As the temperature is further decreased, the ESR $\Delta H$ starts to broaden as a consequence of the development of short range magnetic correlations. At the same
temperature region, the g-factor slightly increases, also suggesting the presence of a weak dominant ferromagnetic component. Finally, below $T_N$ the resonance cannot be detected, likely due to the presence of antiferromagnetic collective modes which broadens the ESR line.

![Graph of temperature dependence of Eu$^{2+}$ ESR $\Delta H$ and g-factor in X-Band.](image)

**FIG. 4**: Temperature dependence of Eu$^{2+}$ ESR $\Delta H$ and g-factor in X-Band.

To further explore the microscopic origin of the Eu$^{2+}$ ESR $\Delta H$ anisotropy we have performed detailed electrical resistivity experiments in both paramagnetic and ordered regimes. Fig. 5a shows the comparison between the anisotropy in Eu$^{2+}$ ESR $\Delta H$ and that in the electrical resistivity. Such comparison is important in this case because an anisotropic exchange interaction between the Eu$^{2+}$ 4f electrons and the ce would result in similar angular dependence of both physical quantities. In fact, we observe that both quantities display a similar anisotropy. This suggests the presence of anisotropic magnetic scattering due to anisotropic short range magnetic correlations between Eu$^{2+}$ ions. In addition, Fig. 5c shows a subtle change of anisotropy in the antiferromagnetic state as compared to the paramagnetic one (Fig. 5b), in agreement with the above picture.

![Graph of angle dependence of in-plane resistivity and ESR linewidth.](image)

**FIG. 5**: a) Angle dependence of in-plane resistivity and ESR linewidth. In-plane resistivity maps as a function of angle and magnetic field at b) $T = 100$ K and c) $T = 2$ K.
CONCLUSION

Here we report the synthesis, macroscopic characterization and ESR experiments on single crystalline samples of EuPtIn$_4$. This compound crystallizes in an orthorhombic structure (space group Cmcm) and presents AFM ordering below $T_N = 13.3$ K. A spin-flop transition is observed at $H_c \sim 2.5T$ for magnetic fields applied along the $ac$-plane of easy magnetization. In the paramagnetic state, a single Eu$^{2+}$ Dysonian ESR line with a Korringa-type relaxation is observed, indicating a metallic environment. The anisotropy of ESR linewidth, resonance field and electrical resistivity at high-$T$ indicates the presence of both second order CEF effects and anisotropic exchange interaction between the Eu$^{2+} 4f$ mediated by $ce$. The latter may be caused by the low dimensionality of [PtIn$_4$] polyanionic networks surrounding the Eu$^{2+}$ ions.

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