Canted antiferromagnetic order in EuZn$_2$As$_2$ single crystals

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Compounds containing Eu show a vast range of unique physical properties due to the interplay of electronic and magnetic properties, which can lead to a nontrivial electronic topology combined with magnetic order. We report on the growth of trigonal (P$\bar{3}$m1 space group) EuZn$_2$As$_2$ single crystals and on the studies of their structural, electronic and magnetic properties. A range of experimental techniques was applied including X-ray diffraction, electron microscopy, magnetic susceptibility, magnetization, heat capacity and Mössbauer spectroscopy in the study. We found that Eu has solely a 2+ valence state and its magnetic moments below $T_N = 19.2$ K form a canted antiferromagnetic structure, tilted from the basal plane.

Rare earth based compounds show multitude of interesting and unique magnetic and electronic properties. Materials containing Eu are not an exception with this regard with their properties being a result of interactions between the localized 4$f$ electrons and conduction electrons via the RKKY coupling$^{1,2}$. Eu is particularly interesting, since it appear in two valence states, which cause very different physical properties. In intermetallic compounds, the magnetic Eu$^{2+}$ configuration (with 4$f^7$, $L=0$, $S=J=7/2$) is more often observed than the non-magnetic Eu$^{3+}$ one (4$f^6$, $L=S=3$, $J=0$). In some materials an intermediate valence state is also possible, e.g. in EuZnSb$_2$ or EuNi$_2$P$_2$.$^3,4$ These two compounds are a good example of a wide range of different physical properties as the first one is an antiferromagnetic semimetal with Dirac states, and the second one shows a heavy fermion behavior and the Kondo effect. Combination of magnetic and electronic properties can lead to effects like colossal magnetoresistance$^5$, but the fact that many Eu compounds show nontrivial electronic topology, which is combined with magnetic order, is even more interesting. The examples of such materials are EuCd$_3$As$_3$.$^6,7$ and EuIn$_3$As$_3$,$^8$ which are a topological semimetal and an insulator, respectively. Both compounds have hexagonal crystal structure, order antiferromagnetically and have similar ordering temperature as EuZn$_2$As$_2$ studied by us, which is expected to be a topological semimetal.$^9$ We undertook the study of EuZn$_2$As$_2$ in order to determine its magnetic structure since such knowledge is crucial for the elucidation of possible nontrivial surface states of magnetic topological materials.

Here, we report on the growth of large, high quality single crystals of EuZn$_2$As$_2$ and the studies of their structural, electronic and magnetic properties by means of X-ray diffraction, electron microscopy, magnetization and AC susceptibility, heat capacity, and $^{151}$Eu Mössbauer spectroscopy.

**Experimental**

Single crystals of EuZn$_2$As$_2$ were grown by the high-temperature solution technique using tin as a flux. Starting materials: europium (3N), zinc (4N), arsenic (4N) and tin (4N) pieces weighed in the atomic ratio Eu: Zn: As: Sn = 1: 2: 2: 20, were placed into an alumina crucible and sealed under vacuum in a silica glass ampule. The ampoule was heated in a resistance furnace to 1050 °C within 10 h, then kept at this temperature for 20 h and finally cooled slowly (2–3 °C/h) to 600 °C. The single crystals were separated from the flux using a centrifuge. Samples quality was checked by scanning electron microscopy (SEM) using a JEOL 5900LV microscope equipped with an energy-dispersive X-ray spectrometer (EDS).

Powder X-ray diffraction (XRD) measurements were made by a Panalytical Empyrean diffractometer. For the low temperature XRD studies an Oxford Instruments Phenix closed-cycle helium refrigerator was used (14–300 K). During the low-temperature measurements the sample position was corrected against thermal displacement of the sample stage. The stabilization of temperature was better than 0.1 K. The XRD patterns were refined using the Rietveld-type package FullProf.$^{10}$

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The DC mass susceptibility/magnetization were measured in the temperature range of 2–300 K in magnetic fields up to 9 T using the vibrating sample magnetometer (VSM) option of a Quantum Design Physical Property Measurement System (PPMS-9). The AC susceptibility was measured in the temperature range of 2–50 K in magnetic fields up to 9 T using the AC measurement system (ACMS) option in a PPMS-9.

The heat capacity measurements were carried out by a two-tau relaxation method with the heat capacity option of a PPMS-9 during heating in the temperature range of 1.85–295 K. The single crystal samples for heat capacity measurements were attached and thermally coupled to the addenda with Apiezon N grease. A background signal from addenda and grease was recorded versus temperature.

$^{151}$Eu Mössbauer spectra were recorded at 300 K and at 4.2 K with a conventional constant acceleration spectrometer using the $^{151}$Sm(SmF$_3$) source. The 21.5 keV $\gamma$-rays were detected with a NaI(Tl) scintillation detector. The absorber surface density was approx. 60 mg/cm$^2$. The spectra were analyzed by means of a least-squares fitting procedure. The absorption line positions and relative intensities were calculated by numerical diagonalization of the full hyperfine interactions Hamiltonian. The fitted hyperfine parameters are $\delta$, $\epsilon$, $B$, and $\theta$, where $\delta$ stands for the isomer shift given relative to the $^{151}$Sm(SmF$_3$) source at room temperature. $\epsilon = \frac{1}{2}c/\mathcal{E}_\gamma eQ_gV_{zz}$ is the quadrupole coupling parameter for Eu, assuming that the electric field gradient (EFG) is axially symmetric. Symbol $c$ stands for the speed of light in vacuum, $\mathcal{E}_\gamma$—Mössbauer photon energy, $e$—elementary charge value, $Q_g$—nuclear electric quadrupole moment in the ground state of $^{151}$Eu. $B$ denotes the hyperfine magnetic field at the nucleus and $\theta$ stands for the angle between the principle component ($V_{zz}$) axis of the EFG and the hyperfine magnetic field at the Eu nucleus.

Results and discussion

Structural properties. The obtained single crystals were up to a few mm in size and have well developed shapes corresponding to the crystal symmetry, according to Fig. 1. The planes with the largest surface are parallel to the [001] family of planes, as checked by X-ray diffraction. Also [100] and [010] directions (with angle of 120°) can be easily distinguished by eye and confirmed by XRD. The crystals exhibit good homogeneity, as apparent from Fig. 1. The elemental distribution over the chosen piece of specimen shows only traces of remaining Sn from the flux on the crystal surface. The results of the X-ray microanalysis confirmed that the ratio of Eu:Zn:As is approximately 1:2:2, indicating that the composition of the sample is stoichiometric EuZn$_2$As$_2$ within the measurement uncertainty of 5%.

The XRD pattern of EuZn$_2$As$_2$ at 300 K can be entirely indexed by the trigonal $P\bar{3}m1$ space group (No. 164). No spurious phases were observed revealing excellent sample quality, as can be seen in Fig. 2. The corresponding lattice parameters are: $a = 4.2127(1)$ Å and $c = 7.1837(2)$ Å. The refined parameters are consistent with previous findings on powder samples$^{11}$. The crystal structure and coordination of the Eu atoms are shown in Fig. 3. The existence of a threefold rotation axis parallel to the [001] direction can be easily noticed by analysis of the triangular Zn and As distribution with respect to the [001] direction (Fig. 3b). Another interesting aspect of this crystal is layered structure, where Zn and As form honeycomb layers, separated by Eu planes. Therefore, the structure promotes complex and strongly anisotropic magnetic properties, especially in the case of antiferromagnetic exchange in the basal $ab$ plane.

At low temperatures (down to 14 K) the crystal structure of EuZn$_2$As$_2$ remains unchanged. The only changes observed in XRD patterns are due to a thermal expansion of the unit cell, as depicted in Fig. 4a,b. In the entire experimental range no significantly anomalous behavior can be noticed. The only small deviation of the $a$ lattice parameter, and consequently the unit cell volume, can be noticed at low temperature at 15 K. Interestingly
enough the lattice parameter does not show contraction at this temperature. Positional parameters of Zn and As do not change within uncertainty levels over the entire temperature range, as can be inferred from the Fig. 4c. Temperature changes of the unit cell volume, presented in Fig. 4d, can be roughly described using the Debye formula12:

\[ V = V_0 + I_C \frac{T^4}{\Theta_D^4} \int_0^{\Theta_D} \frac{x^3}{e^x - 1} \, dx \]

where \( V_0 \) is the unit cell volume at 0 K, \( I_C \) is the coefficient involving the Grüneisen and compressibility parameters and \( \Theta_D \) is the Debye temperature. The \( I_C \) coefficient is a slope of the linear part of the \( V(T) \) dependence. The refined parameters are as follows: \( V_0 = 109.38(1) \, \text{Å}^3 \), \( I_C = 0.0132(1) \, \text{Å}^3/\text{K} \) and \( \Theta_D = 261(8) \, \text{K} \).

Magnetic properties. Results of measurements of magnetic properties are presented in Fig. 5. Inset of panel a) shows the temperature dependence of the low field magnetic susceptibility \( \chi \), for the field perpendicular to the c-axis (B\text{\textperp}c). It increases with decreasing temperature until the kink at temperature \( T_N = 19.2 \, \text{K} \) is reached, where it first saturates and then slightly decreases, indicating a transition to antiferromagnetic (AFM) state. This temperature is close to that reported recently for polycrystalline13 and single crystalline samples14. Panel (a) also presents the temperature dependence of the reciprocal magnetic susceptibility \( 1/\chi \), showing a linear behavior above \( T_N \), together with the fit of the Curie–Weiss dependence: \( \chi(T) = \chi_0 + \frac{C}{T-\Theta_\text{p}} \). The values of \( \chi_0 = -(4.8 \pm 0.4) \times 10^{-7} \, \text{cm}^3/\text{g} \), \( C = (18.05 \pm 0.02) \times 10^{-3} \, \text{cm}^3/\text{K} \) and \( \Theta_\text{p} = 23.8 \pm 0.1 \, \text{K} \) were obtained. From the Curie constant \( C \) we calculated the effective magnetic moment \( \mu_{\text{eff}} = 7.90 \pm 0.01 \mu_B \) per Eu atom (assuming a sole Eu origin of magnetism), which is very close to the theoretical value for paramagnetic Eu\textsuperscript{2+} (7.94\mu_B), of the 4f

Figure 2. Refined X-ray diffraction pattern of EuZn\textsubscript{2}As\textsubscript{2}.

Figure 3. Crystal structure of EuZn\textsubscript{2}As\textsubscript{2}, (a) with coordination of Eu atom, (b) showing that the c-axis is a threefold rotation axis, leading to an axially symmetric electric field gradient at the Eu site. Figure was created using Diamond v. 4.6.3, https://www.crystalimpact.com/diamond/.
electronic configuration. A positive value of the paramagnetic Curie temperature $\theta_p$ indicates dominating ferromagnetic correlations between the Eu magnetic moments in the paramagnetic state.

The temperature dependences of magnetization at various magnetic fields are presented in panels (b) and (c). One can notice that for both orientations of magnetic field with respect to the $c$-axis $T_N$ decreases with increasing field as is expected for an antiferromagnet. At sufficiently high field (2.5 T for $B \perp c$ and at 5 T for $B || c$), the kink corresponding to $T_N$ vanishes.

Panel (d) presents field dependences of magnetization for both orientations of the magnetic field with respect to the crystallographic axes, measured at 2 K, i.e. much below $T_N$. Both curves reach saturation, which occurs for $B \perp c$ at 2.2 T and for $B || c$ at 3.4 T. This suggests that the $c$-axis direction is magnetically harder than that in the plane perpendicular to it. The saturation magnetization values correspond to $7\mu_B$ per Eu atom, which is expected for Eu$^{2+}$ ions in the magnetically ordered state. The $M(H)$ dependences in panel d, show clear nonlinearities at low field for both orientations. In the recent study on EuZn$_2$As$_2$ linear $M(H)$ dependences were observed in the whole field range below saturation. This difference with respect to our results might be caused by different magnetic structure. In ref14 the A-type antiferromagnetic magnetic structure was proposed (Fig. 6a). For EuSn$_2$As$_2$, which also has a trigonal structure, two types of magnetic structures were proposed by different research groups: the A-type and a canted one (Fig. 6b)15,16. Pakhira et al.16 even reported very different temperature dependences of magnetic susceptibility for single crystals grown at different conditions.

Both of our $M(H)$ curves ($B \perp c$ and $B || c$) measured are found to correspond to hard magnetization directions of an antiferromagnet as we do not observe features characteristic for an easy magnetization direction (e.g. spin flop)17. Although Blawat et al.14 claim an A-type antiferromagnetic structure, no spin flop was observed for $B \perp c$ either. In the inset of Fig. 5d results for $B \perp c$ orientation at different temperatures are shown. The $M(H)$ dependence at 10 K is almost the same as at 2 K with somewhat smaller saturation magnetization value. The result at 20 K (i.e. 1 K above $T_N$) still shows similarity to that at 10 K, but magnetization does not reach saturation up to 9 T. At 30 K, in the paramagnetic region, it still shows a nonlinear dependence. Similar non-linear $M(H)$ dependence was observed in EuSn$_2$As$_2$ single crystals, but only for $B \perp c$ orientation, which was attributed to a canted antiferromagnetic structure with a ferromagnetic component in the plane perpendicular to the $c$-axis, as shown in Fig. 6b15. In our case such non-linear behavior is observed for both orientations. This suggests that the ferromagnetic component departs from the basal plane (Fig. 6c).

We approximated the antiferromagnetic component with a straight line (fitted at high fields) and subtracted it from the total $M(H)$, which allowed us to obtain the ferromagnetic component18. This procedure was carried out for measurements at 2 K and 10 K and its results for $B \perp c$ orientation are shown in Fig. 5e. The saturation magnetization value and the field at which saturation of the ferromagnetic component is reached are almost the same at both temperatures. In the inset to the Fig. 5e a zoomed view on the ferromagnetic component at 2 K and 10 K are shown. At 2 K this component shows a non-zero, but very small (1.2 mT) coercive field, which practically vanishes at 10 K. Figure 5e shows also antiferromagnetic components and the $M(H)$ dependence at 20 K
for a comparison. In Fig. 5f we compare the derived ferromagnetic and antiferromagnetic components for $B \perp c$ and $B || c$ orientations measured at 2 K. The saturation magnetization value of the ferromagnetic component is higher for $B \perp c$ orientation ($0.72 \mu_B$ per Eu atom) than for $B || c$ ($0.52 \mu_B$ per Eu atom). Unlike the $B \perp c$, for $B || c$ no coercivity is observed. For $B \perp c$ the magnetization of the ferromagnetic component initially increases rapidly, but the increase slows down at higher fields, and then a saturation is reached. This behavior suggests that the direction perpendicular to the $c$-axis is an intermediate magnetizing direction for the ferromagnetic component, although being close to an easy direction. On the contrary, the $c$-axis magnetization curve is found to correspond to the hard magnetizing direction here, analogously to typical magnetizing curves of ferromagnets. It is worth noting that in our case the Eu sites have six equivalent directions in the plane perpendicular to the $c$-axis and, thus, easier
magnetizing in the plane than along the c-axis, is expected. Taking the above into account we conclude that our EuZn$_2$As$_2$ single crystals exhibit a canted antiferromagnetic structure with magnetic moments tilted from the basal plane (Fig. 6c). This discrepancy with respect to the A-type order proposed by Blawat et al.\textsuperscript{14} is consistent with difference in coupling between Eu magnetic moments, as indicated by a 50% higher paramagnetic Curie temperature in our case. Also the unit cell volume is larger (by 0.3%) in our case, which altogether can explain the different magnetic structures. As we mentioned above, both types of magnetic structures are reported for EuSn$_2$As$_2$ by different groups\textsuperscript{15,16}.

Panels (a) and (b) of Fig. 7 present temperature dependences of the real part of the AC magnetic susceptibility $\chi'$ for the static field perpendicular and parallel to the c-axis, respectively.

Figure 6. Schemes of antiferromagnetic order considered: (a) A-type, (b) with in-plane canting, (c) with tilting from the basal plane. Figure was created using FullProf Studio v. 2.0 https://www.ill.eu/sites/fullprof/ and Inkscape v. 1.0.1 https://inkscape.org/.

Figure 7. (a) and (b) The temperature and the field dependences of the real component of AC magnetic susceptibility $\chi'$ for the static field perpendicular and parallel to the c-axis, respectively.
fields. We denote these points as $T^*$ and attribute them to enforced alignment of magnetic moments along the applied static magnetic field. These features related to $T^*$ and $\theta_D$ show a sharp peak above about 20 K (maximum value at 19.1 K and the inflection point at 19.2 K), which is the signature of long range antiferromagnetic order already destroyed by a smaller static magnetic field.

The magnetic contribution $C_{\text{mag}}(T)$ to the heat capacity is calculated from the fitting of Eq. (2) to the $C_p$ vs $T$ dependence according to formula (3):

$$C_p = C_{\text{ph+el}} = \frac{R}{1 - \alpha T} \left[ 9 \left( \frac{T}{\theta_D} \right)^3 \int_{0}^{\theta_D/T} x^4 e^x (e^x - 1)^2 dx + \sum_{i} \frac{m_i (\theta_E i)}{R} \frac{\theta_E i}{T - 1} + \gamma T \right]$$

where $\theta_D$ is a Debye temperature, $\theta_E$ are Einstein temperatures and $m_i$ are corresponding multiplicities for each individual optical branch, $\gamma$ stands for an anharmonic coefficient, $R$ is the gas constant. In order to facilitate analysis, the summation over 12 independent optical branches was grouped into 2 branches with sixfold degeneracy. The $\gamma$ value could not be separately determined from the low-temperature $C_p$ data because of the presence of $C_{\text{mag}}$. When allowed to vary, it tends to correlate strongly with the more significant for goodness of fit, $\alpha$ parameter. Therefore, $\gamma$ was fixed at zero for the final fit. The fit to experimental data was performed from 38 to 247 K (far from the AFM peak observed around 20 K) and is indicated by the solid blue curve in Fig. 8. The calculated $C_p$ at 300 K attains a value of $\approx 123.5$ J/(mol K), which is close to the Dulong-Petit high temperature limit $C_V = 5nR = 124.7$ J/(mol K), where $n = 5$.

The corresponding fit parameters are collected in Table 1. The value of $\theta_D$ (218 K) obtained in is relatively good agreement with the one obtained from XRD above (261 K). The solid red curve in Fig. 8 shows the calculated magnetic part of the specific heat, $C_{\text{mag}}(T) = C_p(T) - C_{\text{ph+el}}(T)$. The jump of $C_{\text{mag}}$ at $T_N$, amounts to 28.8 J/(mol K), which is significantly higher than predicted from the mean field theory for a simple antiferromagnetic order (20 J/(mol K)$^{11}$. This behavior is also observed in a similar antiferromagnetically ordered, hexagonal EuMg$_2$Bi$_2$ and can be attributed to the presence of dynamic correlations, which are not accounted for in the mean field theory$^{22}$.

The magnetic contribution $S_{\text{mag}}(T)$ to the entropy was calculated from the $C_{\text{mag}}(T)$ derived from our experiment according to formula (3):
Due to the lack of experimental data for $C_{\text{mag}}(T)$ below 1.85 K, the $C_{\text{mag}}/T$ data were extrapolated from 1.85 to 0 K using second order polynomial function (fitted to the low-temperature experimental points). The calculated magnetic entropy between $T=0$ K and 41 K was determined by numerical integration of the dashed curve, representing $C_{\text{mag}}$, shown in the inset in Fig. 8 and is equal to 17.23 J/(mol K). The expected magnetic entropy of one mole of the spin-$J$ particles in a magnetic field is given by $S_{\text{mag}} = R \ln \left( 2J + 1 \right)$ for $S = 7/2$. The $J$ (for $S_{\text{mag}} = 17.23$ J/(mol K)) was estimated to be 3.47—a value well consistent with the presence of Eu$^{2+}$ ions with $J = 7/2$.

For heat capacity measurements at different orientations of the applied magnetic field with respect to crystallographic axes, much smaller (of about 2 mg) bar shape crystal was cut and measured in limited temperature ranges. The magnetic contributions $C_{\text{mag}}(T)$ to $C_p(T)$ obtained after subtracting the lattice contribution approximated with fitted theoretical curve (Eq. (2)) are shown as $C_{\text{mag}}(T)$ dependencies in Fig. 9. At zero external field, the phase transition at 19.1 K could be clearly identified. Upon applying magnetic fields up to 4 T, the peak becomes broader, rounder, shifts to lower temperatures and the transition is monotonously suppressed, similarly to observed in other antiferromagnetically ordered Eu containing compounds. Exact positions of the maxima were calculated from the $C_{\text{mag}}$ versus $T$ dependencies for $B \perp c$ and $B \parallel c$ geometries and are collected as a function of applied magnetic fields in Table 2. One could conclude from these data that as the magnetic field is increased the jump in the $C_{\text{mag}}$ progressively decreases and simultaneously the peak position shifts to lower temperature. Clearly stronger field dependence is observed for the $B \perp c$ geometry, where the jump in the $C_{\text{mag}}$ completely disappeared at 2 T instead of 3 T (for $B \parallel c$), which is consistent with our magnetic susceptibility measurements. The negative peak shift and its disappearance under magnetic field application confirm that there is an antiferromagnetic type order in the compound, which is possibly suppressed at 2 T and 3 T for $B \perp c$ and $B \parallel c$ geometries, respectively. As the magnetic field is further increased above 2 T (3 T) the position of the broad peak in the $C_{\text{mag}}$ vs $T$ dependencies shifts back to higher temperature which is typically observed in ferromagnetic compounds (as larger field further aligns the magnetic moments).

$$S_{\text{mag}}(T) = \int_0^T \frac{C_{\text{mag}}}{T} dT$$

*Figure 9.* Top panels: temperature dependencies of magnetic specific heat ($C_{\text{mag}}$) measured at magnetic fields $B \perp c$ (a) and $B \parallel c$ (b) geometries. The solid symbols denote experimental points and the dashed lines are to guide the eye. The bottom panels display the magnetic entropies calculated from corresponding curves in upper panels. Dotted horizontal line indicates infinite temperature limit for the molar magnetic entropy $S_{\text{mag}} = R \ln (2J + 1)$ for $S = 7/2$. (*) denotes the reference measurement (from the inset in Fig. 8) performed at $B = 0$ T on a larger sample. The insets in (a) and (b) show adiabatic temperature changes ($\Delta T_{\text{ad}}$) as a function of temperature, obtained from heat capacity data. Figure was created using Origin v. 2019b, https://www.originlab.com/.
The magnetic entropy $S_{\text{mag}}(T)$ was calculated from $C_{\text{mag}}(T)/T$ dependencies using Eq. (3) (as before, the $C_{\text{mag}}/T$ data were fitted to the range between 2.8 and 1.85 K, and extrapolated to 0 K) and the results are shown in Fig. 9 (bottom panels). With increasing magnetic field the magnetic entropy approaches the theoretical limit for $\parallel c$ geometries at increasingly higher temperatures. The non-zero contributions to $C_{\text{mag}}$ and $S_{\text{mag}}$ above the ordering temperature likely arise from the dynamic short-range correlations. Some discrepancy is apparent for the $\perp c$ geometry (left panel), but it is most probably caused by the narrower measurement temperature ranges and rather falls into the experimental error range (increased by the low sample mass).

Adiabatic temperature change ($\Delta T_{\text{ad}}$) was calculated as:

$$\Delta T_{\text{ad}}(T, \Delta B) = T(S, B_f) - T(S, B_i),$$

where $T(S, H)$ is temperature as a function of the total entropy $S$ and magnetic field $B$ (initial $B_i=0$ and final $B_f>0$). The estimated $\Delta T_{\text{ad}}$ from heat capacity data for $\parallel c$ and $\perp c$ geometries are shown in the insets in Fig. 9. The maximum obtained $\Delta T_{\text{ad}}$ is 4.7 K at 19.8 K and 4 T for $\perp c$ geometry and relatively larger magnetocaloric effect is seen for $\perp c$ geometry where the maximum $\Delta T_{\text{ad}}$ is 4.2 K at 19.7 K and 3 T. These values indicate quite high magnetocaloric effect in EuZn$_2$As$_2$, which is comparable to that in ferromagnetic EuO or antiferromagnetic EuCu$_5$In and EuAg$_5$In.

Mössbauer spectroscopy. In order to confirm and study in more detail the magnetic structure of EuZn$_2$As$_2$, deduced above, we used $^{151}$Eu Mössbauer spectroscopy. This technique is sensitive to the local surrounding of Eu nuclei. The top panel in Fig. 10 presents the $^{151}$Eu Mössbauer spectrum measured at room temperature. It consists of a single absorption line with the isomer shift, $\delta$, of $-11.6$ mm/s, which is characteristic for Eu$^{3+}$ ions. There is no absorption signal close to 0 mm/s, a value typical for non-magnetic Eu$^{3+}$ ions, indicating a high sample quality (lack of impurities containing Eu$^{3+}$). Since the $c$-axis is a threefold rotation axis (the Eu site has a $3m$ point symmetry, see Fig. 3) one expects that it becomes the principal axis of the electric field gradient tensor and the EFG tensor itself is axially symmetric along it. The Eu$^{3+}$ ion has a half-filled $4f^7$ electronic configuration with the $^8S_{7/2}$ ground state, so that the $4f$ electron contribution to the EFG is zero and, thus, the $V_{zz}$ and the respective quadrupole coupling $\varepsilon$ are expected to be small, coming from the “lattice” and bonding with adjacent atoms. This is what is observed, at room temperature [$V_{zz}$ amounts to $35 \times 10^{20}$ V/m$^2$, which is smaller than e.g. in EuFeAs$_2$ or RbEuFe$_4$As$_4$ (40 to $50 \times 10^{20}$ V/m$^2$)]. Larger magnitudes of quadrupole interaction were also reported for similar compounds e.g. EuCd$_2$As$_2$ or EuFe$_2$As$_2$. It has to be noted, that at room temperature, in the paramagnetic state, Mössbauer spectroscopy is not sensitive to the sign of $V_{zz}$.

The $^{151}$Eu spectrum at 4.2 K consists of several groups of peaks, which correspond to the presence of a magnetic field at the Eu nucleus, indicating magnetic order of Eu moments. In the ordered state the expression for the quadrupole coupling constant becomes:

$$\varepsilon = \frac{1}{4} \frac{ceQ_E V_{zz}}{E_P} \left( \frac{3 \cos^2 \theta - 1}{2} \right)$$

In general, it is possible to obtain the information about the angle $\theta$ between the $c$-axis (principal component axis of the EFG) and the direction of Eu hyperfine field, and, thus, its magnetic moment. However, care should be taken since $V_{zz}$ and $\theta$ are fitted simultaneously in the same term and several solutions could provide similar fit quality. In numerous compounds, the quadrupole coupling $\varepsilon$ at Eu$^{3+}$ has been reported to be negative. Therefore, in the first attempt, the spectrum was fitted with the $V_{zz}$ fixed at the value obtained at room temperature but negative, and we obtained $\theta=58.5 \pm 2^\circ$. Next, both parameters $V_{zz}$ and $\theta$ were allowed to be fitted and $V_{zz}=48 \times 10^{20}$ V/m$^2$ and $\theta=58 \pm 1^\circ$ were obtained (fit shown in Fig. 10b). As was mentioned above, recent neutron diffraction study suggested that Eu moments lie in the plane perpendicular to the $c$-axis and, therefore, we also attempted to fit the spectrum with $\theta$ fixed at $90^\circ$. Such a fit provided a non-physical value of $|V_{zz}|$ six times smaller compared to the value obtained at room temperature, while it is generally observed that the absolute value of $V_{zz}$ increases as the temperature decreases, unless there occurs a structural phase transition or strong or even uneven change of the lattice parameters with temperature. As apparent from the Fig. 3, the gradient of the electric field could originate mainly from As and Zn ligands. According to XRD data, presented in the Fig. 4, $c/a$ ratio changes with temperature by less than 0.1%, while the lattice parameters vary less than 0.4%. Moreover, the As and Zn positional parameters are constant, within the uncertainty level (see Fig. 4c), in the investigated temperature range. The diffraction pattern collected at 14 K shows no sign of possible distortion.

### Table 2. Temperatures of the anomalies in magnetic specific heat ($C_{\text{mag}}$) calculated from the $C_{\text{mag}}$ versus $T$ dependences at selected magnetic fields for $B \perp c$ ($T_{\text{ad}}$) and $B\parallel c$ ($T_{\text{ad}}^\parallel$) geometries.

| $B$ (T) | $T_{\text{ad}}$ (K) | $T_{\text{ad}}^\parallel$ (K) |
|---------|----------------|------------------|
| 0       | 19.1           | 19.1             |
| 1       | 17.3           | 17.7             |
| 2       | 17.6           | 13.8             |
| 3       | 18.9           | 18.1             |
| 4       | –              | 18.6             |
into a lower symmetry space group. Therefore, we conclude that our Mössbauer spectroscopy results indicate that Eu moments are tilted at angle $\theta = 58 \pm 1^\circ$ with respect to the $c$-axis, i.e. about $32^\circ$ from the Eu plane, which is almost exactly an angle at which the closest Eu neighbor, As is located ($38^\circ$), see Fig. 3a.

We note that the obtained value of $\varepsilon = -0.14$ mm/s is smaller than e.g. in EuFe$_2$As$_2$ ($-1.7$ mm/s) or EuCd$_2$As$_2$ ($-0.45$ mm/s). The magnetic field value $B = 28.2$ T is obtained, which is similar to e.g. EuZn$_2$Sb$_2$ (28.5 T) or EuFe$_2$As$_2$, EuCo$_2$As$_2$ (27.4–27.5 T), but somewhat higher than in EuCd$_2$As$_2$ (25.2 T) or EuIn$_2$As$_2$ (26.5 T). To illustrate the difference in the shape of the $^{151}$Eu Mössbauer spectrum for different arrangements of Eu magnetic moments in Fig. 10c we show spectra for EuRu$_2$As$_2$ (Eu magnetic moments parallel to the $c$-axis) and EuFe$_2$As$_2$ (Eu magnetic moments perpendicular to the $c$-axis), after. Figure was created using Origin v. 2019b, https://www.originlab.com/ and Inkscape v. 1.0.1 https://inkscape.org/.

**Magnetic field and temperature dependent phase diagram.** Figure 11 summarizes results of our studies and presents the magnetic field and temperature dependent phase diagram of EuZn$_2$As$_2$ obtained from magnetization, AC susceptibility and heat capacity measurements. At zero field it becomes antiferromagnetic at the temperature $T_N = 19.2$ K. The magnetic ordering temperature decreases with the application of magnetic field at a rate depending on the orientation of the field with respect to the $c$-axis of the crystal. At a sufficiently high magnetic field (of 2.2 T and 3.4 T for $B \perp c$ and $B || c$, respectively) the AFM order is overruled and magnetic
moments align along the direction of the applied magnetic field. This type of forced alignment also occurs at lower field but at higher temperatures (i.e. in between the AFM and PM phases at the phase diagram).

Summary and conclusions

We have successfully grown large (mm size), high quality single crystals of EuZn₂As₂ using Sn flux. They were studied by means of X-ray diffraction, electron microscopy, magnetization, AC susceptibility, heat capacity and ¹⁵¹Eu Mössbauer spectroscopy. We have found that this compound has a trigonal crystal structure (P₃m₁ space group), and that Eu is in a sole 2+ valence state. Its magnetic moments form a canted antiferromagnetic structure below T_N = 19.2 K with moments tilted from the basal plane as deduced from Mössbauer spectroscopy and from the presence of a ferromagnetic contribution to the magnetization, which has both c-axis and the basal plane components.

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Author contributions

Z.B. and D.R. conceived the research. Z.B. grew single crystals. J.Z. and D.R. conducted Mössbauer spectroscopy measurements. M.B. preformed AC susceptibility and magnetization measurements. L.G. conducted XRD and electron microscopy measurements. J.P. carried out heat capacity and magnetic susceptibility measurements. All authors participated in data analysis and discussion. D.R., J.P., L.G. and C.K. wrote the manuscript with contribution of other co-authors.

Competing interests

The authors declare no competing interests.

Additional information

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