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Magnetic properties and ^{151}Eu Mössbauer effects of mixed valence europium copper sulfide, Eu_2CuS_3

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Abstract

Ternary europium copper sulfide Eu_2CuS_3 have been investigated by X-ray diffraction, ^{151}Eu Mössbauer spectroscopy, magnetic susceptibility, magnetization, and specific heat measurements. In this compound, Eu^{2+} and Eu^{3+} ions occupy two crystallographically independent sites. The ^{151}Eu Mössbauer spectra indicate that the Eu^{2+} and Eu^{3+} ions exist in the molar ratio of 1:1, and the Debye temperatures of Eu^{2+} and Eu^{3+} are 180 and 220 K, respectively. In its magnetic susceptibility, the divergence between the zero-field cooled and field cooled susceptibilities appears below 3.4 K. The specific heat has a λ-type anomaly at the same temperature. From the field dependence of magnetization at 1.8 K, the Eu^{2+} ion was found to be in the ferromagnetic state with the saturation magnetization $M_S = 6.7\,\mu_B$.

Keywords: Magnetic properties; Mössbauer spectroscopy; Magnetic susceptibility; Specific heat; Europium; Copper; Sulfide

1. Introduction

Ternary europium copper sulfide Eu_2CuS_3 has been reported to crystallize in the orthorhombic structure with space group *Pnma* [1]. The schematic structure of Eu_2CuS_3 is illustrated in Fig. 1. This compound has the formal oxidation state of $Eu^{2+}Eu^{3+}Cu^{+}S_3^{2-}$ and the Eu^{2+} and Eu^{3+} ions occupy crystallographically different sites. In the case of sulfides, the mixed-valence compounds show an interesting electronic behavior as the valence state and the magnetic interaction. For example, Eu_3S_4 has the Verwey transition at 186 K [2] and the ferromagnetic transition at 3.1 K [3]. $EuPd_3S_4$ shows an electron hopping between Eu^{2+} and Eu^{3+} and has the antiferromagnetic transition at 3 K [4]. $Eu_5Sn_3S_{12}$ is metamagnetic and has two field-dependent antiferromagnetic phases at low temperatures [5].

Generally, the divalent state of Eu is stable in sulfides, but some compounds contain trivalent europium. Flahaut noted that these were classified into two types [6]. In the case that compounds containing only Eu^{3+} ions, there is necessarily a strongly electronegative anion, or a second weakly electronegative cation. For compounds containing mixtures of Eu^{2+} and Eu^{3+}, Eu_3S_4 [7] and $EuPd_3S_4$ [4], ^{151}Eu Mössbauer spectroscopic measurements were performed to investigate the mixed-valence state of Eu. These compounds show the occurrence of the electron transfer and/or the electron hopping between Eu^{2+} and Eu^{3+}, which may stabilize the Eu^{3+} ions. The situation for Eu_2CuS_3 is different from the case for the above-mentioned sulfides, i.e., Eu_2CuS_3 has two crystallographically distinguishable sites for Eu^{2+} and Eu^{3+} ions. However, none of the studies on the electronic and magnetic properties of this mixed valence compound have been carried out.

In this study, we synthesized the polycrystalline samples of Eu_2CuS_3 and have measured the magnetic susceptibility, magnetization, specific heat measurements and ^{151}Eu Mössbauer spectroscopy. The results will be discussed in detail.

2. Experimental

A ternary europium copper sulfide, Eu_2CuS_3, was synthesized by a solid-state reaction. Europium monosulfide (EuS), copper powders, and sulfur were used as

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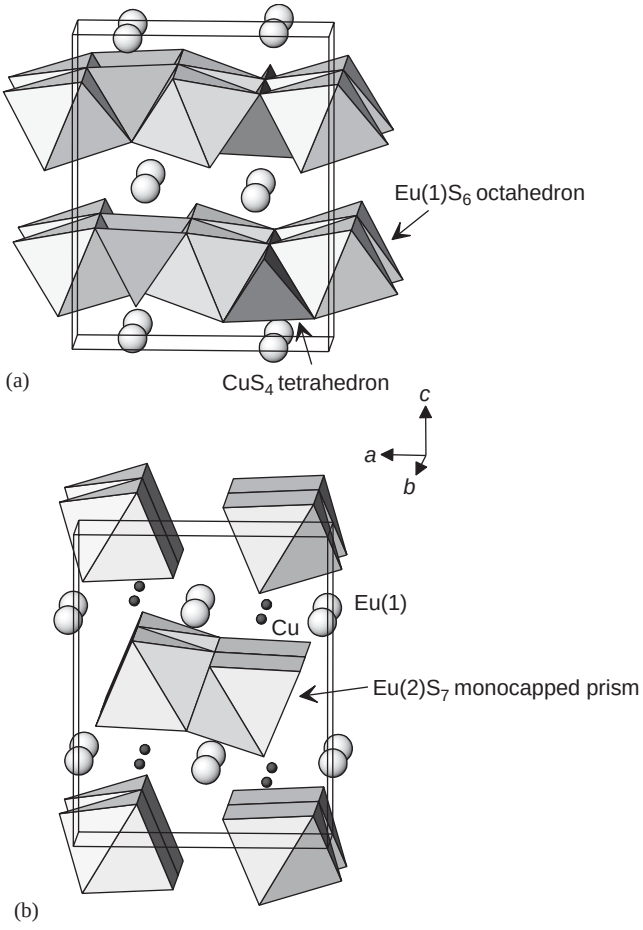

Fig. 1. Polyhedral representation of the Eu_2CuS_3 structure. (a) $CuEu(1)S_3$ layers composed of $Eu(1)S_6$ octahedra and CuS_4 tetrahedra. (b) The double chains of the $Eu(2)S_7$ monocapped trigonal prisms with Eu(1) and Cu represented by the larger and the smaller spheres.

starting materials. To obtain the europium monosulfide, europium sesquioxide (Eu_2O_3) was heated on a graphite boat at 1273 K in a flow of the mixed gas of CS_2 and N_2, which was obtained by bubbling the N_2 gas through liquid CS_2 at room temperature. Stoichiometric mixtures of the starting materials were ground and pressed into a pellet, and then heated in a quartz ampoule. The inner wall of the ampoule was, in advance, coated with a carbon film by decomposing benzene. The reaction was carried out at 1173 K for 12 h, with one interval regrinding.

Powder X-ray diffraction measurements were performed with Cu$K\alpha$ radiation on a Rigaku MultiFlex diffractometer equipped with a curved graphite monochromator. Intensity data were collected by step scanning in the range $2\theta = 10^\circ - 120^\circ$ at intervals of 0.02°. The structure and lattice parameters were refined with a Rietveld program RIETAN 2000 [8].

The ^{151}Eu Mössbauer spectra were measured between 15 and 300 K with a Mössbauer spectrometer VT-6000 (Laboratory Equipment Co.) using a radiation source $^{151}SmF_3$ (1.85 GBq). The sample lapped in an aluminum foil was cooled down to each temperature and the isomer shift was determined relative to the shift of europium fluoride (EuF_3).

Magnetic susceptibility measurements of the powder sample weighing ~20 mg were performed with a SQUID magnetometer (Quantum Design MPMS model) from 1.8 to 300 K. The applied field was 0.1 T. In the neighborhood of the magnetic transition, the magnetic susceptibility was measured under zero-field cooled (ZFC) and field cooled (FC) conditions with 5 mT. The field dependence of magnetization was measured at 1.8 K by changing the applied magnetic field between −5 and 5 T.

The specific heat measurement was carried out using a relaxation technique supplied by commercial specific heat measurement system (Quantum Design, PPMS) in the temperature range from 1.8 to 300 K. The sample in the form of pellet (~7 mg) was mounted on an aluminum plate with apiezon for better thermal contact.

3. Results and discussion

The Eu_2CuS_3 compound was obtained as a single phase. The X-ray diffraction profile was indexed on an orthorhombic cell with the space group *Pnma*, and its crystallographic parameters were refined by the Rietveld method. Fig. 2 shows the X-ray diffraction profile of Eu_2CuS_3. The calculated profile was in good agreement with the observed one ($R_{wp} = 8.10\%$, $R_I = 2.95\%$). The refined lattice and positional parameters are listed in Table 1, and the selected interatomic distances are listed in Table 2. These values for the lattice parameters and the interatomic distances agree with those reported by Lemoine et al. [1].

The crystal structure of Eu_2CuS_3 is shown in Fig. 1. In this structure, the Eu ions occupy two crystallographically independent sites. The Eu(1) ions are coordinated

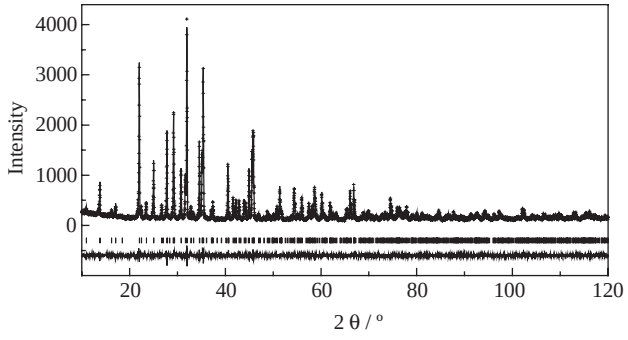

Fig. 2. Powder X-ray diffraction patterns and Rietveld refinements for Eu_2CuS_3. The bottom trace is a plot of the difference between observed + (cross makers) and calculated (solid line) intensities. All allowed Bragg reflections are shown by vertical lines.

Table 1
Lattice parameters and atomic positions of Eu_2CuS_3

Space group: *Pnma*
$Z = 4$
$a = 10.3596(2)$ Å, $b = 3.9586(1)$ Å, $c = 12.8194(3)$ Å

Atom	Site	x	y	z	B (Å^2)
Eu(1)	4*c*	0.0164(2)	1/4	0.7374(1)	0.46(5)
Eu(2)	4*c*	0.7801(2)	1/4	0.0014(2)	0.55(5)
Cu	4*c*	0.2321(4)	1/4	0.2225(3)	0.80(9)
S(1)	4*c*	0.0505(6)	1/4	0.1157(5)	0.55(17)
S(2)	4*c*	0.4068(7)	1/4	0.1021(5)	0.30(16)
S(3)	4*c*	0.2635(7)	1/4	0.8280(5)	0.57(16)

$$R_{wp} = \left[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\right]^{1/2} = 8.10\%,$$

$$R_I = \sum |I_o - I_c| / \sum I_o = 2.95\%,$$

$$R_F = \sum |F_o - F_c| / \sum F_o = 2.13\%.$$

Table 2
Selected interatomic distances (Å) of Eu_2CuS_3

Eu(1)–S(2)	2.795(5) × 2
Eu(1)–S(3)	2.795(8)
Eu(1)–S(3)	2.812(7)
Eu(1)–S(1)	2.818(5) × 2
Eu(2)–S(3)	2.985(5) × 2
Eu(2)–S(1)	3.041(5) × 2
Eu(2)–S(2)	3.070(5) × 2
Eu(2)–S(1)	3.121(6)
Cu–S(1)	2.344(7)
Cu–S(2)	2.363(7)
Cu–S(3)	2.397(4) × 2

by six sulfur ions and the Eu(1)S_6 octahedra share corners along the *a*-axis and edges along the *b*-axis. The Eu(1)S_6 octahedra and CuS_4 tetrahedra form a CuEu(1)S_3 layer perpendicular to the *c*-axis. The Eu(2) ions are coordinated by seven sulfur ions between the CuEu(1)S_3 layers and make the Eu(2)S_7 monocapped trigonal prisms. The bases of the Eu(2)S_7 monocapped trigonal prisms, S(1), S(2), and S(3), are shared by each other to make a chain along the *b*-axis and one corner of this base, S(1), is also coordinated by the Eu(2) belonging to the neighboring chain.

The valences of the cations are calculated by the bond valence sum (V_i) [9]:

$$v_{ij} = \exp\left(\frac{R_0 - d_{ij}}{b}\right), \quad (1)$$

$$V_i = \sum_j v_{ij}, \quad (2)$$

where R_0 and b are known as the bond valence parameters of various cations and a constant value

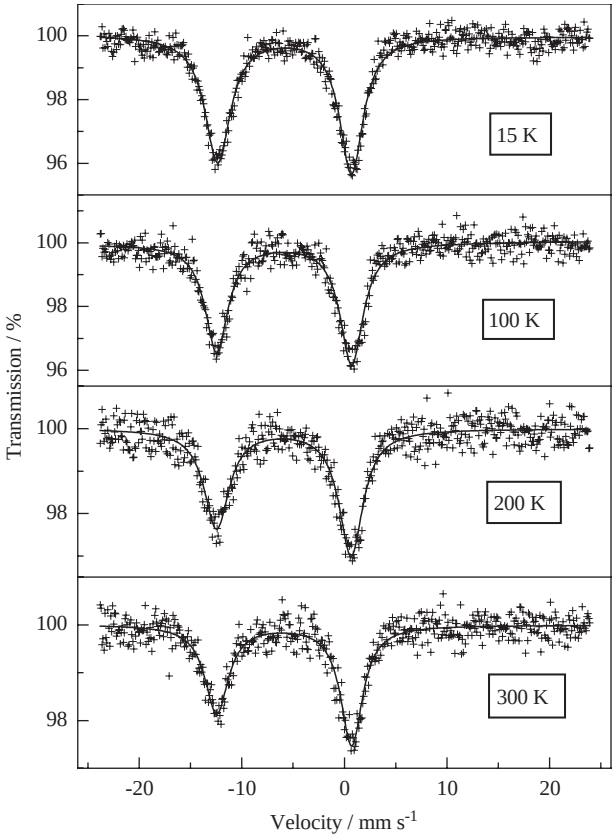

Fig. 3. ^{151}Eu Mössbauer spectra of Eu_2CuS_3 at 15, 100, 200, and 300 K.

(0.37 Å), respectively, and d_{ij} means the interatomic distance between cation *i* and anion *j*. The valences of the Eu(1), Eu(2), and Cu ions were determined to be +3.04, +1.73, and +0.971, respectively. This result indicates that the trivalent and divalent europium ions occupy the Eu(1) and Eu(2) sites, respectively.

Fig. 3 shows the ^{151}Eu Mössbauer spectra of Eu_2CuS_3 between 15 and 300 K. Two absorption peaks appear at ca. −12 and 0 mm s^{-1} in these spectra, indicating the presence of the divalent and trivalent Eu ions. To simplify this analysis, each peak was fitted with a single Lorentzian. The isomer shifts of Eu^{2+} ($\delta \sim -12.4$ mm s^{-1}) and Eu^{3+} ($\delta \sim 0.68$ mm s^{-1}) are nearly constant between 15 and 300 K. It is known that the difference in the isomer shifts between Eu^{2+} and Eu^{3+} decreases with increasing the temperature in mixed valence europium sulfides, Eu_3S_4 [7], $EuPd_3S_4$ [4], and $(EuS)_{1.173}NbS_2$ [10] because of the electron hopping between Eu^{2+} and Eu^{3+}. The temperature dependence of the isomer shifts for Eu_2CuS_3 means that the electron hopping does not occur in this compound.

Fig. 4 shows the temperature dependence of the absorption area of the intensity curves of the Eu^{2+} and Eu^{3+} ions. Both intensities decrease monotonously with increasing temperature. The intensities for Eu^{2+} and

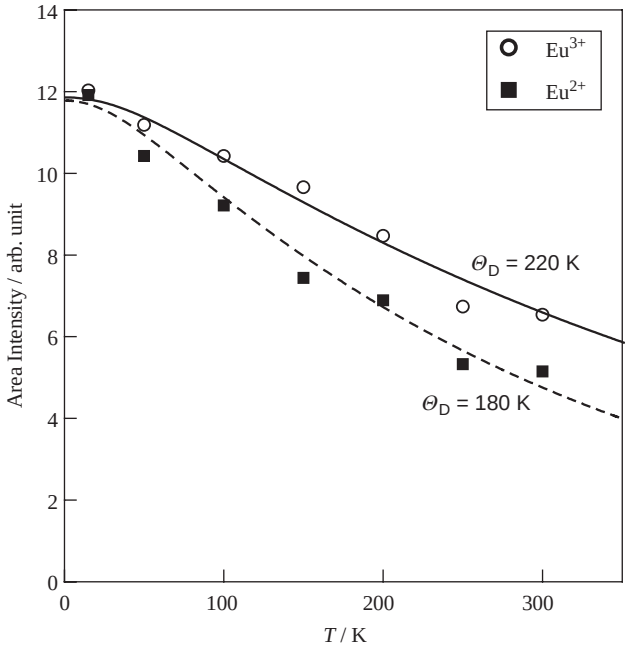

Fig. 4. Temperature dependence of the absorption area of intensities of Eu_2CuS_3. The solid line is the theoretical curve ($\Theta_D = 180$ K) normalized to $A(Eu^{2+})$ at 15 K and the broken line is the theoretical curve ($\Theta_D = 220$ K) normalized to $A(Eu^{3+})$ at 15 K.

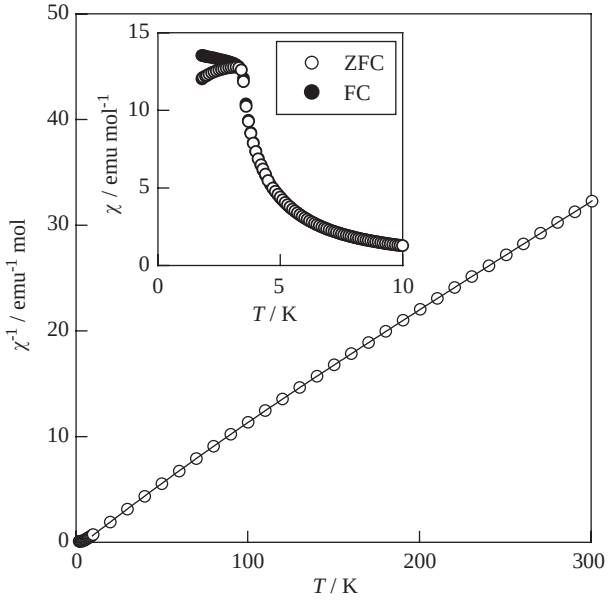

Fig. 5. Temperature dependence of the reciprocal magnetic susceptibility χ^{-1} of Eu_2CuS_3. A solid line is the fitting result by using Eq. (4) (see text). The inset shows χ of Eu_2CuS_3 below 10 K measured in the magnetic field of 5 mT.

Eu^{3+} are equal at 15 K but the ratio of the intensities for Eu^{2+} and Eu^{3+} is found to be 2:3 at 300 K. This difference may be due to a difference in the Debye–Waller factors between Eu^{2+} and Eu^{3+}. The area of the intensity curve is proportional to the recoil-free fraction. The Debye temperatures for Eu^{2+} and Eu^{3+} are estimated from the recoil-free fraction. The recoil-free fraction is represented by [11]

$$f = \exp\left[\frac{-6E_R}{k_B\Theta_D}\left\{\frac{1}{4} + \left(\frac{T}{\Theta_D}\right)^2 \int_0^{\Theta_D/T} \frac{x\,dx}{(e^x - 1)}\right\}\right], \qquad (3)$$

where k_B is the Boltzmann's constant, Θ_D is the Debye temperature, and E_R is the free-atom recoil energy. The theoretical curves with $\Theta_D = 180$ K and $\Theta_D = 220$ K using this equation are in good agreement with the experimental data for Eu^{2+} and Eu^{3+}. The higher Debye temperature for the Eu(1) ion indicates that the Eu^{3+}–S^{2-} bonds in the $Eu(1)S_6$ octahedron are stronger than the Eu^{2+}–S^{2-} bonds in the $Eu(2)S_7$ monocapped trigonal prism, which is attributable to the small coordination-number and the short interatomic distances for $Eu(1)S_6$ as compared with those for the Eu^{2+}–S^{2-} bonds of $Eu(2)S_7$.

Fig. 5 shows the reciprocal magnetic susceptibilities (χ^{-1}) of Eu_2CuS_3 as a function of temperature in the magnetic field of 0.1 T. The molar susceptibilities of Eu_2CuS_3 is given by

$$\chi_M = \chi_M(Eu^{2+}) + \chi_M(Eu^{3+}) + \chi_0, \qquad (4)$$

where χ_0 is the temperature-independent term containing the diamagnetic term. The ground state of the Eu^{2+} ion is $^8S_{7/2}$. Therefore the orbital angular momentum vanishes, and the crystal field does not affect the magnetic properties of Eu^{2+} compounds. The magnetic susceptibility ($\chi_M(Eu^{2+})$) of Eu^{2+} is represented by $N_A\mu_{eff}^2/3k_B(T-\Theta_W)$, where μ_{eff} is the effective magnetic moment and Θ_W is the Weiss constant. The ground state ($^7F_0$) of Eu^{3+} is nonmagnetic, and the excited states ^7F_J ($J = 1, 2, \ldots, 6$) are close enough to give energy differences comparable to k_BT at room temperature. Thus, in consideration of the excited states, the magnetic susceptibility of Eu^{3+} can be written as

$$\chi_M(Eu^{3+}) = \frac{N_A\mu_B^2}{3k_B\gamma T} \frac{24 + (13.5\gamma - 1.5)e^{-\gamma} + (67.5\gamma - 2.5)e^{-3\gamma} + (189\gamma - 3.5)e^{-6\gamma} + \cdots}{1 + 3e^{-\gamma} + 5e^{-3\gamma} + 7e^{-6\gamma} + \cdots}, \qquad (5)$$

where $\gamma = \lambda/k_BT$ is 1/21 of the ratio of the over all multiplet width to k_BT [12]. On the assumption that the screening number is 34, the theoretical value of λ/k_B is

$363\,cm^{-1}$. If λ/k_B was fixed to be $363\,cm^{-1}$ [12], the values of μ_{eff} and Θ_W of Eu^{2+} were determined to be $7.96(1)\,\mu_B$ and $+4.74(2)\,K$, respectively. The effective magnetic moment is in good agreement with the theoretical one ($7.94\,\mu_B$). The positive Weiss constant indicates the existence of the ferromagnetic coupling of Eu^{2+} ions.

The inset of Fig. 5 shows the magnetic susceptibility measured in the applied field of 5 mT. The divergence between the ZFC and FC magnetic susceptibility have been observed below 3.4 K. To clarify this behavior, we measured the field dependence of the magnetization at 1.8 K as shown in Fig. 6. The magnetization linearly increases and then reaches an almost constant value. Actually it still increases with a further increase of the magnetic field strength. The coersive force is very small ($\sim$1 mT). The extrapolation of the high-field magnetic moment to zero field yields a saturation moment of $6.7\,\mu_B$. The magnetic contribution of Eu^{3+} to the magnetization of Eu_2CuS_3 is negligible at 1.8 K because of its nonmagnetic ground state ($^7F_0$). This saturation moment corresponds to the ferromagnetic-ordering magnetization of Eu^{2+} which is expected to be $7\,\mu_B$.

The temperature dependence of the specific heat C_p of Eu_2CuS_3 is shown in Fig. 7(a). The sharp λ-type anomaly at 3.4 K indicates that the existence of a long-range magnetic ordering corresponds to the ferromagnetic transition at 3.4 K observed from the magnetic susceptibility. The specific heat of insulating Eu_2CuS_3 consists of a magnetic contribution (C_{mag}) and a lattice contribution (C_{lat}). The C_{lat} is represented by the usual harmonic lattice series in odd powers of T:

$$C_{lat} = B_3T^3 + B_5T^5 + B_7T^7 + \cdots. \quad (6)$$

On the assumption that the C_{mag} is negligible above 16 K, the constants B_3, B_5, B_7 were determined by fitting Eq. (6) to the observed specific heat data between 16 and 25 K. The C_{mag} is obtained by subtracting C_{lat} from the total C_p. A dashed line in the $C_p - T$ curve represents the extrapolated specific heat below 1.8 K. This is calculated by fitting to the function $C_p = BT^{3/2} + C_{lat}$ in the temperature range $1.8\,K \leqslant T \leqslant 2.2\,K$, because C_{mag} for a ferromagnetic ordering is proportional to $T^{3/2}$ [13]. The temperature dependence of the C_{mag}/T and the magnetic entropy calculated by $S_{mag} = \int (C_{mag}/T)\,dT$ are shown in Fig. 7(b). From the $S_{mag} - T$ curve, the magnetic entropy change is estimated to be $\sim 15\,J\,mol^{-1}\,K^{-1}$, and it is close to $R\ln(2S+1) = R\ln 8$.

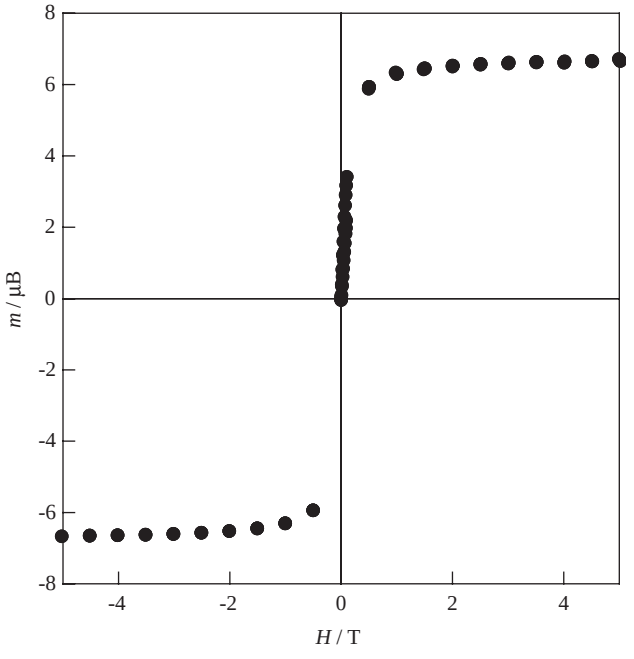

Fig. 6. Field dependence of magnetization measured at 1.8 K for Eu_2CuS_3.

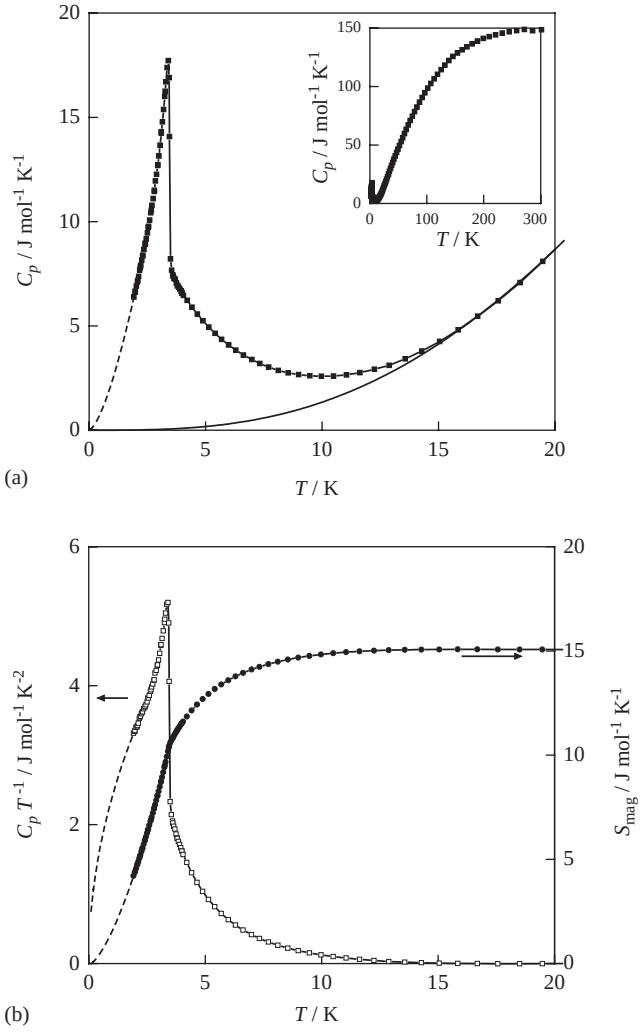

Fig. 7. (a) Temperature dependence of the specific heat below 20 K for Eu_2CuS_3. The inset shows the specific heat behavior up to 300 K. (b) Temperature dependence of the magnetic specific heat divided by temperature (left ordinate) and magnetic entropy (right ordinate) for Eu_2CuS_3.

This result strongly indicates that the ferromagnetic ordering of Eu_2CuS_3 is caused by only the Eu^{2+} ion and the eight-fold degeneracy remains in the ground state of Eu^{2+}, which is consistent with the results obtained through the magnetic susceptibility and the magnetization measurements.

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