Anisotropic magnetic properties of EuAl$_2$Si$_2$

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Abstract. EuAl$_2$Si$_2$ is known to crystallize in the CaAl$_2$Si$_2$-type trigonal structure. We have grown single crystals of EuAl$_2$Si$_2$ by flux method, using Al-Si eutectic (87.8% Al) as self-flux, and investigated their anisotropic magnetic properties by means of magnetization, electrical resistivity and heat capacity in zero and applied magnetic fields, and $^{151}$Eu Mössbauer spectroscopy. Magnetic susceptibility data show an antiferromagnetic transition at $T_N = 33.3$ K in agreement with the previously reported value on polycrystalline sample. The isothermal magnetization at 2 K measured along and perpendicular to the $c$-axis shows anisotropic behaviour, which is rather unexpected as Eu$^{2+}$ is an $S$-state ion. The spin flip fields along the two directions are 2.8 and 4.8 T, respectively, while two closely spaced spin-flop transitions in the $ab$-plane are observed near 1.4 and 1.6 T. The electrical resistivity shows an upturn between $T_N$ and 60 K as the temperature is lowered below ~ 60 K, suggesting the presence of antiferromagnetic correlations in the paramagnetic state. Magnetoresistivity at 2 K in 14 T is nearly 1070 % for H // [0001]. The results of heat capacity and $^{151}$Eu Mössbauer spectroscopy are in conformity with a bulk transition at 33.3 K.

1. Introduction

Divalent Eu and trivalent Gd ions are $S$-state ions as the orbital magnetic moment of their half-filled 4f-shell is zero. As a result the single-ion magnetocrystalline anisotropy vanishes in the first order in compounds of these ions. Despite this, anisotropic magnetic behavior is seen in some Eu$^{2+}$ and Gd$^{3+}$ compounds ordering magnetically [1-5]. Typically, the anisotropy is attributed to anisotropic exchange, crystal field effects to higher order and dipolar interactions. In the present work we have probed the magnetic behavior of EuAl$_2$Si$_2$ single crystal using the techniques of magnetization, electrical resistivity and heat capacity in zero and applied fields, and $^{151}$Eu Mössbauer spectroscopy. The single crystals were grown by flux method using the eutectic mixture of Al-Si as flux. EuAl$_2$Si$_2$ is known to crystallize in the trigonal CaAl$_2$Si$_2$-type structure. The magnetic properties of polycrystalline EuAl$_2$Si$_2$ have been reported in the literature [6-7]. Eu ions are in the divalent state (with $L=0$, $S=7/2$) in this compound and order antiferromagnetically at ~ 35 K. Powder neutron diffraction [6] shows that the Eu magnetic moments order according to a collinear antiferromagnetic structure with the wave vector $k = (0,0,1/2)$, made up by an alternating stacking of ferromagnetic layers perpendicular to the [0001] axis, with the moments in the (0001) plane. However, the direction of the moments in the (001) plane is not known.

2. Experimental

Single crystals of EuAl$_2$Si$_2$ were grown by high temperature flux technique using the eutectic composition of Al-Si as flux. The grown crystals were characterized by electron dispersive analysis by x-rays (EDAX) for their stoichiometry. Powder x-ray diffraction data were recorded on a Panalytical x-ray diffractometer to check for phase purity. Crystals were oriented by the back-reflection Laue technique using a Huber Laue diffractometer, and subsequently cut by a spark erosion cutting m
machine for directional dependent measurements. Electrical resistivity and heat capacity in zero and applied magnetic fields were performed in a Quantum Design Physical Properties Measurement System (PPMS). Magnetic susceptibility was measured in a Quantum Design SQUID magnetometer and also in a Quantum Design vibrating sample magnetometer (VSM). The $^{151}$Eu Mössbauer absorption spectra were recorded with a SmF$_3$ $\gamma$-ray source mounted on a constant acceleration electromagnetic drive.

3. Results and Discussion

3.1. Powder x-ray and Laue diffraction

EuAl$_2$Si$_2$ is known to crystallize in a trigonal unit cell with P-3m1 space group (#164, Pearson symbol hP5) in the CaAl$_2$Si$_2$-structure type [6]. The Eu atoms form a hexagonal net in the $ab$-plane and the adjacent layers are separated by distance c. Nonmagnetic Al and Si atoms occupy 2$d$ positions possessing $3m$ symmetry. Figure 1a shows the powder x-ray diffraction data of a few crystals crushed into fine powder.

![Figure 1](image)

Figure 1. (a) Rietveld refinement of powder x-ray diffraction data and (b) Laue diffraction pattern of EuAl$_2$Si$_2$ when incident x-ray beam is perpendicular to the (0001) plane.

The Rietveld refinement provides an excellent fit to the xrd pattern confirming the phase purity of the sample. The estimated lattice parameters are $a = 4.178(3)$ and $c = 7.255(2)$ Å, which are in good agreement with the values previously reported on polycrystalline sample [6]. A Laue pattern (figure 1b) with well-defined spots also reveals the good quality of flux-grown crystals.

3.2. Magnetization

The magnetization of EuAl$_2$Si$_2$ as a function of temperature and field measured along the principal crystallographic directions of [10$ar{1}$0] and [0001] is shown in figure 2(a-d). The inset of figure 2a reveals a nearly isotropic paramagnetic susceptibility following Curie-Weiss behavior over a wide range of temperature. Anisotropy gradually builds up below ~50 K as seen in the main panel of figure 2a. The effective paramagnetic moments $\mu_{\text{eff}}$ are 7.8 and 8.1$\mu_B$/f.u. (theoretical value 7.94 $\mu_B$/Eu$^{2+}$), and the paramagnetic Curie temperatures $\theta_p$ are 36.4 and 33.0 K for H // [10$ar{1}$0] and [0001], respectively. The antiferromagnetic transition is clearly manifested by the peak in the susceptibility at $T_N = 33.3$ K in both directions. Keeping in view the results of Ref. 6, the positive $\theta_p$ values indicate that the dominant interaction is the nearest neighbor ferromagnetic exchange within the (0001) planes, the 3-dimensional ordering being triggered by the weaker antiferromagnetic interplane exchange, the interplane separation c being much larger than the separation between the Eu ions in the $ab$-plane. Below $T_N$, the susceptibility along the $c$-axis is almost constant, which is expected since the ordered moments are perpendicular to c. The susceptibility along the $a$-axis shows a more complex behavior, indicating at least that the Eu moments are not along the $a$-axis, which is confirmed by the magnetization data to be described below.
Figure 2b reveals the evolution of $M/H(T)$ at different values of the field applied along the $a$-axis. The upturn in $M/H$ near 23 K observed at 0.1 T is gradually suppressed as the field is increased, turning into a downturn near 26 K at 1 T. The plateau region between $T_N$ and the temperature at which the downturn occurs is widened as the field is further increased to 2 T. The downturn in $M/H$ at lower temperature is most likely a field induced phase transition due to spin re-orientation, which is also captured in the heat capacity and resistivity data. At 2.5 T, the downturn at lower temperature is pushed below 2 K and the sharp peak at $T_N$ appears as a broad anomaly around 23 K. At 3 T and higher fields the susceptibility plots do not apparently present any evidence of an antiferromagnetic transition. On the other hand for magnetic field parallel to $c$-axis (figure 2c), $T_N$ decreases with field (the peak shifts to lower temperatures) but no additional anomaly (downturn in $M/H$) is observed. At 5 T, the susceptibility below 10 K is nearly temperature independent like in a ferromagnet at temperatures far below the Curie point. The apparent lack of any evidence for an antiferromagnetic transition at 3 T and higher fields in figure 2b, and at 5 T and higher fields in figure 2c is understandable given the values of spin flip fields as determined from the data in figure 2d (see below).

The spin-flip fields at 2K along the $[\overline{1}0\overline{1}0]$ and $[0001]$ directions are 2.8 and 4.8 T, respectively which indicate that $[0001]$ direction is the hard direction of magnetization (figure 2d). The magnetization above the spin-flip field is nearly 7 $\mu_B$/Eu, in excellent agreement with the value expected for the divalent state of the Eu ions. Two closely spaced spin flop transitions occur near $H_{c1}=1.4$ and $H_{c2}=1.6$ T along $[\overline{1}0\overline{1}0]$ but the magnetization does not vanish below $H_{c1}$, indicating that the Eu moments do not lie along the $a$-axis. The unequal spin-flip fields point to the presence of anisotropic exchange and/or of non negligible dipolar interactions.

3.3. Electrical Transport
Electrical resistivity as a function of temperature $\rho(T)$ is presented in figure 3a for current density $J$ parallel to $a$ and $c$-axis, respectively. The variation of $\rho(T)$ is typical of a metal and a pronounced anomaly is observed at the antiferromagnetic transition. A shallow minimum occurs in the vicinity of $T_N$ in the paramagnetic region which is attributed to antiferromagnetic fluctuations.
At temperatures well above \( T_N \), \( \rho(T) \) can be fitted to the Bloch-Grüneisen formula:

\[
\rho(T) = A + B \left( \frac{T}{\theta_R} \right)^5 \int_0^{\theta_R} \frac{x^5}{(e^x-1)(1-e^{-x})} \, dx.
\]

In the above equation, A is temperature independent part of electrical resistivity, which can be considered as a sum of spin disorder resistivity (\( \rho_{sd} \)) and residual resistivity (\( \rho_0 \)) arising from lattice imperfections and/or dislocations, and B is a material dependent parameter. The values of A and the Debye temperature \( \theta_R \) determined from the fit are listed in Table 1.

Table 1 Parameters derived from the Bloch-Grüneisen fit to the resistivity data and observed residual resistivity ratio (RRR).

| \( J/\{10\bar{1}0\} \) | \( J/\{0001\} \) |
|--------------------------|--------------------------|
| \( \rho_0 + \rho_{sd} \) (\( \mu\Omega \text{ cm} \)) | \( \rho_0 + \rho_{sd} \) (\( \mu\Omega \text{ cm} \)) |
| 55.4 | 20.2 |
| \( \rho_0 \) at 2 K (\( \mu\Omega \text{ cm} \)) | \( \rho_0 \) at 2 K (\( \mu\Omega \text{ cm} \)) |
| 7.9 | 6.2 |
| \( \theta_R \) (K) | \( \theta_R \) (K) |
| 478 | 514 |
| RRR | RRR |
| 29 | 16 |
| \( \rho(300K)/\rho(2K) \) | \( \rho(300K)/\rho(2K) \) |
| 478 | 514 |

Unlike the magnetic susceptibility, we observe a significant anisotropy in the resistivity even in the paramagnetic region which is most likely due to an anisotropic Fermi surface of tetragonal EuAl\(_2\)Si\(_2\). Figure 3b shows the plot of magnetoresistivity, MR, at 2 K for \( I/\{10\bar{1}0\} \) and \( H/\{0001\} \). The MR is defined as \( \text{MR(\%)} = \frac{\rho(H) - \rho(0)}{\rho(0)} \times 100 \% \). A colossal value of MR = 1070 \% is observed at 2 K in 14 T. A positive MR is typically seen in antiferromagnets. We plan to probe in detail in a future work the origin of the giant value of MR in EuAl\(_2\)Si\(_2\).

3.4. Heat Capacity

The heat capacity \( C_p(T) \) of EuAl\(_2\)Si\(_2\) is shown in figure 4. There is a sharp anomaly at \( T_N = 33.3 \text{ K} \) marking the bulk magnetic phase transition. The main anomaly shifts down to 32.5 K in a magnetic field of 1 T, as expected in an antiferromagnet, applied parallel to \( [10\bar{1}0] \) while an additional field-induced anomaly appears at 25.9 K, in very good correspondence with the susceptibility (figure 2b).

We have fitted the following expression to the zero field \( C_p(T) \) data in the range 100-300 K.

\[
C = \gamma T + C_E + C_D,
\]

Where the first term is the conduction electron contribution, \( \gamma \) being the Sommerfeld coefficient, \( C_E \) and \( C_D \) are contributions to the heat capacity furnished by the Einstein and Debye formulae, respectively, given by the following expressions.
\[ C_E = 3 n_E R \frac{y^2 e^y}{(e^y-1)^2} \]  
and  
\[ C_D = 9 n_D R \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} x^4 e^x \frac{dx}{(e^x-1)^2} \]  \tag{3}

Here \( x = \theta_D/T \), \( y = \theta_E/T \), \( \theta_D \) and \( \theta_E \) are the Einstein and Debye temperatures, respectively. \( n_E \) is the number of Einstein modes and \( n_D \) is the number of Debye oscillators per formula unit in the phonon spectrum, used as integral fitting parameters under the constraint \( n_D + n_E = 5 \) (i.e. number of atoms per formula unit). We have obtained the best fit to the data for \( \theta_D = 481 \text{ K}, \theta_E = 114 \text{ K}, \gamma = 20 \text{ mJ/mol K}^2, n_D = 4 \) and \( n_E = 1 \). The Einstein mode is presumably contributed by the heavier Eu ions while Al and Si account for the Debye modes in the phonon spectrum. The classical Dulong and Petit high temperature limit \( 3nR \) of the heat capacity is not fully reached at room temperature, which is most likely due to the high Debye temperature of this material. It may be noted that Debye temperature determined from the temperature dependence of electrical resistivity and heat capacity are in close agreement.

The entropy associated with the magnetic ordering of the Eu ions was obtained by subtracting the phonon contribution provided by the fitted data. A limiting value of 16.4 J/mol K is obtained, which is just about 5% less than the theoretical value of \( R \ln 8 \) (17.3 J/mol K).

Figure 4. (a) Heat capacity data \( C_p(T) \) of EuAl\(_2\)Si\(_2\) in 0 and 1 T // [10\(\overline{1}0\)], (b) The solid black line is obtained by fitting the zero field heat capacity data between 100 to 300 K to equation 2.

3.5. Mössbauer spectra

Figure 5. (a) \(^{151}\)Eu Mössbauer spectra at selected temperatures in EuAl\(_2\)Si\(_2\). The lines are fits to a single hyperfine field pattern, (b) thermal variation of the hyperfine field in EuAl\(_2\)Si\(_2\).
\(^{151}\) Eu absorption Mössbauer spectra were recorded in EuAl\(_2\)Si\(_2\) in the temperature range 4.2-34 K. Spectra at selected temperatures are represented in Figure 5. The spectra between 4.2 K and 33 K are single hyperfine field spectra; at 34 K, the spectrum consists of a narrow single line, i.e. the whole sample is paramagnetic. The spectra are typical for divalent Eu, with an Isomer Shift of -10.1(1) mm/s. The hyperfine field decreases monotonically up to 33 K; its thermal variation is represented in figure 5b.

The mean field law for \(S=7/2\) is seen to match the temperature variation of the hyperfine field with a Néel temperature of 35 K, close to \(T_N\) of 33.3 K determined by bulk measurements. From Mössbauer spectra we conclude that EuAl\(_2\)Si\(_2\) behaves as a standard Eu\(^{2+}\) material, with a saturated hyperfine field of 27.3 T, a single moment (antiferro)magnetic structure (i.e. no incommensurate modulation), the paramagnetic phase being reached through a 2\(^{\text{nd}}\) order transition with \(T_N\) close to 34 K. The saturated hyperfine field at 4.2 K is in excellent agreement with 28 T reported in Ref.2. However, in this latter work, the Mössbauer spectra between 37 and 32 K were fitted with two superimposed subspectra, with only one of them showing a magnetic hyperfine field splitting. While such a situation may arise due to a first order phase transition (assuming the sample is phase pure and there is no impurity divalent phase which orders below 32 K), with the co-existence of paramagnetic and magnetically ordered phases in the transition region, we do not observe such a behavior in our sample.

4. Conclusion

We have grown a single crystal of EuAl\(_2\)Si\(_2\) for the first time using Al-Si flux. We observe signatures in magnetic susceptibility, electrical resistivity and magnetic susceptibility that EuAl\(_2\)Si\(_2\) orders antiferromagnetically at 33.3 K with (0001) being the easy plane. The susceptibility is largely isotropic in the paramagnetic region, but it exhibits anisotropy in the ordered state. The upturn in the resistivity near Néel temperature in the paramagnetic region can be inferred as persistence of antiferromagnetic fluctuations above \(T_N\). A huge magnetoresistance is observed for field parallel to the \(c\)-axis below \(T_N\). The heat capacity data confirm the bulk nature of the magnetic transition at \(T_N\) and also the field induced spin reorientation below \(T_N\) for 1 Tesla field parallel to the \(a\)-axis. The \(^{151}\) Eu Mössbauer spectra are characteristic of divalent Eu in EuAl\(_2\)Si\(_2\), with a single moment antiferromagnetic structure and a saturated hyperfine field of 27.3 T. The thermal variation of the hyperfine field follows a \(S=7/2\) mean field curve, indicating a second order transition.

References

[1] Garnier A, Gignoux A, Schmitt D, Shigeoka T 1996 Physica B 222 80.
[2] W. Bauhofer, E. Gmelin, M. Möllendorf, R. Nesper, H.G. Von Schnering 1985 J. Phys. C 18 3017.
[3] Bonville P, Hodges J A, Shirakawa M, Kasaya M, D. Schmitt 2001 Eur. Phys. J. B 21 349.
[4] Kumar N, Dhar S K, Thamizhavel A, Bonville P and Manfrinetti P 2010 Phys. Rev. B 81 144414.
[5] Maurya A, Bonville P, Thamizhavel A, Dhar S K 2014 J. Phys.: Condens. Matter 26 216001.
[6] Schobinger-Papamantellos P, Hulliger F 1989 J. Less-Common Met. 146 327.
[7] Kranenberg C, Johrendt D, Mewis A, Pöttgen R, Kotzyba G, Rosenhahn C, Mosel B D 2000 Solid State Sci. 2 215.