Emergence of 1/3 magnetization plateau and successive magnetic transitions in Zintl phase Eu_3InAs_3

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Single crystals of Eu_3InAs_3 have been successfully synthesized by indium flux reactions. Eu_3InAs_3 crystallizes in the Ca_3AlAs_3 -type structure with an orthorhombic space-group $Pnma$. Theoretical calculations indicate that Eu_3InAs_3 is a semiconductor with a direct band gap of 0.3 eV. Eu_3InAs_3 has large negative Seebeck coefficients in the range of 300–450 $\mu\text{V/K}$ at room temperature. Eu_3InAs_3 displays two antiferromagnetic transitions ($T_{N1} = 13$ and $T_{N2} = 10$ K) for both $H \parallel b$ and $H \perp b$ which can be suppressed by magnetic fields. At 2 K, field-induced ferromagnetic states are reached for both $H \parallel b$ and $H \perp b$. Particularly, the $H \parallel b$ magnetization curves show a plateau at 1/3 of the saturated magnetization and an anomaly at 2/3 of the saturated magnetization. Eu_3InAs_3 is a Zintl phase material showing a 1/3 magnetization plateau here.

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I. INTRODUCTION

The classical Zintl phase was discovered in the 1930s as valence-specific compounds formed between electropositive elements, such as alkali metal or alkali-earth metal and the main groups 13–16 elements [1,2]. A large number of Zintl phase compounds have been reported [3–7], and they have been attracting great attention owing to their thermoelectric properties [8–15], magnetic properties [16–27], and superconductivity [28–30].

Recently, M_3TPn_3 Zintl phase compounds, where M represents alkal- earth metal or europium, T represents In or Al, and Pn represents As or P elements, show high Seebeck coefficients and have the potential for thermoelectric application. The antimonide series Sr_3GaSb_3 and $\text{Ca}_5\text{Al}_2\text{Sb}_6$, for instance, bear high Seebeck coefficients above 300 $\mu\text{V K}^{-1}$ [11,13]. A maximum Seebeck coefficient of 500 $\mu\text{V K}^{-1}$ has been observed in Sr_3AlSb_3 [8,12]. Recently, Eu_3InAs_3 has been reported to have an unusually large negative Seebeck coefficient (absolute value >400 $\mu\text{V K}^{-1}$ at 700 K) and a paramagnetic behavior down to 5 K [21]. Europium-containing Zintl

phase materials usually exhibit interesting magnetic behaviors [17–25]. For example, $\text{Eu}_3\text{Sn}_2\text{P}_4$ and $\text{Eu}_{14}\text{InSb}_{11}$ are antiferromagnetically ordered [18,19]. EuAs_3 displays steplike behavior in the magnetization curves. Eu_3InP_3 has three successive magnetic orders and field-induced spin-flop transitions at low temperatures [17,23]. In comparison to other europium-containing Zintl phase materials displaying rich magnetic behaviors, a paramagnetism down to 5 K for Eu_3InAs_3 is unexpected. So, in this paper, we reinvestigate the structure, the Seebeck coefficient, and, particularly, the magnetic properties of Eu_3InAs_3 . Our paper shows that Eu_3InAs_3 has large negative Seebeck coefficients similar to that reported in Ref. [21]. But, our magnetic measurements indicate that Eu_3InAs_3 shows successive magnetic orders and field-induced metamagnetic transitions, particularly, the magnetization curves show plateaus at 1/3 of the saturation magnetization (M_S) and anomalies at 2/3 of the M_S . The phenomenon of the observation of fractional values ($1/n$) of the M_S is usually related to the geometric frustration resulting from triangular lattices or the competition of exchange interactions. Eu_3InAs_3 is a Zintl phase showing a 1/3 magnetization plateau here.

II. EXPERIMENT

Single crystals of Eu_3InAs_3 were prepared by indium flux reactions. Elements Eu ($>99.9\%$, Alfa Aesar), In (4N, Alfa Aesar), and As (4N, Alfa Aesar) with a mole ratio of 1:30:1 were loaded into an alumina crucible. Then the crucible was placed into a silica tube. All these processes were carried out in an argon-filled glovebox to protect the elements. Then, the silica tube was transferred outside of the glovebox and sealed under dynamic vacuum using a $\text{C}_2\text{H}_2/\text{O}_2$ torch, heated at 1100° for 10 h, then cooled slowly ($2^\circ/\text{h}$) to 850°. After

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being dwelt for 5 h at 850°, the sealed tube was centrifuged immediately to remove the excess molten indium. Needle-shaped single crystals of Eu_3InAs_3 up to several millimeters in length were obtained. It should be noted that different $\text{Eu}:\text{In}:\text{As}$ mole ratios of 1:15:1 and 1:20:1 were also tried, but obtained Eu_3InAs_3 single crystals are relatively small. Eu_3InAs_3 is moderately air stable as previously reported [21] and can survive in the air for hours. The surface of Eu_3InAs_3 will turn black after being oxidated. We also tried to grow La_3InAs_3 using a similar method, however, the prepared samples are very sensitive to air, becoming yellowish powders after being exposed to air for a few minutes.

Single-crystal x-ray diffraction (SCXRD) was carried out on a Bruker D8 Venture diffractometer at 200 K using $\text{Mo } K\alpha$ radiation ($\lambda = 0.71071 \text{ \AA}$). The single crystal was protected by flowing N_2 gas during the measurement. A total of 1198 frames were collected. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 22 619 reflections to a maximum θ angle of 36.38° ($0.60\text{-\AA}$ resolution) of which 2123 were independent (average redundancy 10.654, completeness = 100.0%, $R_{\text{int}} = 8.16\%$, $R_{\text{sig}} = 3.77\%$) and 1739 (81.91%) were greater than $2\sigma(F_2)$. The final cell is based upon the refinement of the XYZ centroids of 4537 reflections above $20 \sigma(I)$ with $5.850^\circ < 2\theta < 72.60^\circ$. Data were corrected for absorption effects using the multiscan method. The ratio of the minimum to the maximum apparent transmission was 0.626. The crystal structure of Eu_3InAs_3 was solved and refined by analyzing the SCXRD data using the Bruker SHELXTL software package. The final anisotropic full-matrix least-squares refinement on F^2 with 43 variables converged at $R_1 = 2.73\%$ for the observed data and $wR_2 = 4.88\%$ for all data. The goodness of fit was 1.064, indicating the good quality of our sample and the result.

The composition of the single crystals was checked using energy dispersive x-ray spectroscopy (EDX) operated in a Hitachi S-4800 scanning electron microscopy at an accelerating voltage of 15 kV and an accumulation time of 90 s.

First-principles calculations for Eu_3InAs_3 were performed using the Vienna *ab initio* simulation package. Spin-polarized calculations are conducted with the generalized gradient approximation and the Perdew-Burke-Ernzerhof exchange-correlation function was adopted. The lattice constant is optimized until the energy difference is less than 10^{-7} eV , and the force convergence criteria is set to be $0.01 \text{ eV/\AA}$.

The temperature dependence of magnetic susceptibility $\chi(T)$ was measured in a superconducting quantum interference device VSM-7T (Quantum Design, Inc.) between 2 and 300 K with varied applied magnetic fields parallel (or vertical to the b axis) of Eu_3InAs_3 crystals under field-cooled and zero-field-cooled conditions. Isothermal magnetization curves were measured at 2, 10, 20, and 300 K with applied magnetic fields between -7 and 7 T . The temperature dependence of specific-heat $C_p(T)$ was measured in a physical property measurement system-14 T, Quantum Design, Inc. from 2 to 300 K with varied magnetic fields parallel and vertical to the b axis, respectively.

In the low-temperature range (4–350 K), the Seebeck coefficient and thermal conductivity of the Eu_3InAs_3 single crystal

TABLE I. Crystallographic data of Eu_3InAs_3 .

Chemical formula	Eu_3InAs_3
Formula weight	795.46 g/mol
Radiation	$\text{Mo } K\alpha$, $0.71073 \text{ \AA}$
Temperature	200(2) K
Crystal system	Orthorhombic
Space group	$Pnma$
Unit-cell dimensions	$a = 12.8973(4) \text{ \AA}$ $b = 4.39530(10) \text{ \AA}$ $c = 13.9273(5) \text{ \AA}$
Volume	$789.50(4) \text{ \AA}^3$
Z	4
Density (calculated)	6.692 g/cm^3
Absorption coefficient	38.753 mm^{-1}
$F(000)$	1348
θ range for data collection	$2.15\text{--}36.38^\circ$
Index ranges	$-21 \leq h \leq 21$ $-7 \leq k \leq 7$ $-23 \leq l \leq 22$
Independent reflections	2123 [$R_{\text{int}} = 0.0816$]
Structure solution program	SHELXT 2014/5
Refinement program	SHELXT-2018/3
Function minimized	$\Sigma W(F_o^2 - F_c^2)^2$
Goodness of fit in F^2	1.064
$R_1 (I > 2\sigma_1)$	0.0273
$wR_2 (I > 2\sigma_1)$	0.0444
R_1 (all data)	0.0436
wR_2 (all data)	0.0488
Weighting scheme	$W = 1/[\sigma^2(F_o^2) + (0.0146P)^2 + 0.1060P]$ where $P = (F_o^2 + 2F_c^2)$

were measured in a homemade setup loaded in a liquid helium dewar. In the high-temperature range (300–750 K), the Seebeck coefficient was measured by CTA-3 (Cryoall).

III. RESULTS AND DISCUSSION

Crystal structure. The SCXRD data for Eu_3InAs_3 collected in this paper can be well refined with the orthorhombic space-group $Pnma$ as reported by Rajput *et al.* [21]. Eu_3InAs_3 shares the same Ca_3AlAs_3 -type structure with similar compounds Eu_3InP_3 and Sr_3InP_3 [6,16]. The refined cell parameters, $a = 12.8973(4)$, $b = 4.39530(10)$, and $c = 13.9273(5) \text{ \AA}$, are in good agreement with the values reported [21]. The detailed crystallographic data of Eu_3InAs_3 are summarized in Table I. The EDX results, $\text{Eu } 43.20\%$ (expected 42.86%), $\text{In } 14.33\%$ (14.29%), and $\text{As } 42.27\%$ (42.86%) indicate a stoichiometric composition of Eu_3InAs_3 . Atomic positions and temperature factors for Eu_3InAs_3 obtained from the refinements of the SCXRD data are summarized in Table II. The crystallographic information file can be found in the Supplemental Material [31].

The crystal structure of Eu_3InAs_3 is shown in Fig. 1(a). It can be described as long chains of $\text{InAs}_2\text{As}_{2/2}$ propagating along the b direction, which are separated by Eu^{2+} ions. The linear $\text{InAs}_2\text{As}_{2/2}$ chains are composed of the corner-sharing InAs_4 tetrahedral, and the $\text{As}_{2/2}$ indicates two of the As atoms in InAs_4 are shared with the neighbor-two InAs_4 tetrahedral. In Eu_3InAs_3 , Eu_1 and Eu_3 atoms are surrounded by six As

TABLE II. Atomic coordinates and equivalent isotropic thermal parameters of Eu_3InAs_3 .

	x/a	y/b	z/c	$U(\text{eq.})$
Eu ₁	0.64735(2)	0.75	0.00136(2)	0.00886(6)
Eu ₂	0.72755(2)	−0.25	0.29054(2)	0.00821(6)
Eu ₃	0.56827(2)	0.25	0.60819(2)	0.00863(6)
In	0.55605(3)	0.25	0.20071(3)	0.00744(8)
As ₁	0.60173(5)	0.25	0.38858(5)	0.00769(11)
As ₂	0.74879(5)	0.25	0.12519(5)	0.00772(11)
As ₃	0.45344(5)	−0.25	0.14214(5)	0.00759(11)

atoms, forming EuAs_6 octahedra as shown in Fig. 1(b). Eu₂ are surrounded by five As atoms, forming EuAs_5 pyramids. The corresponding bond distances obtained from the refinement of the SCXRD data are listed in Table III. The distances between Eu and As range from 3.0541 Å to 3.5972 Å, which are comparable to the values of 3.0653–3.6041 Å reported by Rajput *et al.* [21]. These data are also close to the ones reported for Eu_3InP_3 where the Eu-P bond lengths range from 2.989(2) to 3.644(2) Å [16].

Electronic structure. The calculated band structure with spin-orbit coupling for Eu_3InAs_3 is shown in Fig. 2(a). It indicates that Eu_3InAs_3 is a semiconductor with a direct band gap of 0.3 eV. The effective mass at the Γ point of the conduction band along different directions is calculated, the effective mass along Γ -Y, Γ -X, and Γ -S is $0.743m_0$, $0.191m_0$, and $0.207m_0$, respectively. The effective masses of the valence band along the corresponding direction are $-0.752m_0$, $-2.269m_0$, $-1.685m_0$, where m_0 is the static mass of the electron. To better understand the electronic structure, the atom-projected partial density of states of Eu_3InAs_3 is plotted in Fig. 2(b). The states close to the valence-band maximum are mainly contributed from As and Eu atoms, indicating a certain degree of covalent bonding. Although the conduction band is mainly contributed by the Eu atoms.

Thermoelectric property. The temperature-dependent Seebeck coefficient for Eu_3InAs_3 measured between 170 and 750 K is shown in Fig. 3(a). Negative Seebeck coefficient values are observed for the whole temperature range measured, indicating the charge carriers are dominantly electrons. The Eu_3InAs_3 displays large Seebeck coefficients between -270 and $-500 \mu\text{V K}^{-1}$ from room temperature to 750 K. It should

TABLE III. Selected bond lengths in Eu_3InAs_3 .

Bond	Bond length (Å)
Eu ₁ -As ₁	3.5972(7)
Eu ₁ -As ₂	3.0847(5)
Eu ₁ -As ₃	3.0847(5)
Eu ₁ -As ₃	3.2424(5)
Eu ₁ -As ₃	3.2424(5)
Eu ₁ -As ₃	3.1779(7)
Eu ₂ -As ₁	3.0541(5)
Eu ₂ -As ₁	3.0541(5)
Eu ₂ -As ₂	3.1950(5)
Eu ₂ -As ₂	3.1950(5)
Eu ₂ -As ₃	3.0605(7)
Eu ₃ -As ₁	3.0889(7)
Eu ₃ -As ₁	3.1046(5)
Eu ₃ -As ₁	3.1046(5)
Eu ₃ -As ₂	3.2331(5)
Eu ₃ -As ₂	3.2331(5)
Eu ₃ -As ₃	3.4885(7)

be noted that the measured Seebeck coefficients for Eu_3InAs_3 are sample dependent as displayed in Fig. 3(a). These large negative Seebeck coefficients are comparable to the values of -310 to $-430 \mu\text{V K}^{-1}$ in the temperature range from 300 to 700 K reported by Rajput *et al.* [21]. Both samples S1 and S2 show bumps around 420 K. This behavior has also been reported by Rajput *et al.*, and it is possibly due to a small amount of residual In flux which has a melting point of 430 K [21]. We tried to measure the resistivity of Eu_3InAs_3 samples from room temperature to low temperatures and found that the resistivity was too large to measure, indicating the as-grown Eu_3InAs_3 single crystals have very low carrier concentration. The temperature-dependent thermal conductivity was measured in the temperature range of 4.2–350 K as shown in Fig. 3(b). Since the Eu_3InAs_3 sample has very low electrical conductivity, the electronic contribution of thermal conductivity can be reasonably ignored. The thermal conductivity result of Fig. 3(b) could be regarded as mainly dominated by the lattice contribution. As the increasing of temperature, the thermal conductivity undergoes a typical first increasing to a peak value of $35.8 \text{ W K}^{-1} \text{ m}^{-1}$ and then decreasing to an asymptotic high-temperature value of $4.0 \text{ W K}^{-1} \text{ m}^{-1}$. The decreasing of thermal conductivity in the high-temperature range is mainly due to the phonon-phonon umklapping scattering.

Magnetism. Temperature-dependent magnetic susceptibility curves $\chi(T)$ of Eu_3InAs_3 , measured at varied applied magnetic fields ($H \parallel b$) are shown in Figs. 4(a) and 4(b). The $\chi(T)$ curve measured under 1 kOe shows two kinks at 13 and 10 K, respectively, indicating possible successive antiferromagnetic (AFM) transitions. The two AFM transitions are further confirmed from the temperature-dependent specific-heat curve $C_p(T)$, measured without a magnetic field [see Fig. 5(a)], which displays two λ -type anomalies evolving at 13 K (noted as $T_{N1\parallel}$) and 10 K (noted as $T_{N2\parallel}$), respectively. When the magnetic fields increase up to 10 kOe, the $T_{N2\parallel}$ shifts to lower temperatures with increasing of the magnetic fields as shown in Fig. 4(a), indicating that the magnetic fields

FIG. 1. Crystal structure of Eu_3InAs_3 showing the (a) $\text{InAs}_2\text{As}_2/2$ chains and (b) Eu-As bonds. Purple, orange, and green balls represent the Eu, In, and As atoms, respectively. The structure is tripled along the b axis in (a).

FIG. 2. (a) The band structure of Eu_3InAs_3 with spin-orbit coupling; (b) atom-projected density of states of Eu_3InAs_3 .

suppress the second AFM order. The second AFM transition disappeared, and the first AFM transition is suppressed to $T_{N1\parallel} = 11$ K when the magnetic fields are 20 kOe [see Fig. 4(b)], which is also confirmed from the $C_p(T)$ curves measured at 20 kOe showing only one λ -type anomaly around 11 K [see Fig. 5(a)]. The $T_{N1\parallel}$ is further suppressed with increasing magnetic fields and disappears when the magnetic fields are at 50 and 70 kOe as shown in Fig. 4(b). The suppression of AFM order can also be seen from $C_p(T)$ curves shown in Fig. 5(a) that a λ -type anomaly is around 7 K when measured at 30 kOe and disappeared when measured at 50 kOe. The $\chi(T)$ curves measured at 50 and 70 kOe show ferromagneticlike behavior. The Curie temperatures T_c , determined from the corresponding $d\chi/dT$ curves are 17 and 20 K for the curves measured at 50 and 70 kOe, respectively.

The $\chi(T)$ curves of Eu_3InAs_3 measured at varied magnetic fields ($H \perp b$) are shown in Fig. 4(c). The $\chi(T)$ curve shows two kinks at 10 and 13 K under $H = 1$ kOe, which is similar to the $H \parallel b$ data and indicate two AFM transitions. The two AFM transitions are confirmed by the data of the $C_p(T)$ curves measured without a field, showing two λ -type anomalies around 13 ($T_{N1\perp}$) and 10 K ($T_{N2\perp}$), respectively [see Fig. 5(c)]. When the magnetic fields increase up to 10 kOe, the ($T_{N2\perp}$) moves toward lower temperatures, 10.5 K for $H = 5$ kOe and 9.5 K for $H = 10$ kOe. The ($T_{N2\perp}$) disappears and the ($T_{N1\perp}$) shifts to a lower temperature of 12.5

K when the magnetic field is 20 kOe. Correspondingly, the $C_p(T)$ curve measured under 20 kOe shows only one anomaly around 12.5 K [see Fig. 5(c)]. The ($T_{N1\perp}$) shifts to a lower temperature of 11 K with $H = 30$ kOe, which can be seen from both the $\chi(T)$ and the $C_p(T)$ curves measured under 30 kOe. When H is 50 and 70 kOe, the $\chi(T)$ curves show ferromagneticlike behavior, and the T_{cs} are 15 and 17 K, respectively, as determined from the corresponding $d\chi/dT$ data.

Figure 4(d) displays the $\chi^{-1}(T)$ curves of Eu_3InAs_3 measured under a magnetic field of 10 kOe with $H \parallel b$ and $H \perp b$, respectively. Fitting the 50- to 300-K data with Curie-Weiss law, $\chi = C/(T - \theta_w)$, where C and θ_w are the Curie constant and the Weiss temperature, respectively, values of $C = 24.34 \text{ emu K mol}^{-1}$ and $\theta_w = 16$ K were obtained for $H \parallel B$ and $C = 25.45 \text{ emu K mol}^{-1}$ and $\theta_w = 17$ K for $H \perp b$. According to the C values, effective moment μ_{eff} of 8.06 and $8.24 \mu_B/\text{Eu}^{2+}$ were obtained for $H \parallel B$ and $H \perp b$, respectively, which are close to the theoretical value of $7.94 \mu_B$ for Eu^{2+} ($S = 7/2$) and are comparable with the ones reported for other Eu^{2+} compounds Eu_3InP_3 , Eu_3GaAs_3 , and Eu_3AlAs_3 [27].

To further study the field-induced magnetic states in Eu_3InAs_3 , isothermal magnetization curves $M(H)$ have been measured at 2, 10, 20, and 300 K with $H \parallel b$ [see Fig. 6(a)]. At 2 K, the magnetization of Eu_3InAs_3 shows a sharp increase

FIG. 3. (a) Temperature-dependent Seebeck coefficient and (b) thermal conductivity for Eu_3InAs_3 . S1, S2, and S3 indicate three different single crystals.

FIG. 4. (a) and (b) Temperature dependence of magnetic susceptibility for $H \parallel b$ with varied magnetic fields. The inset in (a) shows the single crystal used for measurements. (c) Temperature dependence of magnetic susceptibility for $H \perp b$ with varied magnetic fields. The inset plots an enlarged view for temperature ranges of 8–15 K. (d) Temperature dependence of the inverse magnetic susceptibility and Curie-Weiss fitting.

to $1.7 \mu_B/\text{f.u.}$ with the magnetic field increasing from 0 to 183 Oe. The magnetizations then increase linearly with the increase in magnetic fields up to 12.6 kOe and reach a plateau of about $7.1 \mu_B/\text{f.u.}$ The magnetizations increase sharply to

FIG. 5. (a) and (b) Temperature dependence of specific heat of Eu_3InAs_3 measured with $H \parallel b$ and $H \perp b$, respectively.

FIG. 6. (a) and (b) The isothermal magnetization curves of Eu_3InAs_3 for $H \parallel b$ and $H \perp b$, respectively.

FIG. 7. (a) Temperature dependence of specific heat of Eu_3InAs_3 measured without a magnetic field, and the red curve indicates the Debye-Einstein fitting. (b) The magnetic contributions of the specific heat and the corresponding entropy.

$14.4 \mu_B/\text{f.u.}$ when H increases from 23.2 to 26.6 kOe, then the magnetizations increase less sharply and are nearly saturate ($22.2 \mu_B/\text{f.u.}$) when H is larger than 37.0 kOe. The M_S of $22.2 \mu_B/\text{f.u.}$ is consistent with the moments of three paralleled Eu^{2+} ions, indicating a field-induced ferromagnetic state with all Eu^{2+} moments are parallel arranged. It should be noted that the values of $7.0 \mu_B/\text{f.u.}$ (the plateau) and $14.4 \mu_B/\text{f.u.}$ (the slope change) are close to $1/3$ and $2/3$ of the M_S for Eu_3InAs_3 . At 10 K, the $M(H)$ curve does not show the plateau but only anomalies around $1/3$ and $2/3$ of M_S . The $M(H)$ curve measured at 20 K is smooth and is not saturated under 70 kOe. The $M(H)$ curve measured at 300 K is linear and is following the paramagnetic behavior. The phenomenon of observation of fractional values of M_S is usually related to the geometric frustration resulted from triangular lattices or competition of exchange interactions [32]. The ground state of Eu_3InAs_3 is AFM, but positive θ_W values indicate that ferromagnetic interactions are dominant in Eu_3InAs_3 . One possible reason for the emergence of the plateau at $1/3$ of M_S is due to the competing AFM and ferromagnetic exchange interactions in Eu_3InAs_3 . Moreover, the Eu_1 , Eu_2 , and Eu_3 atoms can form a pseudotriangular lattice in Eu_3InAs_3 [see Fig. 1(b)], which may result in a kind of frustration.

Figure 6(b) shows the $M(H)$ curves of Eu_3InAs_3 measured with $H \perp b$. At 2 K, the magnetizations increase linearly with the increase in the magnetic fields and are nearly saturated ($21.5 \mu_B/\text{f.u.}$) when the magnetic fields reach 50 kOe, indicating a field-induced ferromagnetic state. The $M(H)$ curves measured at 10 and 20 K are similar but the magnetizations are not saturated at 70 kOe. Paramagnetic behavior is observed at 300 K.

The $C_p(T)$ curve without the magnetic field for Eu_3InAs_3 up to 270 K is shown in Fig. 7(a). To estimate the specific contribution from a phonon and an electron, the data between 50 and 200 K are fitted with the Debye-Einstein model,

$$C_p = \lambda T + 9nR\alpha \left(\frac{T}{T_D} \right)^3 \int_0^{T_p/T} \frac{x^4 e^x}{(e^x - 1)^2} dx + \frac{3nR(1 - \alpha)e^{T_E/T}}{(e^{T_E/T} - 1)^2},$$

where C_p , λ , n , R , and α represent the isobaric specific heat, the electronic specific heat, the moles, the Boltzmann constant, and the weight of different contributions, respectively.

The T_E and T_D represent Einstein and Debye temperatures, respectively. The fitting curve is shown in Fig. 7(a), and the resulting values for T_D and γ are 239 K and $15 \text{ mJmol}^{-1}\text{K}^{-2}$, respectively. The corresponding magnetic entropy is calculated by subtracting the phonon and electron contributions [see Fig. 7(b)]. The calculated entropy is larger than $2R\ln 8$ but is smaller than $3R\ln 8$ (expected for three Eu^{2+} ions), where R is the gas constant. The small deviation from $3R\ln 8$ may indicate that the fitted phonon and electron contributions are overestimated.

IV. CONCLUSION

Single crystals of Eu_3InAs_3 have been successfully synthesized by indium flux reactions. SCXRD analysis indicates that Eu_3InAs_3 crystallizes in an orthorhombic space-group $Pnma$ with cell parameters, $a = 12.8973(4)$, $b = 4.39530(10) \text{ \AA}$, and $c = 13.9273(5) \text{ \AA}$, which are close to the reported values [21]. Theoretical calculations indicate that Eu_3InAs_3 is a semiconductor with a direct band gap of 0.3 eV. Measurements of Seebeck coefficients found that Eu_3InAs_3 has large negative Seebeck coefficients similar to that reported in Refs. [9,21]. Currently, the as-grown samples have relatively high electrical resistivity, indicating a quite low intrinsic carrier concentration. Future doping studies are needed to optimize the thermoelectric properties of Eu_3InAs_3 .

Anisotropic magnetic properties are measured for both $H \parallel b$ and $H \perp b$, respectively. Temperature-dependent magnetic susceptibility and specific-heat measurements confirm two AFM transitions for both $H \parallel b$ ($T_{N1\parallel} = 13$ and $T_{N2\parallel} = 10$ K) and $H \perp b$ ($T_{N1\perp} = 13$ and $T_{N2\perp} = 10$ K). Increasing magnetic field suppresses T_{N2} first then T_{N1} for both $H \parallel b$ and $H \perp b$. Isothermal magnetization measurements at 2 K with $H \parallel b$ indicate successive field-induced metamagnetic transitions, particularly, the magnetization curves show a plateau at $1/3$ of M_S and an anomaly at $2/3$ of M_S before reaching M_S . In comparison, isothermal magnetizations at 2 K with $H \perp b$ increase linearly with the increase in magnetic fields and nearly saturate when the magnetic fields are larger than 50 kOe. The origin of the plateau at $1/3$ of M_S observed in Eu_3InAs_3 may be related to competing AFM and ferromagnetic exchange interactions in Eu_3InAs_3 . Future studies, such as neutron diffraction to determine magnetic structures under varied magnetic fields, are needed to understand it. Eu_3InAs_3 is a Zintl phase showing a $1/3$ magnetization plateau.

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