Anisotropic magnetotransport properties coupled with spiral spin modulation in a triangular-lattice magnet EuZnGe

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We investigate the thermodynamic, magnetic, and electrical transport properties of a triangular-lattice antiferromagnet EuZnGe using single crystals grown from Eu-Zn flux in sealed tantalum tubes. Magnetic properties are found to be isotropic in the paramagnetic state while we observe an enhancement of in-plane magnetic susceptibility at the temperature near \( T^* = 11.3 \) K, suggesting an easy-plane anisotropy at low temperatures. Magnetic transition temperature is lower than \( T^* \) as specific heat shows a peak at \( T_N = 7.6 \) K. We reveal the magnetic modulation along the \( c \) axis by resonant x-ray scattering at Eu \( L_2 \) edge, which suggests competing magnetic interaction among Eu triangular-lattice layers. We observe a double-peak structure in the intensity profile along (0, 0, \( L \)) below \( T_N \), which is mainly composed of a dominant helical modulation with \( q \sim (0, 0, 0.4) \) coexisting with a secondary contribution from \( q \sim (0, 0, 0.5) \). We reproduce the intensity profile with a random mixture of five- and four-sublattice helices with spin rotation skipping due to hexagonal in-plane anisotropy. The metallic conductivity is highly anisotropic with the ratio \( \rho_{xx}/\rho_{zz} \) exceeding 10 over the entire temperature range and additionally exhibits a sharp enhancement of \( \rho_{xx} \) at \( T_N \) giving rise to \( \rho_{xx}/\rho_{zz} \sim 50 \), suggesting a coupling between out-of-plane electron conduction and the spiral magnetic modulations. In-plane magnetic field induces a spin-flop like transition, where the \( q = 0.4 \) peak disappears and an incommensurate peak of approximately \( q_{CM} \sim 0.47 \) emerges, while the \( q = 0.5 \) modulation retains a finite intensity. This transition correlates with non-monotonic magnetoresistance and Hall resistivity, suggesting a significant interplay between electrons and spin structures through Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.

I. INTRODUCTION

Interplay between conduction electrons and underlying magnetic textures is one of the central interests in modern condensed matter physics. Discoveries of new quantum materials showing novel magnetotransport responses are essential to facilitate future application to spintronic devices. Recent advances of this research field are, for example, discoveries of quantum anomalous Hall effect in magnetic topological insulators, spontaneous anomalous Hall effect and Nernst effect in magnetic Weyl metal, and topological Hall effect (THE) associated with non-coplanar spin textures such as skyrminon lattice states.

Europium-based intermetallics are a group of materials having been investigated for long time and attracting recent interests as a source of various topological spin textures and exotic transport phenomena including anomalous Hall effect associated with topological band structures, giant magnetoresistance, coexistence of superconductivity and helimagnetism, three-dimensional quantum Hall effect, and valence transitions.

EuZnGe, the material of interest in this study, crystallizes in the centrosymmetric ZrBeSi type (\( P6_3/mmc \)) structure (Fig. 1(a)), which belongs to one of the \( RMX \) phases (\( R \): alkali earths/eurpium/ytterbium, \( M \): Cu, Au, Zn, Cd, \( X \): anionic main group elements) with AlB\(_2\) as the aristotype structure. Every other layer of the Zn-Ge honeycomb network is rotated by 60° with respect to each other, and they are stacked along the \( c \) axis sandwiching triangular lattices of Eu. Formal valence of each atom is Eu\(^{2+}\)/Zn\(^{2+}\)/Ge\(^{4-}\), which can be described as an electron-precise Zintl phase. Finite density of state at \( E_F \) is ascribed to the overlap between the conduction and valence bands, resulting in a metallic behavior. Previous studies of magnetism were performed with polycrystalline samples, reporting divalent Eu\(^{2+}\) nature with localized magnetic moments. Two antiferromagnetic-like transitions at 12.2 K and 9.5 K were observed though the dominant magnetic interaction was suggested to be ferromagnetic by the Weiss temperature \( \Theta_W = 11 \) K. Together with a signature of metamagnetic transition at 0.6 T before the saturation, magnetic properties suggest the presence of inherent magnetic frustration in Eu-sublattice in EuZnGe.

In this work, we report the nature of magnetism and electric properties of single crystals of EuZnGe. We combine transport and thermodynamic measurements with resonant x-ray scattering (RXS) to reveal a strong correlation between magnetotransport properties and the spin structures with a double-modulation peak along the \( c \) axis. We simulate the spin structure to reproduce the magnetic diffraction profile to propose a helical configuration that is modified by the spin-skipping due to hexagonal in-plane anisotropy.
II. EXPERIMENTAL METHODS

Single crystals of EuZnGe were grown from Eu-Zn flux in a sealed tantalum crucible. The method proposed in Ref. [29] was applied to avoid the reaction of Eu with quartz tube and prevent the loss of volatile Eu-Zn flux. As shown in the ternary phase diagram (Fig. 1(b)), synthesis of the EuZnGe phase in Zn-rich flux (m.p.: 420°C) is inhibited by the tetragonal phase EuZn$_2$Ge$_2$ [30] (green line). We focused on the Eu-Zn flux as the binary phase diagram (Fig. 1(c)) exhibits low-temperature liquidus line below 800°C. The europium ingots (99.9%), zinc wires (99.99%), and germanium pieces (99.999%) were put into a tantalum tube with the molar ratio Eu:Zn:Ge = 2:2:1 (the composition for the flux 3, red cross in Fig. 1(b)), which was sealed by an arc furnace under Ar atmosphere. Eu ingots were handled in an Ar-filled glovebox. The tantalum tube was put into an evacuated quartz tube and heated to 950°C. After being held for 24 hours, it was then cooled to 750°C in 200 hours. After annealing for 4 days at this temperature, the excess flux was removed by centrifugation.

The atomic composition and the phase were checked by energy dispersive x-ray spectroscopy (EDS, JEOL model JSM-6010LA) and a Rigaku SmartLab diffractometer using Cu K$_\alpha$ radiation, respectively. The crystal structure was investigated by a single-crystal x-ray diffractometer at the synchrotron facility SPring-8 (see Appendix). A He-gas-blowing device was employed to cool the crystal to 50 K.

Magnetization was measured with a superconducting quantum interference device magnetometer (Quantum Design MPMS-XL). Electrical transport measurements were performed by a conventional five probe method at typical frequency near 17 Hz. The transport properties at low temperatures in a magnetic field was measured using a commercial superconducting magnet and cryostat. The obtained longitudinal and transverse resistivities were symmetrized and antisymmetrized, respectively by field to correct contact misalignment. Thermal expansion and the magnetostriction was measured by the fiber-Bragg-grating (FBG) technique using an optical sensing instrument (Hyperion si155, LUNA) in an Oxford Spectromag as described in Ref. [32]. Optical fibers were glued using epoxy (Stycast1266) on the (001) and (100) surfaces of as-grown crystals to measure the elongation/compression along the a and c axes, respectively.

Single-crystal RXS measurement was carried out at BL-3A, Photon Factory, KEK, Japan, by using the horizontally polarized x-ray in resonance with Eu L$_2$ absorption edge (7.615 keV). We attached a crystal with the as-grown (001) plane on an aluminum plate with GE varnish, and loaded it into a vertical-field superconducting magnet with the b axis parallel to the magnetic field direction. The scattering plane was set to be (H, 0, L). Unless stated, scattered x-rays were detected without polarization analysis.

III. RESULTS

We obtained single crystals of thin hexagonal-prism shape with the typical dimension 1×1×0.5 mm$^3$, as shown in Fig. 1(d). The atomic composition was checked to be Eu:Zn:Ge = 0.35:0.33:0.32, which fairly agrees with the nominal chemical formula. No trace of tantalum was detected in the crystals. Powder x-ray diffraction (XRD) patterns confirmed the single phase of EuZnGe. In the single-crystal XRD with synchrotron radiation, we observed odd $l = 2n + 1$ reflections as shown in Fig. 1(e), exemplifying a doubled-cell of the ZrBeSi-type structure along the c axis with respect to the AlB$_2$-type unit cell due to the Zn/Ge-site ordering as shown in Fig. 1(a) (see Appendix). We refined the crystal structure and discerned negligible site mixing for Zn/Ge atoms or substitution of Ge for Zn as reported in Ref. [33]. The
refined lattice constants at room temperature are \(a = 4.3700(5) \text{ Å}\) and \(c = 8.5994(5) \text{ Å}\), which is consistent with the previously reported values\(^{25}\) in polycrystalline samples. We also succeeded in synthesizing single crystals of \(\text{BaZnGe}\) with the same method. The lattice constants are \(a = 4.47 \text{ Å}\) and \(c = 9.62 \text{ Å}\), consistent with that reported in Ref. \(^{25}\). Single crystals of \(\text{EuZnGe}\) are stable in air while those of \(\text{BaZnGe}\) are oxidized within a few days. Prior to the growth with flux 3, we attempted different growth paths starting from flux 1 and 2 (brown crosses in Fig. 1(b)), which are on the line connecting \(\text{EuZnGe}\) and \(\text{Eu}_{0.73}\text{Zn}_{0.27}\), the lowest \(\text{Eu}-\text{Zn}\) eutectic point. We failed obtaining \(\text{EuZnGe}\) phase in these runs. \(\text{EuZn}\) or \(\text{EuGe}\) appeared instead as the dominant phases, potentially because of their compositional proximity and/or high melting point.

We summarize the temperature dependence of physical properties of single crystalline \(\text{EuZnGe}\) in Fig. 2. The magnetic transition at \(T_N = 7.6 \text{ K}\) can be detected as the specific heat peak at zero field (Fig. 2(a)). The high-temperature feature is dominated by phonons with no signature of structural phase transition as is similar with that of isostructural \(\text{BaZnGe}\). The absence of structural transition is also confirmed by single-crystal XRD and thermal expansion at zero field (Fig. 2(b)). The magnetic susceptibilities \((M/H)\) for \(H \parallel c\) and \(H \parallel a\) (Fig. 2(c)) exhibit Curie-Weiss feature characteristic for localized spins of \(\text{Eu}^{2+}\) in the paramagnetic state (Fig. 2(c)). The inverse susceptibility \((H/M)\) gives the estimation of effective moments as \(p_{\text{eff} \perp c} = 7.89 \mu_B\) for \(H \parallel c\) and \(p_{\text{eff} \parallel c} = 7.92 \mu_B\) for \(H \parallel a\), both of which are close to 7.94 \mu_B for free \(\text{Eu}^{2+}\) ions with \(S = \frac{7}{2}\). Weiss temperatures are \(\Theta_{\parallel c} = 16.2 \text{ K}\) and \(\Theta_{\perp c} = 15.7 \text{ K}\) for \(H \parallel c\) and \(H \perp c\), respectively, suggesting ferromagnetic interaction as the dominant coupling. At low temperatures, easy-plane type anisotropy starts to develop just above \(T_N\). Figure 2(d) compares resistivity for in-plane and out-of-plane current directions. The resistivity ratio \(\rho_{\perp}/\rho_{\parallel}\) (see inset) exceeds ten at all temperatures, consistent with the layered crystal structure with quasi-2D nature of Fermi surface. At \(T_N\), \(\rho_{\perp}/\rho_{\parallel}\) reaches near fifty, which we attribute to enhanced spin-electron scattering for out-of-plane transport.

Next we move on to the low-temperature behavior associated with the magnetic ordering. We summarize the physical properties near \(T_N\) in Fig. 3. A clear single peak in \(C_{\text{mag}}\) was observed at \(T_N\). The magnetic entropy \(S_{\text{mag}}\) is obtained by the integration of \(C_{\text{mag}}/T\) with respect to \(T\) (Fig. 2(a)), and approaches \(R \ln(2S + 1)\) with \(S = \frac{7}{2}\) at well above \(T_N\). This is consistent with the idea that the \(\text{Eu}^{2+}\) ions dominate the magnetism. The onset of the magnetic order at \(T_N\) coincides with a steep change in the lattice distortion for both along \(a\) and \(c\) axes (Fig. 3(b)), which is clear in the thermal expansion coefficient.
in $M/H$ for $H \perp c$ at $T \approx 10.5$ K and 9.0 K is similar to the previous result.\textsuperscript{23} By taking temperature derivative of $M$, we observe a peak at $T_N$ in $dM/dT$. For $H \parallel c$, the transition near $T_N$ manifests as a dip and a broad peak near $T^* \approx 11.3$ K implies another critical temperature while no obvious anomaly is observed in $C_p$ or $\Delta L/L$ (see dashed lines in Figs. 3(a)-(b)). We observed distinct responses between in-plane and out-of-plane resistivities to these transition-like temperatures (Fig. 3(d)). A sharp peak in $\rho_{zz}$ occurs only at $T_N$, which correlates with the onset of the out-of-plane modulation as observed in similar Eu-based helimagnets.\textsuperscript{23,33,36} $\rho_{xx}$, on the other hand, takes a broad peak at $T^*$ and exhibit a weak kink at $T_N$. These transport anomalies imply that $T^*$ corresponds to the steep growth of in-plane magnetic correlations, which may originate from low-dimensionality of Eu triangular-lattice layers.

In order to clarify the magnetic structure of EuZnGe, we performed RXS. We used the Eu $L_2$-edge resonance to observe the magnetic scattering due to Eu spin ordering. The intensity profile in the $(0, 0, L)$ scan is shown in Fig. 4(a). We observed magnetic Bragg scattering around $L = 7.5 - 7.6$, which disappears at $T = 15$ K (above $T_N$ and $T^*$). We found a double-peak feature with a dominant peak at $L = 7.6$ and a weak peak at $L = 7.5$, which correspond to magnetic modulations along the $c^*$ axis with $q = \frac{2}{5}$ and $q = \frac{1}{5}$, respectively. The energy profiles at $(0, 0, 7.6)$ and $(0, 0, 7.5)$ (see Fig. 4(b)) show a resonant peak near the Eu $L_2$ edge, $E \sim 7.615$ keV, clarifying the Eu origin of the magnetic Bragg scattering. We performed polarization analysis for the $q = \frac{2}{5}$ peak and confirmed the comparable intensities for $\pi'$ and $\sigma'$ channels, which is consistent with a spiral modulation.

We note that the double-peak feature as well as the diffusive intensity in intermediate $0.4 < q < 0.5$ cannot be reconciled with the proper-screw (helical) spin configuration with $q = 0.4$, which corresponds to undistorted interlayer-rotation of $72^\circ$ to exhibit a single peak at $L = 7.6$. Applying the broken-helix recently proposed in a related Eu-based intermetallics EuIn$_2$As$_2$,\textsuperscript{33} it is unlikely because in the present case the magnetic unit cell of $q = 0.5$ (four-sublattice) is incompatible in that of $q = 0.4$ (five-sublattice). To reproduce the intensity profile, we introduce two types of spin configuration as shown in Figs. 4(c)-(d), and consider the actual spin structure as a random mixture of the two. Figure 4(c) shows a five-sublattice spin configuration for $q = 0.4$ with a four-fold $60^\circ$ inter-layer spin rotation followed by a $120^\circ$ rotation ($60^\circ - 60^\circ - 60^\circ - 60^\circ - 120^\circ$). Figure 4(d) corresponds to a four-sublattice model with $60^\circ - 120^\circ - 60^\circ - 120^\circ$ spin rotations. Such a model with discretized spin rotations by $60^\circ$ or $120^\circ$ is hypothesized in the limit of strong hexagonal in-plane anisotropy, which is consistent with the site symmetry of Eu ions. We construct a real-space spin configuration on a 1D-chain with $\sum n_i$ sites (see Fig. 4(e)), where $n_i$ is the number of sites in each local $i$-th section in which the spins modulate in either of the above two models. We randomly distribute the config-

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\alpha (= d(\Delta L/L)/dT)\] The profiles of $C_{mag}$ and $\alpha$ reasonably agree with each other for the second order phase transition, indicating that the spin-lattice coupling does not appear to significantly facilitate the magnetic transition at $T_N$.\textsuperscript{33}

We note that in the previous polycrystalline study,\textsuperscript{23} the magnetic susceptibility suggests successsive magnetic transitions at $12.2$ K and $9.5$ K. We also observed anomalous features in $M$-$T$ curves under the application of $\mu_0 H = 5$ mT, as shown in Fig. 3(c). Double-peak feature

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f(0,0,L)\] scans near $L = 6$ at various temperatures in zero field. (b) The integrated intensity of the main magnetic peaks at $\alpha \approx 0.4$ (red, $I_{4\times4}$), $\alpha \approx 0.5$ (blue, $I_{4\times5}$), and remnant component (cyan, $I_{ICM}$) in the $L$-scan for (g) (see the inset).

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\rho_{xx}\] on the other hand, takes a broad peak at $T^*$ and exhibit a weak kink at $T_N$. These transport anomalies imply that $T^*$ corresponds to the steep growth of in-plane magnetic correlations, which may originate from low-dimensionality of Eu triangular-lattice layers.

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utation for \( q = 0.4 \) or \( q = 0.5 \) onto the \( i \)-th section by a ratio of 7:3, and determined the number \( n_i \) by a random variable among \( 0 \sim 50 \). Figure 4(f) compares the square of the fast Fourier transformation (FFT) of the spin configuration and the observed magnetic scattering intensity, where we obtain a reasonable agreement. In particular, the present model reproduces the intensity in the intermediate \( q \) region, which cannot be reconciled with a simple multi-domain model for \( q = 0.4 \) and 0.5.

Figure 4(g) shows the intensity profile in the \((0, 0, L)\) scan near \( L = 6 \) at selected temperatures. The intensity for \( q(=L-6)=0.5 \) \((I_{0.5})\) together with the intermediate diffuse intensity \((I_{\text{ICM}})\) disappear above \( T = 8 \) K, while that of \( q \sim 0.4 \) (\( I_{0.4} \)) persists with the shift to \( q = 0.38 \). We propose a realization of incommensurate smooth helical structure (namely the proper-screw) near \( T_N \), likely due to thermal fluctuations. As shown in Fig. 4(h), the double-peak structure disappears above \( T_N \), which is correlated with the sharp peak in \( \rho_{zz} \) (Fig. 3(d)).

Responses in a magnetic field clarify the coupling between magnetism and the underlying electric structure. We measure magnetization for both \( H \parallel c \) and \( H \parallel a \) (Fig. 5(a)), and observe the saturation to near \( 7 \, \mu_B \) for \( H > 4 \) T, consistent with the divalent nature of Eu. We note that the metamagnetic transition at \( \sim 0.6 \) T is reproduced only for the \( H \parallel c \). It apparently corresponds to the transition from spiral to fan or transverse conical spin structure, as predicted in the magnetization process of helimagnet.\(^{32}\) The resistivity shows distinct responses with respect to the direction of the electric currents (Fig. 5(b)). \( \rho_{zz} \) shows a sharp peak at the critical field, as is commonly observed in metamagnetic transitions.\(^{33,39}\) In the metamagnetic phase (SF phase), \( \rho_{zz} \) shows a large negative magnetoresistance, implying the suppression of the out-of-plane modulation. In contrast to this, \( \rho_{xx} \) shows a dip, which may be attributed to enhanced conduction at domain walls between regions with different \( q \). We also observe magnetostriiction associated with the metamagnetic transition (Fig. 5(c)). In contrast to \( \Delta L_a/L_a, \Delta L_c/L_c \) is nonmonotonic at the phase boundary, suggesting the coupling between spin configuration and inter-layer distance of triangular-lattices. We place the anomalies observed in various physical properties measurements for \( H \parallel c \) in the \( H-T \) phase diagram (Fig. 5(d)). The peaks of \( M-T \) curve for \( H \parallel c \) (green squares) slightly deviate from the transition temperatures estimated for \( M-T \) in \( H \parallel c \), and \( dM/dT, C_p, \rho_{xx}, \) and \( \rho_{zz} \) in zero field.

The Hall resistivity also exhibits an intriguing field evolution with \( H \parallel b^* \) (Fig. 5(e)). At \( T = 1.8 \) K, \( \rho_{xx} \) shows...
a valley-like feature selectively in the SF phase compared with a monotonic negative slope at $T = 12$ K, suggesting the dominant electron-type carrier transport at low temperatures. It is reminiscent of the THE due to the emergence of noncoplanar spin configuration as proposed in the distorted-spiral compound YMn$_5$Sn$_6$. Nevertheless in the present case, it is difficult to disentangle possible topological Hall response from field-modulation of the scattering time evidenced in $\rho_{xx}$ (Fig. 5(b)) as the Hall signals across the metamagnetic transition in intermetallics with high-mobility carriers closely resemble that of $\rho_{xx}$ through the multi-carrier transport. In Fig. 5(c), $\rho_{xx}$ shows a sign change above 100 K, clearly indicating the multi-carrier nature.

To gain the insight on the field-induced SF phase, we measured the RXS profile under different magnetic fields. Figure 6(a) shows that entering the SF phase at 0.8 T (see the peak in dM/dH in Fig. 6(b) defining the phase boundary) induces an enhancement of the peak at $q = 0.5$ and in contrast an abrupt shift of the modulation at $q = 0.4$ to $q_{ICM} \sim 0.47$. Interestingly, the double-peak structure with $q = 0.5$ and $q_{ICM}$ survives up to $\mu_0H = 1.8$ T and disappears in the FM phase at $\mu_0H = 3$ T. Through the removal of the applied $H$, the double-peak structure recovers from the SF phase (0.8 T), and eventually settles near identical profile (but weaker intensity at $q = 0.4$) in the zero field. The hysteretic behaviors of the $q$ position and the intensity of the magnetic scatterings are summarized in Figs. 6(c)-(d). The step wise shift from $q = 0.4$ to $q_{ICM}$ (Fig. 6(c)) coincides with the increase of the integrated intensity for $q = 0.5$, $l_{0.5}$ (Fig. 6(d)). The double $q$-peak structure in the SF phase excludes the simple fan or transverse conical spin configuration (described by a single-$q$) with no scalar spin chirality. Further study is necessary to reveal possible noncoplanar spin configuration in the SF phase to understand the THE-like response in $\rho_{xx}$ (Fig. 5(e)).

IV. CONCLUSION

In conclusion, we succeeded in growing single crystals of stoichiometric magnetic semimetal EuZnGe and found magnetotransport properties strongly coupled with underlying spin structure. Resonant x-ray scattering revealed the helical modulation along the $c$-axis, which is not a simple proper-screw, but randomized with spin-skipping in terms of the rotation in the hexagonal plane. We found that the in-plane magnetic field induces the spin-flop-like metamagnetic transition. The strong correlation with the longitudinal and transverse transport responses suggests that the present magnetic semimetal is potentially promising for emergent phenomena due to spin-conduction-electron coupling in spiral magnet.

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Appendix: Crystal structure of EuZnGe at 300 K

Due to the small difference in the number of electrons between Zn (30) and Ge (32) it is difficult to distinguish two atoms by in-house XRD experiment. Therefore, we performed synchrotron XRD experiments on BL02B1 at SPring-8 in Japan using a high-quality single crystal of EuZnGe. A two-dimensional detector CdTe PILATUS, which had a dynamic range of $\sim 10^7$, was used to record the diffraction pattern. Diffraction data collection for crystal structural analysis was performed using a RIGAKU RAXIS IV diffractometer. Intensities of equivalent reflections were averaged and the structural parameters were refined by using Jana2006.

The results of the structural analysis of EuZnGe at 300 K are summarized in Tables I and II. When the Zn and Ge sites are completely mixed, the length of the $c$-axis can be regarded as half, resulting in the absence of the $l = 2n + 1$ reflections. We, however, found $l = 2n + 1$ reflections (Fig. 1(e)). The degree of the site mixing at the Zn and Ge sites was further analyzed. Although the occupancy of each of the Zn and Ge sites was refined by restricting the total value to 1, no signs of the site mixing were found, where the $R$ factors were not improved and each occupancy of the Zn and Ge sites remained almost unchanged (see Tables II).
TABLE I. Structural parameters of EuZnGe at 300 K. The space group is $P6_3/mmc$ (No. 194), and $a = b = 4.3700(5)$ Å, $c = 8.5994(5)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$.

| Wyckoff | x    | y    | z    | $U_{11}(=U_{22})$ (Å$^2$) | $U_{33}$ (Å$^2$) | $U_{12}$ (Å$^2$) |
|---------|------|------|------|---------------------------|------------------|------------------|
| Eu      | 2a   | 0    | 0    | 0.00915(2)                | 0.00967(3)       | 0.004574(12)     |
| Zn      | 2d   | 2/3  | 1/3  | 1/4 | 0.00680(3)                | 0.01649(5)       | 0.002901(13)     |
| Ge      | 2c   | 1/3  | 2/3  | 1/4 | 0.00746(3)                | 0.01649(6)       | 0.003728(13)     |

TABLE II. Crystallographic data of EuZnGe

| Temperature (K) | 300 |
| Wavelength (Å)  | 0.310109 |
| Crystal dimension (µm$^3$) | 50×50×50 |
| Space group     | $P6_3/mmc$ |
| $a$ (Å)         | 4.3700(5) |
| $c$ (Å)         | 8.5994(5) |
| $Z$              | 2 |
| $F(000)$        | 250 |
| (sin $\theta$/λ)$_{max}$ (Å$^{-1}$) | 1.79 |
| $N_{Total}$     | 13080 |
| $N_{Unique}$    | 1281 |
| Average redundancy | 10.211 |
| Completeness (%) | 99.96 |

$R$ factors when assuming the perfect ordering of Zn and Ge

| $N_{parameters}$ | 8 |
| $R_1$ ($I > 3\sigma$) [number of reflections] | 1.23% [868] |
| $R_1$ (all) [number of reflections] | 2.51% [1281] |
| $wR_2$ (all) [number of reflections] | 2.95% [1281] |
| GOF (all) [number of reflections] | 1.85% [1281] |

$R$ factors when allowing the site mixing of Zn and Ge

| $N_{parameters}$ | 10 |
| $R_1$ ($I > 3\sigma$) [number of reflections] | 1.23% [868] |
| $R_1$ (all) [number of reflections] | 2.52% [1281] |
| $wR_2$ (all) [number of reflections] | 3.77% [1281] |
| GOF (all) [number of reflections] | 1.84% [1281] |

Occupancy of Zn/Ge at (2/3, 1/3, 1/4) 1.034(8) / −0.034(8)

Occupancy of Ge/Zn at (1/3, 2/3, 1/4) 0.994(7) / 0.006(7)
1. C.-Z. Chang, J. Zhang, X. Feng, J. Shen, Z. Zhang, M. Guo, K. Li, Y. Ou, P. Wei, L.-L. Wang, et al., “Experimental observation of the quantum anomalous Hall effect in a magnetic topological insulator,” Science 340, 167 (2013).

2. Y. Deng, Y. Yu, M. Z. Shi, Z. Guo, Z. Xu, J. Wang, X. H. Chen, and Y. Zhang, “Quantum anomalous Hall effect in intrinsic magnetic topological insulator MnBi2Te4,” Science 367, 895 (2020).

3. S. Nakatsuji, N. Kiyohara, and T. Higo, “Large anomalous Hall effect in a non-collinear antiferromagnet at room temperature,” Nature 527, 212 (2015).

4. E. Liu, Y. Sun, N. Kumar, L. Muechler, A. Sun, L. Jiao, S.-Y. Yang, D. Liu, A. Liang, Q. Xu, et al., “Giant anomalous Hall effect in a ferromagnetic Kagome-lattice semimetal,” Nat. Phys. 14, 1125 (2018).

5. A. Neubauer, C. Pleiferder, B. Binz, A. Rosch, R. Ritz, P. G. Niklowitz, and P. Böni, “Topological Hall effect in the a phase of MnSi,” Phys. Rev. Lett. 102, 186602 (2009).

6. S. Mühlbauer, B. Binz, F. Jonietz, C. Pleiferder, A. Rosch, A. Neubauer, R. Georgii, and P. Böni, “Skyrmion lattice in a chiral magnet,” Science 323, 915 (2009).

7. T. Kurumaji, T. Nakajima, M. Hirschberger, A. Kikkawa, Y. Yamasaki, H. Sagayama, H. Nakao, Y. Taguchi, T.-h. Arima, and Y. Tokura, “Skyrmion lattice with a giant topological Hall effect in a frustrated triangular-lattice magnet,” Science 365, 914 (2019).

8. M. Kakihana, D. Aoki, A. Nakamura, F. Honda, M. Nakashima, Y. Amako, S. Nakamura, T. Sakakibara, M. Hedo, T. Nakama, et al., “Giant Hall resistivity and magnetoresistance in cubic chiral antiferromagnet EuPtSi,” J. Phys. Soc. Jpn. 87, 023701 (2018).

9. T. Shang, Y. Xu, D. J. Gawryluk, J. Z. Ma, T. Shiroka, M. Shi, and E. Pomjakushina, “Anomalous Hall resistivity and possible topological Hall effect in the EuAl4 antiferromagnet,” Phys. Rev. B 103, L020405 (2021).

10. R. Takagi, N. Matsuyama, V. Ukleev, L. Yu, J. S. White, S. Francoual, J. R. L. Mardegan, S. Hayami, H. Saito, K. Kaneko, et al., “Square and rhombic lattices of magnetic skyrmions in a centrosymmetric binary compound,” Nat. Commun. 13, 1 (2022).

11. J. M. Moya, S. Lee, E. M. Clements, K. Allen, S. Chi, S. Sun, Q. Li, Y. Y. Peng, A. Husain, M. Mitran, et al., “Incommensurate magnetic orders and possible field-induced skyrmions in the square-net centrosymmetric EuGa2Al2 system,” Phys. Rev. Mater. 6, 074201 (2022).

12. J.-Z. Ma, S. M. Nie, C. J. Yi, J. Jandke, T. Shang, M.-Y. Yao, M. Naamneh, L. Q. Yan, Y. Sun, A. Chikina, et al., “Spin fluctuation induced Weyl semimetal state in the paramagnetic phase of EuCd2As2,” Sci. Adv. 5, eaaw4718 (2019).

13. Y. Xu, Z. Song, Z. Wang, H. Weng, and X. Dai, “Higher-order topology of the axion insulator EuIn2As2,” Phys. Rev. Lett. 122, 256402 (2019).

14. J.-R. Soh, F. De Juan, M. G. Vergniory, N. B. M. Schröter, M. C. Rahn, D. Y. Yan, J. Jiang, M. Bristow, P. Reiss, J. N. Blandy, et al., “Ideal Weyl semimetal induced by magnetic exchange,” Phys. Rev. B 100, 201102 (2019).

15. X. Gui, I. Pleitikosie, H. Cao, H.-J. Tien, X. Xu, R. Zhong, G. Wang, T.-R. Chang, S. Jia, T. Valla, et al., “A new magnetic topological quantum material candidate by design,” ACS Cent. Sci. 5, 900 (2019).

16. Y. Xu, L. Das, J. Z. Ma, C. J. Yi, S. M. Nie, Y. G. Shi, A. Tiwari, S. S. Tsirkin, T. Neupert, M. Medarde, et al., “Unconventional transverse transport above and below the magnetic transition temperature in Weyl semimetal EuCd2As2,” Phys. Rev. Lett. 126, 076602 (2021).

17. G. M. Pierantozzi, A. De Vita, C. Bigi, X. Gui, H.-J. Tien, D. Mondal, F. Mazzola, J. Fuji, I. Vobornik, G. Vinal, et al., “Evidence of magnetism-induced topological protection in the axion insulator candidate EuSn2P2,” PNAS 119, e2116575119 (2022).

18. H. W. Meul, M. Decroux, R. Odermatt, R. Noer, and Ø. Fischer, “Transport properties and the nature of the low-temperature phase of EuMo6S8,” Phys. Rev. B 26, 6431 (1982).

19. S. Süßow, I. Prasad, M. C. Aronson, J. L. Sarrao, Z. Fisk, D. Hristova, A. H. Lacerda, M. F. Hundley, A. Vigliante, and D. Gibbs, “Structure and magnetic order of EuB6,” Phys. Rev. B 57, 5860 (1998).

20. J. Yin, C. Wu, L. Li, J. Yu, H. Sun, B. Shen, B. A. Frandsen, D.-X. Yao, and Y. Wang, “Large negative magnetoresistance in the antiferromagnetic rare-earth dichalcogenide EuTe2,” Phys. Rev. Mater. 4, 013405 (2020).

21. P. Rosa, Y. Xu, M. Rahn, J. Souza, S. Kushwaha, L. Veiga, A. Bombardi, S. Thomas, M. Janoschek, E. Bauer, et al., “Colossal magnetoresistance in a nonsymmorphic antiferromagnetic insulator,” npj Quantum Mater. 5, 1 (2020).

22. K. Iida, Y. Nagai, S. Ishida, M. Ishikado, N. Murai, A. D. Christianson, H. Yoshida, Y. Inamura, H. Nakamura, A. Nakao, et al., “Coexisting spin resonance and long-range magnetic order of eu in EuRbFe4As4,” Phys. Rev. B 100, 014506 (2019).

23. H. Masuda, H. Salai, M. Tokunaga, Y. Yamasaki, A. Miyake, J. Shioigai, S. Nakamura, S. Awaji, A. Tsukazaki, H. Nakao, et al., “Quantum Hall effect in a bulk antiferromagnet EuMnBi2 with magnetically confined two-dimensional Dirac fermions,” Sci. Adv. 2, e1501117 (2016).

24. Y. Ōnuki, M. Hedo, and F. Honda, “Unique electronic states of Eu-based compounds,” J. Phys. Soc. Jpn. 89, 102001 (2020).

25. F. Merlo, M. Pani, and M. L. Fornasini, “RMX compounds formed by alkaline earths, europium and ytterbium II: Ternary phases with M≡ Zn, Cd and X≡ Si, Ge, Sn, Pb,” J. Less-Common Met 171, 329 (1991).

26. R. Pöttgen and D. Johrendt, “Equiatomic intermetallic europium compounds: syntheses, crystal chemistry, chemical bonding, and physical properties,” Chem. Mater. 12, 875 (2000).

27. Samir F Matar and Rainer Pöttgen, “Coloring in the ZrBeSi-type structure,” Z. Naturforsch. B 74, 307 (2019).

28. R. Pöttgen, “The crystal structure of EuZnGe and its relation with EuGe2,” Z. Kristallogr. Cryst. Mater. 210, 924 (1995).

29. A. Jesche and P. C. Canfield, “Single crystal growth from light, volatile and reactive materials using lithium and calcium flux,” Phil. Mag. 94, 2372 (2014).

30. A. Grytsiv, D. Kaczorowski, A. Leithe-Jasper, P. Rogl, C. Godart, M. Potel, and H. Noël, “EuZn4Si2 and EuZn4Ge2 grown from Zn or Ga (In)/Zn flux,” J. Solid State Chem. 163, 37 (2002).
31 H. Okamoto, *Phase diagrams for binary alloys*, Vol. 44 (ASM international Materials Park, OH, 2000).
32 M. Gen, A. Miyake, H. Yagiuchi, Y. Watanabe, A. Ikeda, Y. H. Matsuda, M. Tokunaga, T. Arima, and Y. Tokunaga, “Enhancement of giant magnetoelectric effect in Ni-doped CaBaCoO$_4$,” Phys. Rev. B 105, 214412 (2022).
33 T.-S. You, S. Lidin, O. Gourdon, Y. Wu, and G. J. Miller, “To what extent does the Zintl-Klemm formalism work? the Eu(Zn$_{1-x}$Ge$_x$)$_2$ series,” Inorg. Chem. 48, 6380 (2009).
34 L. R. Testardi, “Elastic modulus, thermal expansion, and specific heat at a phase transition,” Phys. Rev. B 12, 3849 (1975).
35 S. X. M. Riberolles, T. V. Trevisan, B. Kuthanazhi, T. W. Heitmann, F. Ye, D. C. Johnston, S. L. Bud’ko, D. H. Ryan, P. C. Canfield, A. Kreysig, *et al.*, “Magnetic crystalline-symmetry-protected axion electrodynamics and field-tunable unpinned Dirac cones in EuIn$_2$As$_2$,” Nat. Commun. 12, 1 (2021).
36 W. Bauhofer, E. Gmelin, M. Mollendorf, R. Nesper, and H. G. Von Schnering, “Electrical and magnetic properties of single crystalline EuAs$_3$, β-EuP$_3$ and their mixed crystals,” J. Phys. C: Solid State Phys. 18, 3017 (1985).
37 T. Nagamiya, “Helical spin ordering—1 theory of helical spin configurations,” in *Solid State Physics*, Vol. 20 (Elsevier, 1968) p. 305.
38 E. D. Mun, S. L. Bud’ko, H. Ko, G. J. Miller, and P. C. Canfield, “Physical properties and anisotropies of the RNiGe$_3$ series (R= Y, Ce-Nd, Sm, Gd-Lu),” J. Magn. Magn. Mater. 322, 3527 (2010).
39 N. V. Baranov, P. E. Markin, A. I. Kozlov, and E. V. Sinitsyn, “Effect of magnetic interphase boundaries on the electrical resistivity in metallic metamagnets,” J. Alloys Compd. 200, 43 (1993).
40 N. J. Ghimire, R. L. Dally, L. Poudel, D. C. Jones, D. Michel, N. T. Magar, M. Bluenel, M. A. McGuire, J. S. Jiang, J. F. Mitchell, *et al.*, “Competing magnetic phases and fluctuation-driven scalar spin chirality in the Kagome metal YMn$_6$Sn$_6$,” Sci. Adv. 6, eabe2680 (2020).
41 Q. Wang, K. J. Neubauer, C. Duan, Q. Yin, S. Fujitsu, H. Hosono, F. Ye, R. Zhang, S. Chi, K. Krycka, *et al.*, “Field-induced topological Hall effect and double-fan spin structure with a $c$-axis component in the metallic Kagome antiferromagnetic compound YMn$_6$Sn$_6$,” Phys. Rev. B 103, 014416 (2021).
42 L. Ye, T. Suzuki, and J. G. Checkelsky, “Electronic transport on the Shastry-Sutherland lattice in Ising-type rare-earth tetraborides,” Phys. Rev. B 95, 174405 (2017).
43 T. Yokouchi, F. Kagawa, M. Hirschberger, Y. Otani, N. Nagaosa, and Y. Tokura, “Emergent electromagnetic induction in a helical-spin magnet,” Nature 586, 232 (2020).
44 N. Jiang, Y. Nii, H. Aisawa, E. Saitoh, and Y. Onose, “Electric current control of spin helicity in an itinerant helimagnet,” Nat. Commun. 11, 1 (2020).
45 K. Sugimoto, H. Ohsumi, S. Aoyagi, E. Nishibori, C. Moriyoshi, Y. Kuroiwa, H. Sawa, and M. Takata, “Extremely high resolution single crystal diffractometry for orbital resolution using high energy synchrotron radiation at SPring-8,” in *AIP Conf. Proc.*, Vol. 1234 (American Institute of Physics, 2010) p. 887.
46 V. Petříček, M. Dušek, and L. Palatinus, “Crystallographic computing system JANA2006: general features,” Z. Kristallogr. Cryst. Mater. 229, 345 (2014).