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Anisotropic magnetic behavior in $EuIr_2Ge_2$ single crystal

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Abstract

We present a complete characterization of the magnetic properties of indium-flux grown single crystals of $EuIr_2Ge_2$ using electrical resistivity, magnetization, specific heat, magnetoresistance and ^{151}Eu Mössbauer spectroscopy. All results indicate that Eu ions in $EuIr_2Ge_2$ are in the divalent state with Eu moments ordering antiferromagnetically at $T_N = 20.5$ K. While at higher temperatures the susceptibility χ is isotropic as expected for the pure spin nature of the Eu local moment, below 40 K a pronounced anisotropy emerges, with χ_{ab} in the basal plane being a factor of two larger than χ_c along c at T_N. We observed a pronounced metamagnetic transition in the in-plane magnetization, which is also reflected in a step-like increase of the magnetoresistance. Further analysis of the data indicates that the metamagnetic transition is related to a spin–flop transition. The origin of this strong anisotropy and of the pronounced metamagnetic transition is discussed.

1. Introduction

The intermetallic rare earth compounds RT_2X_2 (R = rare earth, T = transition metal and X = Si, Ge) are well known for their diverse physical properties, e.g. intermediate valence, Kondo effect, metamagnetic transition, heavy fermion behavior, superconductivity etc. Most of these phenomena are due to unstable 4f shells. Among these compounds the Eu based ones attract attention because of its unstable valence, which can be tuned from a magnetic ($J = 7/2$) Eu^{2+} ($4f^7$) to a nonmagnetic ($J = 0$) Eu^{3+} ($4f^6$) configuration by applying pressure or by changing the local chemical environment. The RIr_2X_2 (R = rare earth, X = Ge, Si) series of compounds presents interesting magnetic properties. For example, $LaIr_2Ge_2$ exhibits superconductivity at 1.5 K [1] and the Kondo lattice system $CeIr_2Ge_2$ shows heavy fermion and non-Fermi-liquid behavior [2, 3], while the heavy fermion system $YbIr_2Si_2$ exhibits Fermi liquid behavior at low temperature [4] and pressure induced magnetic order [5]. A valence fluctuating behavior of Eu ions in $EuIr_2Si_2$ has been reported from ^{151}Eu Mössbauer spectroscopy and magnetic susceptibility measurements by Chevalier *et al* [6] and Patil *et al* [7]. With the expectation that replacing Si by larger Ge would move the system towards the magnetic–nonmagnetic boundary we have synthesized and investigated $EuIr_2Ge_2$. This compound is reported to form in the $ThCr_2Si_2$ structure [1]. Here we present the magnetic and transport properties of $EuIr_2Ge_2$ single crystals based on magnetic susceptibility, specific heat, electrical resistivity, magnetoresistance and Mössbauer spectroscopy measurements.

2. Experimental details

We have grown $EuIr_2Ge_2$ single crystals using an indium-flux growth method similar to that described in [8]. Dilute HCl was used to remove single crystals from indium flux. We obtained plate-like $EuIr_2Ge_2$ single crystals with dimensions as large as 4 mm × 2 mm × 0.5 mm. The phase purity was checked by powder x-ray diffraction of crushed single crystals and scanning electron microscope (SEM) images. The composition of the crystal was checked by energy dispersive x-ray analysis (EDAX). Magnetization measurements were performed using a commercial superconducting quantum interference device (SQUID) magnetometer. Electrical resistivity and specific heat measurements were carried out using AC transport and heat capacity options of a physical property measurement system (PPMS, Quantum Design). ^{151}Eu Mössbauer spectra were recorded at various temperatures using a conventional constant

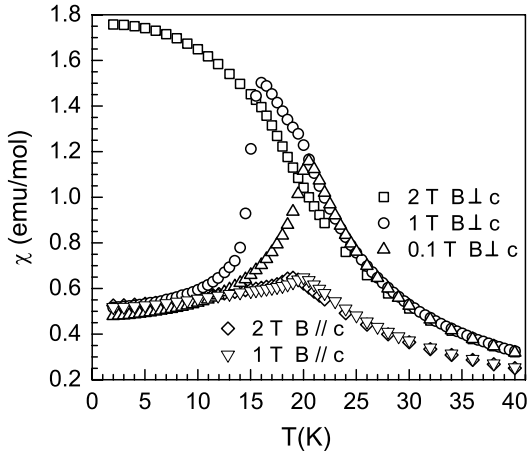

Figure 1. Magnetic susceptibility data of an $EuIr_2Ge_2$ single crystal as a function of temperature for $B \parallel c$ and $B \perp c$ at three different fields, $B = 0.1$, 1 and 2 T.

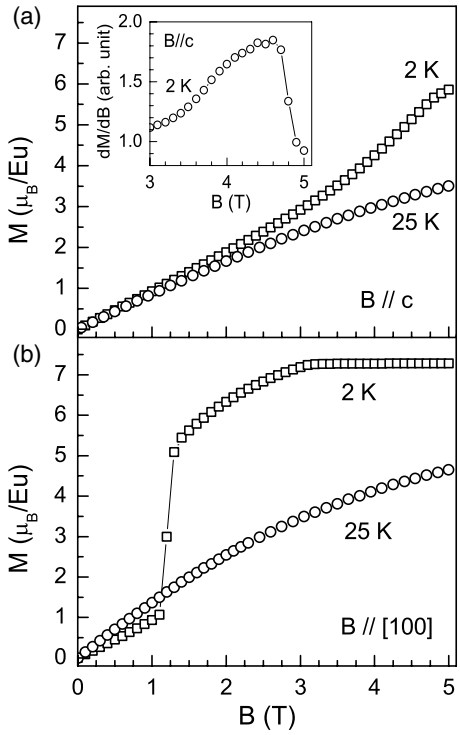

Figure 2. Isothermal magnetization data of $EuIr_2Ge_2$ as a function of magnetic field at 2 and 25 K for magnetic field applied (a) along the c-axis and (b) in the basal plane along [100]. The inset in (a) shows the derivative of magnetization data for $B \parallel c$ at 2 K.

acceleration spectrometer equipped with a $^{151}SmF_3$ source (21.6 keV transition) at room temperature. The Mössbauer studies were performed on an absorber prepared by powdering the crystals (no sieving was done). Our spectrometer gives a typical line width of about 2.9 mm s^{-1} for the EuF_3 absorber. The velocity was calibrated using an α-Fe absorber and the isomer shifts were measured with respect to EuF_3.

3. Results and discussion

Powder x-ray diffraction pattern of crushed $EuIr_2Ge_2$ single crystals revealed the single phase nature of the samples which form in $ThCr_2Si_2$-type tetragonal structure (space group $I4/mmm$) with lattice parameters $a = 4.1677(6)$ Å and $c = 10.5509(23)$ Å. The lattice parameters are in fair agreement with the reported ones $a = 4.172(4)$ Å and $c = 10.543(9)$ Å [1]. The EDAX analysis shows the sample to have the desired composition, 1:2:2.

The temperature dependence of the magnetic susceptibility of the $EuIr_2Ge_2$ single crystal is shown in figure 1 for two different orientations of magnetic field, i.e. B in the ab-plane and B along the crystallographic c-axis. At high temperature the susceptibility is almost isotropic, as usually observed for a stable divalent Eu state. Since it bears a spin only ($J = S = 7/2$) moment, one expects only a very weak anisotropy. In contrast, we observe an increasing anisotropy below 40 K, with the susceptibility for B in the basal plane (χ_{ab}) being a factor of 3.5 larger than that for B along the c-axis at 2 K and 2 T (figure 1) implying that the easy axis lies in the ab-plane. χ_{ab} increases quite strongly below 40 K and exhibits a well defined peak at $T_N = 20.5$ K for $B = 0.1$ T, which indicates an antiferromagnetic transition (see figure 1). For $B = 1$ T the data show a change of slope at $T_{N2} = 19.5$ K and a sharp drop below $T_{N1} = 16$ K. We further notice a strong change in low temperature magnetization between 1 and 2 T. For $B = 2$ T, the pronounced drop in $\chi_{ab}(T)$ has disappeared and χ_{ab} continuously increases with decreasing temperature before saturating below 4 K. This type of behavior indicates the presence of a field induced metamagnetic transition. A clear signature of magnetic transition at $T_N = 20$ K is also seen for $B \parallel c$; however, the magnitude of the anomaly is much weaker. Application of a larger field does not induce significant changes. In the paramagnetic regime the inverse susceptibility (at $B = 2$ T) follows a Curie–Weiss behavior, $\chi = C/(T - \theta_p)$, in the temperature range 50–300 K, with an effective magnetic moment $\mu_{eff} = 7.84\ \mu_B$ and a Weiss temperature $\theta_p^{ab} = +18.8$ K for B in the basal plane and $\mu_{eff} = 7.76\ \mu_B$, $\theta_p^c = +11.6$ K for B along c. The values of effective moments are close to the theoretically expected value 7.98 μ_B for Eu^{2+} ions, while the positive θ_p values indicate predominantly ferromagnetic inter-site interactions.

The presence of a metamagnetic transition is confirmed by magnetization measurements. The magnetization $M(B)$ measured at 2 and 25 K for B along [100] in the ab-plane and B along c are shown in figure 2. For $B \parallel$ [100] the magnetization at 2 K shows a sudden increase at the critical field $B_{C1} = 1.2$ T followed by a linear increase up to $B_{C2} = 3.2$ T, where the magnetization reaches its saturation value of 7.3 μ_B/Eu. Therefore, we can associate B_{C1} and B_{C2} with the $T_{N1}(B)$ and $T_{N2}(B)$ phase boundaries, respectively. This allows us to draw the phase diagram for field along [100] in the basal plane (figure 3). The B–T phase diagram is based on the magnetization measurements for different values of magnetic fields and temperatures. The low field antiferromagnetic phase AF_1 is separated from the high field AF_2 phase by the metamagnetic transition at $T_{N1}(B)$, while the phase AF_2 is separated from the paramagnetic phase by a weak anomaly

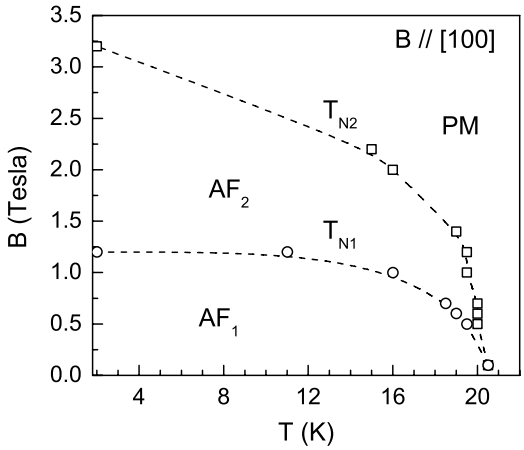

Figure 3. The tentative phase diagram of $EuIr_2Ge_2$ for magnetic field applied along [100] in the basal plane.

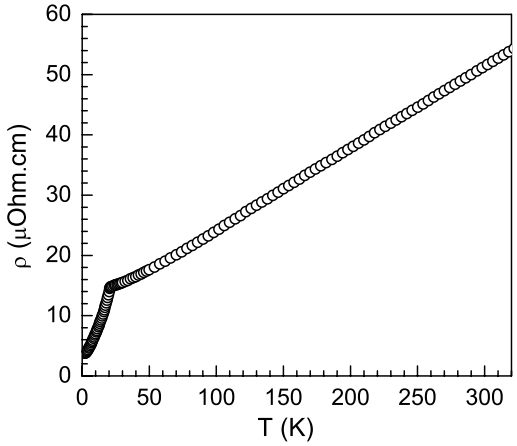

Figure 5. Zero field in-plane resistivity of $EuIr_2Ge_2$ as a function of temperature in the temperature range 2–300 K.

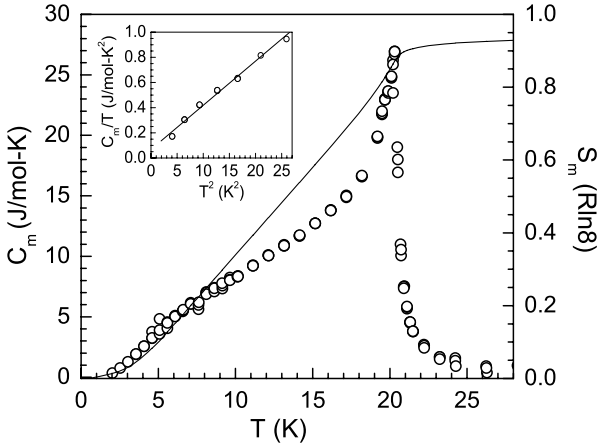

Figure 4. The temperature dependence of the magnetic contribution to the specific heat of $EuIr_2Ge_2$. The solid line represents the magnetic entropy obtained by integrating the C_m/T versus T curve. The inset shows the low temperature specific heat data plotted as C_m/T versus T^2.

(change of slope) at $T_{N2}(B)$. The phase diagram for B along [110] is very similar to that for B along [100], except that $T_{N1}(B)$ is shifted to slightly higher field. Although not so well pronounced, a field induced metamagnetic transition is also observed at $B = 4.6$ T for $B \parallel c$ in the magnetically ordered state at 2 K. This is more clearly seen in the dM/dB versus B plot (inset of figure 2(a)). The saturation magnetization is not reached up to $B = 5$ T.

In figure 4 we have plotted the magnetic part C_m of the specific heat obtained by subtracting the specific heat of the nonmagnetic compound $LaIr_2Ge_2$ as well as the magnetic entropy obtained by integrating the C_m/T curve. The prominent peak in the specific heat data at ∼20.3 K with a peak height of ∼27 J mol^{-1} K^{-1} corresponds to the magnetic transition. In the magnetically ordered state, below 5 K, i.e. far below T_N, the magnetic part of specific heat follows a power law, $C_m = \gamma T + \beta T^3$, with $\gamma = 68 \pm 14$ mJ mol^{-1} K^{-2} and $\beta = 35 \pm 1$ mJ mol^{-1} K^{-4} (inset of figure 4). The specific heat coefficients are large compared to $\gamma = 6.18$ mJ mol^{-1} K^{-2} and $\beta = 27.96$ mJ mol^{-1} K^{-4} for Eu metal [9]. A large γ value was also observed in antiferromagnetically ordered $EuCu_2Ge_2$ [10]. While the relatively large value of γ can be attributed to a slightly enhanced Sommerfeld coefficient, the βT^3 term is attributed to the AF magnons. The observation of a T^3 term in the magnetic part of the specific heat far below T_N indicates that the excitation gap in the magnon dispersion curve is very small, implying that the moments are free to rotate within at least one plane, here probably the ab-plane. The magnetic entropy at T_N is ∼0.9 R ln(8), which is close to the R ln(8) expected for the $J = 7/2$ state of Eu^{2+} ions.

The electrical resistivity of $EuIr_2Ge_2$ as shown in figure 5 has metallic behavior with room temperature resistivity $\rho_{300} \sim 52$ $\mu\Omega$ cm and a residual resistivity ratio (RRR) of ∼14. The high residual resistivity ratio together with a low residual resistivity $\rho_0 \sim 3.6$ $\mu\Omega$ cm at 2 K confirms the good quality of our sample. The resistivity data also show a sharp transition at T_N followed by a rapid decrease in resistivity below the transition temperature due to reduction in spin disorder scattering.

We have also investigated the field dependence of the electrical resistivity. The normalized magnetoresistance, defined as $[\rho(B) - \rho(0)]/\rho(0)$ for $T = 2$ and 25 K, is shown in figure 6 for both $B \parallel c$ and $B \perp c$. A sharp positive step at $B \sim 1.2$ T for $B \perp c$ and a broad maximum at ∼5.5 T for $B \parallel c$ at 2 K reflect the metamagnetic transition observed in the magnetization data for $B \perp c$ and $B \parallel c$, respectively. For $B \perp c$, T_{N2} is also nicely seen as an inflection point in $\rho(B)$ (marked with an arrow in figure 6). The behavior is thus well consistent with the magnetization data along both directions. In the paramagnetic state (at 25 K) the magnetoresistance is negative, as expected from the reduction of spin disorder scattering caused by spin alignment along the external magnetic field. This type of positive and negative magnetoresistance data in the magnetically ordered and in the paramagnetic state had also been observed in single crystals of $EuCu_2Ge_2$ [10] and $EuCo_2Ge_2$ [11]. Qualitatively, our results on $EuIr_2Ge_2$ are similar to those reported for $EuCo_2Ge_2$, with the difference that the anisotropy and the metamagnetic transition are much more pronounced in $EuIr_2Ge_2$.

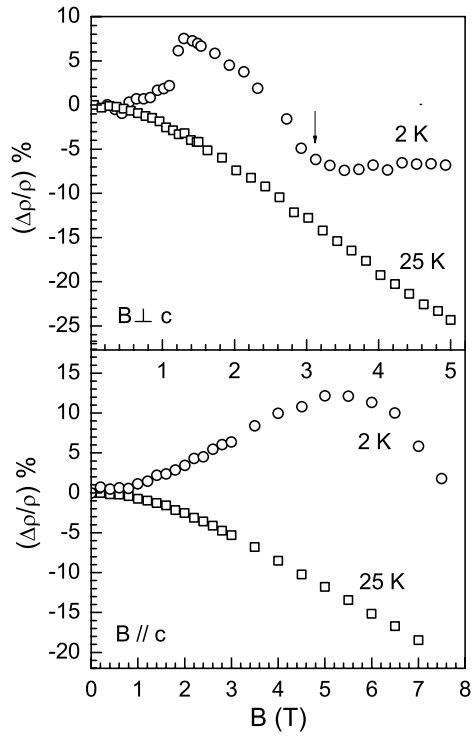

Figure 6. Magnetoresistance at 2 and 25 K as a function of magnetic field for $B \perp c$ and $B \parallel c$. Electric current was flowing within the *ab*-plane.

The magnetic order in $EuIr_2Ge_2$ was further investigated using ^{151}Eu Mössbauer spectroscopy. Mössbauer spectra were recorded at selected temperatures in the paramagnetic state and the magnetically ordered state (figure 7). The spectra showed strong asymmetry at all temperatures. Below 21 K the line width increases, indicating the onset of magnetic order. The best fit to the experimental spectra was obtained by including a quadrupole interaction parameter in the least squares fit procedure. The isomer shift observed was -9.7 mm s^{-1} (relative to EuF_3 at 300 K), firmly establishing the divalent character of Eu ions in $EuIr_2Ge_2$, consistent with the magnetic susceptibility data. In the paramagnetic state, we obtain an effective quadrupole interaction ($q_{\rm eff}$) of about -13 ± 0.5 mm s^{-1}, whereas in the magnetically ordered state at 4.2 K the effective quadrupole interaction is about 6 ± 0.5 mm s^{-1}. In the magnetically ordered state one measures only the gradient component along the magnetic hyperfine field, i.e. $q_{\rm eff} \propto (3\cos^2\theta - 1)$. Thus the angle θ between the magnetic hyperfine field and the *c*-axis can be calculated and is found to be about 90°. This shows that below $T_{\rm N}$ the Eu spins order in the basal plane, in agreement with the magnetization data. The hyperfine field $B_{\rm hf} \sim 33.1$ T obtained at 4.2 K is in fair agreement with that expected for the Eu^{2+} ion ($B_{\rm hf} = -34$ T) [12, 13]. Our Mössbauer results on $EuIr_2Ge_2$ are very similar to those of $EuRu_2Ge_2$ except that the latter has much larger quadrupole interaction of -25 mm s^{-1} and 12 mm s^{-1} in the paramagnetic and magnetically ordered state respectively [14]. This is most probably related to the short *c* parameter of 10.180 Å and long *a* of 4.263 Å for $EuRu_2Ge_2$ compared to the lattice parameters of $EuIr_2Ge_2$ ($c = 10.5509(23)$ Å and $a = 4.1677(6)$ Å).

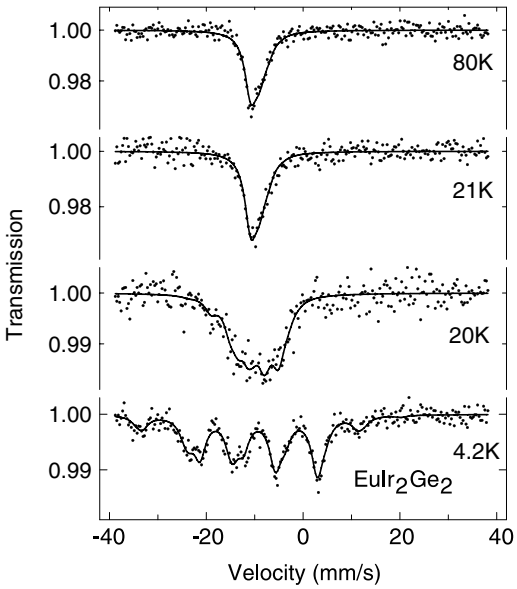

Figure 7. Mössbauer spectra of $EuIr_2Ge_2$ in the paramagnetic and magnetically ordered states.

4. Conclusion

The susceptibility, specific heat and Mössbauer spectra conclusively evidence a stable divalent Eu state, which undergoes a transition to an antiferromagnetic state at $T_{\rm N} = 20.5$ K. In contrast to the expectation for the pure spin nature of the Eu^{2+} local moment, we observe a pronounced anisotropy below 40 K in the susceptibility, magnetization and magnetoresistance. The low temperature magnetization and the Mössbauer spectroscopy results reveal that in the magnetically ordered state the magnetic moments lie in the basal plane. A pronounced field induced metamagnetic transition is observed.

With increasing field in the basal plane, two transitions emerge from $T_{\rm N}$ at $B = 0.1$ T, one at a lower field $B_{\rm C1}$ and lower temperature $T_{\rm N1}$ corresponding to a very sharp metamagnetic transition, while the second one at higher field $B_{\rm C2}$ and higher temperature $T_{\rm N2}$, showing only a weak anomaly, corresponds to the transition from the antiferromagnetic to paramagnetic state. Both transitions are also well observed in the magnetoresistance. Below 40 K and above $T_{\rm N1}$, the susceptibility in the basal plane is much larger than that along the *c*-axis. This suggests that the moments order within the basal plane, which is further confirmed by Mössbauer spectroscopy results. However, the metamagnetic transition observed for magnetic field applied in the basal plane and its weak anisotropic behavior within the basal plane is then not easy to explain. We suspect that this unusual behavior is the result of competing RKKY exchange and dipolar interactions, which get comparatively large because of the large Eu moments and the rather weak RKKY exchange as deduced from a comparatively low $T_{\rm N}$. A further interesting aspect of this compound is that since Eu in $EuIr_2Ge_2$ is in the stable divalent state, which orders magnetically below 21 K, application of isostatic pressure or a chemical substitution of

Ge by Si should suppress the magnetic order, leading to some kind of critical point.

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