Structural distortion and incommensurate noncollinear magnetism in EuAg\textsubscript{4}As\textsubscript{2}

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Layered pnictide materials have provided a fruitful platform to study various emergent phenomena, including superconductivity, magnetism, charge density waves, etc. Here we report the observation of structural distortion and noncollinear magnetism in layered pnictide EuAg\textsubscript{4}As\textsubscript{2} via transport, magnetic, single crystal X-ray and neutron diffraction data. EuAg\textsubscript{4}As\textsubscript{2} single crystal shows a structural distortion at 120 K, where two sets of superlattice peaks with the propagation vectors of \(q_1 = \pm (0.25, 0.5)\) and \(q_2 = \pm (0.25, 0.1)\) exist. Before the hexagonal Eu\textsuperscript{2+} sublattice enters into an incommensurate noncollinear antiferromagnetic state below 9 K with a propagation vector of (0,-0.1,0.12), a short-range antiferromagnetic order with reduced magnetic anisotropy takes place between 15 K to 9 K. The magnetic structure below 9 K is helical along the \(c\) axis and cycloidal along the \(b\) axis with a moment of 3.7 \(\mu_B/\text{Eu}^{2+}\).

\section{I. INTRODUCTION}

Rare earth elements are characterized with the localized 4f electrons. Often coupled through Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction with conduction electrons, they can develop long-range magnetic order with large local magnetic moments, leading to various magnetic ground states. The intensive studies of the magnetism in rare earth elements and compounds have shaped our understanding of complex magnetism. In rare earth magnet, the magnetism is determined as a result of the interplay of crystal electric field (CEF) anisotropy, the dipole-dipole interaction, the magnetoelastic coupling between the moment and the lattice, as well as the oscillatory RKKY interaction which favors incommensurate periodicity \cite{1}. Besides these rich interactions which govern the magnetism, other exotic ground states can interplay with the magnetism in rare earth compounds. Layered Eu\textsuperscript{2+} based pnictides are well-known for being a material platform to study these interplays. For example, EuFe\textsubscript{2}As\textsubscript{2} is an antiferromagnet with a spin density wave phase transition of the FeAs layer at about 190 K and an A-type antiferromagnetic order arising from the Eu\textsuperscript{2+} sublattice at around 19 K \cite{2,3}. With K doping on the Eu site, which destroys the Eu magnetism, the SDW transition was suppressed and SC emerged \cite{4,5}. Eu magnetism is more persistent with chemical doping of As sites with P \cite{6,7}, and Fe sites with Cu \cite{8}, or under pressure up to 6 GPa \cite{9}, leading to coexistence of ferromagnetism and superconductivity.

Recently, we have studied a layered pnictide SrAg\textsubscript{4}As\textsubscript{2}, where a structural distortion is observed at around 110 K and quantum oscillation reveals the existence of small Fermi pockets with light effective mass and unexpected high mobility \cite{10}. In this paper, we present our studies of its magnetic analog, EuAg\textsubscript{4}As\textsubscript{2}, where the Eu\textsuperscript{2+} magnetic ions have a half-filled 4f shell and form a hexagonal sublattice. At room temperature, it crystalizes in the centrosymmetric trigonal CaCu\textsubscript{4}P\textsubscript{2} structure with the space group of \(R3m\) \cite{11}. The crystal structure can be taken as inserting an additional itinerant Ag\textsuperscript{2+} layer within the Ag\textsubscript{2}As\textsubscript{2} layer of the trigonal CaAl\textsubscript{2}Si\textsubscript{2}-type stacking of -Eu-Ag\textsubscript{2}As\textsubscript{2}-Eu- (Fig. 5(a)). Unlike in the CaCu\textsubscript{4}P\textsubscript{2} where the Cu\textsubscript{2} layer locates on one unique fully occupied site, in EuAg\textsubscript{4}As\textsubscript{2}, the itinerant Ag\textsubscript{2} layer occupies more than one partially occupied sites, leading to metallic Ag-Ag bonding \cite{11}. The CaAl\textsubscript{2}Si\textsubscript{2}-type EuTM\textsubscript{2}P\textsubscript{2} (TM = Mn, Zn, Cd and Pu = As and Sb), which are the trigonal version of the 122 pnictide family, were all reported to be antiferromagnetic (AFM) somewhere under 20 K and many are found with excellent thermoelectric properties \cite{12-19}. Antiferromagnetism was also revealed at around 15 K in EuAg\textsubscript{4}As\textsubscript{2} in a study by susceptibility and Mössbauer spectroscopy measurement \cite{20}. However, very little is known for this compound. Using a combination of transport, single crystal X-ray and neutron diffraction measurements, we revealed the coexistence of a high temperature structural distortion and a low temperature incommensurate noncollinear antiferromagnetism in EuAg\textsubscript{4}As\textsubscript{2}.

\section{II. SINGLE CRYSTAL GROWTH AND EXPERIMENTAL METHODS}

Single crystals of EuAg\textsubscript{4}As\textsubscript{2} were synthesized using Ag\textsubscript{2}As as the self-flux. Ag\textsubscript{2}As precursor was made by the solid state reaction of the stoichiometric ratio of Ag and As powders. The mixture was sealed in a quartz tube, slowly heated to 600 °C, stayed for 10 hours, and then heated up to and held at 850 °C for another 10 hours before being cooled to room temperature. Eu pieces were first scraped and arc-melted to remove oxidation layers. The precursor Ag\textsubscript{2}As and the Eu pieces were mixed
at a molar ratio of 4:1 and placed in an alumina crucible which was then sealed under vacuum in a quartz tube. The tube was heated up to 1100 °C, stayed for 3 hours, and cooled at a rate of 5°C/hour to 750°C. Then the single crystals were separated from the flux using a centrifuge. Several sizable plate-like single crystals with typical dimensions of $5 \times 4 \times 2 \text{mm}^3$ were obtained. A picture of a single crystal is shown in the inset of Fig. 2(a).

Powder X-ray diffraction data using a PANalytical Empyrean diffractometer (Cu Kα radiation) were collected to confirm the phase. Multiple pieces of single crystals ($\sim 20\times30\times30 \mu m^3$) were picked up and mounted on the tips of Kapton loops to examine the structure. The data were collected on a Bruker Apex II X-ray diffractometer with Mo radiation $K_{α1}$ radiation ($\lambda = 0.71073$ Å) and the temperature ranges from 100 K to 300 K. The SHELXTL package was employed to solve the crystal structure using the direct methods and full-matrix least-squares on $F^2$ models [21]. The incommensurate vectors were examined using JANA 2006 [22, 23].

The temperature dependence of the resistivity and the heat capacity was measured in a Quantum Design (QD) DynaCool Physical Properties Measurement System (DynaCool PPMS) from 300 K to 2 K. The temperature dependence of the magnetization was measured in a QD Magnetic Properties Measurement System (MPMS3).

In order to determine the magnetic structures, single crystal elastic neutron diffraction was performed at the HB-3A four circle diffractometer with the neutron wavelength of 1.550 Å from a bent perfect Si(111) monochromator at the High Flux Isotope Reactor (HFIR) at the Oak Ridge National Laboratory (ORNL) [24]. Representational analysis with the SARAh software was performed to determine the possible magnetic symmetries [25]. The nuclear and magnetic structures were refined with the FullProf Suite software [26].

III. RESULTS AND DISCUSSION

A. Superlattice peaks revealed by single crystal X-ray diffraction

The single crystal X-ray diffraction precession images of the $(hk\ell)$, $(0\ell l)$ and $(h0\ell)$ planes generated with $2\theta = 65^\circ$ at 170 K and 100 K, respectively. Space group $R3m$ requires a reflection condition of $-h + k + l = 3n$. At 170 K, in all three planes, only the points satisfying this condition are observed, as shown in Figs. 1(a), (d) and (g). As the temperature decreases to 100 K, additional superlattice peaks arising from the modulation reflections are discernable on the $(0\ell l)$ and $(h0\ell)$ planes, which are highlighted in Figs. 1(h) and (e). No detectable superlattice peaks are observed in the $(hk\ell)$ plane as shown in Fig. 1(h) and the zoom-in plot in Fig. 1(i). Fig. 1(c) presents the close examination of the selected region of the $(0\ell l)$ plane. The blue arrow connects a main nuclear peak and a superlattice peak next to it, suggesting a propagation vector of $q_1 = \pm(0.0,0.25,0.5)$. Fig. 1(f) shows the close examination of the selected region of the $(h0\ell)$ plane. In addition to the symmetry-related vectors of $q_1$ at (-0.25,0,0.5) marked by the blue arrow, the other set of superlattice peaks appears with a commensurate vector $q_2 = \pm(0.25,0,1)$, which is marked by the olive arrow. The emergence of these superlattice peaks suggests the existence of a structural distortion at low temperature.

The attempt to solve the crystal structure with superlattice model using all X-ray peaks at 100 K yielded a significantly high R value ($\sim 50\%$), suggesting the failure of the refinement. Therefore, to get an idea on the main crystal structure at 100 K, only the main X-ray nuclear peaks are used and all superlattice peaks are excluded in the refinement. The refinement suggests that the main crystal structure at 100 K remains the same as the one at 170 K. Tables I and II summarize the crystal structures of EuAg$_4$As$_2$ at 300 K and 100 K based on the main X-ray diffraction peaks and further investigation is needed to solve the low temperature modulated crystal structure. Unlike the crystal structure determined in Ref. [11], in our single crystalline EuAg$_4$As$_2$, the Ag$_2$ layer located on two partially occupied Ag sites, instead

![Figure 1. Single crystal X-ray diffraction precession image of EuAg$_4$As$_2$: (a), (d) and (g): the $(0\ell l)$, $(h0\ell)$ and $(h0\ell)$ planes in the reciprocal lattice at 170 K. (b), (e) and (h): the $(0\ell l)$, $(h0\ell)$ and $(h0\ell)$ planes in the reciprocal lattice at 100 K. (c), (f) and (i): the zoom-in plot of the selected area of (b), (e) and (h). The blue and olive arrows indicate the propagation vectors. Some main Bragg peaks are indexed.](image-url)
Table I. Single crystal crystallographic data for EuAg$_4$As$_2$ at 100(2) and 300(2) K.

| Formula       | EuAg$_{3.9(2)}$As$_2$ | EuAg$_{3.9(3)}$As$_2$ |
|---------------|-----------------------|-----------------------|
| Temperature (K) | 100(2) K             | 300(2) K             |
| F.W. (g/mol);  | 720.34                | 721.41                |
| Space group    | R3m(No.166)           | R3m(No.166)           |
| a (Å)          | 4.514(1)              | 4.543(2)              |
| c (Å)          | 23.554(5)             | 23.704(10)            |
| V (Å$^3$)      | 415.7(2)              | 423.7(4)              |
| Extinction Coefficient | 0.00027(5) | 0.0011(1) |
| θ range (deg) | 2.594-36.974          | 2.578-36.978          |
| Rint          | 2447; 0.0623          | 2375; 0.0781          |
| No. parameters | 21                    | 21                    |
| R1; wR2 (all I) | 0.0290; 0.0353        | 0.0334; 0.0455        |
| Goodness of fit | 1.078                 | 1.051                 |
| Diffraction peak | 2.653; -2.046         | 2.661; -2.092         |

Table II. Atomic coordinates and equivalent isotropic displacement parameters of EuAg$_4$As$_2$ at 100(2) K and 300(2) K. $U_{eq}$ is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor (Å$^2$).

| Atom Wyckoff | Occ. | x     | y     | z     |
|--------------|------|-------|-------|-------|
| 100(2) K     |      |       |       |       |
| Eu           | 3a   | 1     | 0     | 0     |
| Ag1          | 6c   | 0.63(3)| 0     | 0     | 0.1466(2) |
| Ag2          | 18h  | 0.10(1)| 0.743(5) | 0.257(5) | 0.1797(8) |
| Ag3          | 6c   | 1     | 0     | 0     | 0.43004(3) |
| As           | 6c   | 1     | 0     | 0     | 0.25880(4) |

| Atom Wyckoff | Occ. | x     | y     | z     |
|--------------|------|-------|-------|-------|
| 300(2) K     |      |       |       |       |
| Eu           | 3a   | 1     | 0     | 0     |
| Ag1          | 6c   | 0.65(4)| 0     | 0     | 0.1464(4) |
| Ag2          | 18h  | 0.10(1)| 0.74(1)| 0.26(1)| 0.180(2) |
| Ag3          | 6c   | 1     | 0     | 0     | 0.42970(4) |
| As           | 6c   | 1     | 0     | 0     | 0.25857(5) |

of three. This is confirmed based on the refinement of our single crystal neutron diffraction data. The discrepancy may come from the different synthetic processes used in making EuAg$_4$As$_2$.

B. Physical Properties

Figure 2 summarizes the temperature dependence of the resistivity, susceptibility and heat capacity of the EuAg$_4$As$_2$ single crystals. The resistivity, shown in Fig. 2(a), was measured with current applied along the $a$ axis and shows metallic behavior, with a resistivity drop near $T_1 \sim 120$ K and a sharp peak below 20 K. The left inset shows the zoom-in resistivity around 120 K, which has a slight hysteresis with $\Delta T \approx 1.1$ K. Combined with the single crystal X-ray diffraction data in Figure 1, this resistivity drop is associated with the structural distortion and suggests the transition temperature $T_1 \sim 120$ K. A closer examination of the resistivity data below 20 K is shown in the right inset of Fig. 2(a). Two peaks can be seen in the first derivative of resistivity (blue curve), one around 9 K and the other around 15 K. As will be discussed in more details later, the two peaks are closely associated with the onset of magnetic ordering, and the
sharp decrease in the resistivity can be attributed to the loss of spin scattering below the transition temperature. The two transitions below 20 K can also be observed in the magnetic susceptibility $M/H$ with $H//c$, as shown in Fig. 2(b). The zoom-in $M/H$ plot below 20 K is shown in the right inset of Fig. 2(b). Two slope changes can be clearly seen at 9 K and 15 K, which agree well with the magnetic phase transition temperatures determined from the first derivative of resistivity shown in the right inset of Fig. 2(a). A Curie-Weiss (CW) fit is made using $H/M = C/(T + \Theta)$, where $\Theta$ is the Weiss temperature and $C$ is the Curie constant, being related to the effective moment $\mu_{eff}$ and $\Theta_{eff} = \sqrt{8C}$. The fits of the $H/M$ data with $H//ab$ using the data from 50 K to 300 K and $H//c$ with the data from 50 K to 200 K are presented in the left inset of Fig. 2(b). The $\mu_{eff}$ is 7.7$\mu_B$/Eu and 7.6$\mu_B$/Eu for $H//c$ and $H//ab$, respectively, being slightly smaller than 7.94$\mu_B$/Eu, the theoretical value of Eu$^{2+}$. This may suggest that a small percentage of non-magnetic Eu$^{3+}$ atoms is present, consistent with the existence of Ag deficiency from the refinement of the diffraction data. The $\Theta_{ab} = -20$ K and $\Theta_{c} = -10$ K, suggesting the average $\Theta = -17$ K. This negative Weiss temperature suggests dominant ferromagnetic interaction. Considering that the envelope of the low temperature phase transition $M/H$ indicates antiferromagnetism, this may suggest a complex magnetic structure here. The absence of feature of the 120 K transition in the $M/H(T)$ again agrees that this transition has a non-magnetic origin. A sharp heat capacity anomaly is observed at around 120 K in Fig. 2(c), combined with the hysteresis shown in the left inset of Fig. 2(a), indicating the structural distortion is of the first-order type. The zoom-in plot of heat capacity below 20 K shows multiple anomalies with the largest entropy release at 15 K, suggesting complex low temperature magnetic transitions which will be discussed with more details in the section C. The entropy release is consistent with RLn8, the one for Eu$^{2+}$.

Figure 3. Black symbols: The intensity of the magnetic Bragg peaks (1,0,1)+$k_m$ and (1,0,4)+$k_m$, where $k_m$ is the magnetic prorogation vector (0,-0.1,0.12). Pink Curve: The temperature dependent $d\rho_{xx}/dT$. The dashed vertical lines mark the transition temperatures.

Figure 4. (a) The noncollinear magnetic structure of EuAg$_4$As$_2$ in one unit cell at 4 K. Blue sphere: Eu. Grey sphere: As. Orange sphere: Fully occupied Ag. Light orange sphere: Partially occupied Ag. (b),(c): Periodicity beyond one unit cell along the $c$ and and $b$ direction, respectively. Only Eu$^{2+}$ ions are shown.

C. Incommensurate noncollinear magnetism

To reveal the nature of the low temperature phase transitions, single crystal neutron diffraction data on EuAg$_4$As$_2$ were collected using HB-3A single crystal neutron diffractometer at HFIR at ORNL. Magnetic peaks are observed. The magnetic propagation vector is determined to be incommensurate with $k_m = (0,-0.1,0.12)$ and used for collecting magnetic reflections and solving the magnetic structure. Figure 3 shows the temperature dependent (1,0,1)+$k_m$ and (1,0,4)+$k_m$ magnetic peak intensity. As a comparison, temperature dependent $d\rho_{xx}/dT$ is also plotted. Upon cooling, both magnetic order parameter (OP) curves show a sudden increase near 9 K, consistent with the $d\rho_{xx}/dT$ data shown in pink in Figure 3, which suggests a long-range antiferromagnetic ordering at $T_N = 9$ K. By fitting the magnetic intensity below $T_N$ with $(T - T_N)\beta$, we determined the critical exponent to be $\beta = 0.34$, close to the expected value of 0.367 from the Heisenberg model. Although slight piece-to-piece variations are present, besides the rapid intensity increase in the OP plot at 9 K, one subtle slope change of the (1,0,1)+$k_m$ OP curve is discernible at 15 K, being in good agreement with those seen in the $d\rho_{xx}/dT$.

The diffraction lattice of the magnetic phase collected at 4 K is well-defined. Unlike in single crystal X-ray diffraction, we did not observe the superlattice peaks in the single crystal neutron diffraction. This may be due to the fact that the superlattice peaks are too weak for the neutron diffraction to detect. In the magnetic structure refinement carried out using the RI symmetry, only the Eu$^{2+}$ magnetic ions were considered. The refined magnetic structure is shown in Figure 4. It is a complex noncollinear magnetic structure. At 4 K, the spin of Eu$^{2+}$
lies on the $ab$ plane and the moment of each Eu$^{2+}$ site was found to be 3.7 $\mu_B$, as shown in Fig. 4(a). The small values of the propagation vector $k_m = (0, -0.1, 0.12)$ along both $a$ and $c$ directions indicate long periodicity along these two directions. Fig. 4(b) shows the demonstration of the magnetic structure in the $ac$ plane with only Eu$^{2+}$ ions being present. The Eu$^{2+}$ spin rotates around the $c$ axis, suggesting a helical arrangement. Fig. 4(c) shows a cartoon of the magnetic structure in the $ab$ plane. The Eu spin rotates along the $b$ axis, suggesting a cycloidal arrangement. Therefore, the periodicity resembles that of a typical helical structure with a period of about 8$c$ along the $c$ axis, which is nearly 20 nm, and a cycloidal structure with a period of 10$b$ along the $b$ axis.

Since Eu$^{2+}$ ions form hexagonal sublattice, frustration may play a role in the incommensurate periodicity. However, in EuAg$_4$As$_2$, the frustration parameter which is measured by $|\Theta|/T_N$ is around 1.8, suggesting the magnetic frustration is not significant here. Since Eu$^{2+}$ has half-filled $4f$ orbitals, the lack of orbital moment leads to very weak CEF anisotropy. Furthermore, the dipole-dipole interaction is usually one or two orders smaller than the RKKY interaction. Therefore, the RKKY interaction dominates here, which readily explains the existence of the incommensurate magnetic periodicity. Incommensurate noncollinear magnetism has been found in Eu-containing materials. For example, the tetragonal EuCo$_2$As$_2$ and EuCo$_2$P$_2$ adopt incommensurate magnetic structure in the $ab$ plane with a helical axis along the $c$ direction. Similar AFM structure was also observed in GdSi, GdCo$_2$Ge$_2$ and GdNi$_2$Ge$_2$. Where Gd$^{3+}$ ions share a similar electronic state as Eu$^{2+}$.

The evolution of magnetism can be visualized in detail by examining the diffraction image in the reciprocal space. The overall intensity of the scan is integrated within each solid angle and projected on a sphere centered at (2,0,1). Figures 5(a) and (b) show the image of the diffraction sphere sliced in the reciprocal $ab$ plane with $\Delta k_z = 0.0026$ Å$^{-1}$ and -0.0026 Å$^{-1}$, respectively. The coordinates are relative to (2,0,1). At 4 K, as shown in Figs. 5(a) and (b), in total six ellipsoid-like magnetic Bragg peaks are observed around (2,0,1). The six peaks are located $|k_m|$ away from the (2,0,1) and can be related by symmetry operations in the point group of $D_{3d}$, indicating the existence of long-range antiferromagnetic ordering. Fig. 5(c) shows the mapping of the diffraction sphere with the latitude (azimuthal angle) $\theta$ and longitude (polar angle) $\phi$. The three peaks in Figs. 5(a) and (b) correspond to the bottom and top three peaks in Fig. 5(e), respectively. The slight asymmetries of the peak shapes and intensities may be due to the different extent of absorption along different directions.

Figures 5(c), (d) and (f) contain the same slices and angular projections of the diffraction sphere at 10.3 K as Figs. 5(a), (b) and (e) do. Diffraction intensities in Figs. 5(c) and (d) can be observed at approximately the same locations (thus the same propagation vector) as the six peaks in Figs. 5(a) and (c), but they are much weaker and diffusive. This indicates that although the long-range antiferromagnetic order is destroyed above 9 K, antiferromagnetic correlations persist up to higher temperature. As shown in Fig. 5(f), upon warming, six distinct ellipsoids in Fig. 5(e) evolve into two U-shaped bands, suggesting the lowering of magnetic anisotropy, where the symmetry of the magnetic Bragg peaks is reduced to $C_i$. A similar phenomenon of reduced anisotropy in the magnetic correlations has also been observed in MnSi. Upon warming, the magnetic reflections in MnSi evolve from several distinct peaks to an isotropic spherical shell. That is, the helimagnetic fluctuations persist above $T_N$ but they become much more isotropic. Therefore, EuAg$_4$As$_2$ antiferromagnetically orders below 9 K and shows short-range magnetic fluctuation between 9 K to 15 K with reduced magnetic anisotropy.
IV. CONCLUSION

In conclusion, EuAg$_4$As$_2$ undergoes a first-order structural distortion at around 120 K, where superlattice peaks are observed with two independent propagation vectors of $(0.25,0,0.5)$ and $(0.0,25,1)$. It shows short-range antiferromagnetic ordering with reduced magnetic anisotropy between 15 K and 9 K. Below 9 K, EuAg$_4$As$_2$ enters into a long-range incommensurate antiferromagnetic state with a propagation vector of $(0.1,0.1,0.12)$, where the Eu$^{2+}$ spins are helical along the c axis and cycloidal along the b axis with a moment of 3.7 $\mu_B$/Eu$^{2+}$.

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[34] M. Janoschek, M. Garst, A. Bauer, P. Krautscheid, R. Georgii, P. Böni, and C. Pfleiderer, Phys. Rev. B 87, 134407 (2013)

[35] C. Pappas, L. J. Bannenberg, E. Lelièvre-Berna, F. Qian, C. D. Dewhurst, R. M. Dalgliesh, D. L. Schlagel, T. A. Lograsso, and P. Falus, Phys. Rev. Lett. 119, 047203 (2017)