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Metamagnetic transition in $EuFe_2As_2$ single crystals

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Abstract. We report the measurements of the anisotropic magnetization and magnetoresistance (MR) on single crystals of $EuFe_2As_2$, a parent compound of ferro-arsenide high-temperature superconductor. Apart from the antiferromagnetic (AFM) spin density wave (SDW) transition at 186 K associated with Fe moments, the compound undergoes another magnetic phase transition at 19 K due to AFM ordering of Eu^{2+} spins ($J = S = 7/2$). The latter AFM state exhibits metamagnetic (MM) transition under magnetic fields. Upon applying magnetic field with $H \parallel c$ at 2 K, the magnetization increases linearly to $7.0\,\mu_B$ f.u.$^{-1}$ at $\mu_0 H = 1.7$ T and then remains at this value for saturated Eu^{2+} moments under higher fields. In the case of $H \parallel ab$, the magnetization increases step-like to $6.6\,\mu_B$ f.u.$^{-1}$ with small magnetic hysteresis. An MM phase was identified with the saturated moments of $4.4\,\mu_B$ f.u.$^{-1}$. The MM transition accompanies negative in-plane MR, reflecting the influence of Eu^{2+} moments ordering on the electrical conduction of FeAs layers. These results were explained in terms of spin-reorientation and spin-reversal based on an A-type AFM structure for Eu^{2+} spins. The magnetic phase diagram has been established.

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Contents

1. Introduction

The discovery of high-temperature superconductivity in $LnFeAsO_{1-x}F_x$ (Ln = lanthanides) [1]–[3] has stimulated intense research in the field of condensed matter physics. A superconducting transition temperature of 55 K or more has been achieved by either high-pressure synthesis [4, 5] or the Th-doping strategy [6]. It has been accepted that the key structural unit of the superconductors is the antifluorite-type $[Fe_2As_2]^{2-}$ layers. This point of view is manifested by the observation of superconductivity up to ~38 K in $Ba_{1-x}K_xFe_2As_2$ [7], $Sr_{1-x}K_xFe_2As_2$ [8, 9], $Ca_{1-x}Na_xFe_2As_2$ [10] and $Li_{1-x}FeAs$ [11], all of which contain similar $[Fe_2As_2]^{2-}$ layers. Another important point is that the Fe sublattice of the parent compound is antiferromagnetic (AFM) in the ground state [12, 13] and superconductivity is induced by suppressing the AFM order through appropriate carrier doping.

$EuFe_2As_2$ [14] belongs to the so-called '122' family, AFe_2As_2 (A = Ba, Sr, Ca and Eu), and it stands out due to the magnetic moments of Eu^{2+}. We have recently performed systematic physical property measurements on a $EuFe_2As_2$ polycrystalline sample [15]. A very similar magnetic transition related to Fe_2As_2 layers was revealed between $EuFe_2As_2$ and $SrFe_2As_2$. By assuming that Eu^{2+} moments are compatible with superconductivity, we had anticipated that superconductivity might be realized by proper doping in $EuFe_2As_2$ systems. As a matter of fact, superconductivity was indeed obtained in $Eu_{0.5}K_{0.5}Fe_2As_2$ and $Eu_{0.7}Na_{0.3}Fe_2As_2$, according to very recent reports [16, 17].

Although the free Eu^{2+} moments do not directly affect superconductivity, the study of the ordering of Eu^{2+} moments may shed light on the mechanism of high-temperature superconductivity in iron arsenides. Our previous work [15] indicated that the magnetic ordering of Eu^{2+} moments in $EuFe_2As_2$ was very intriguing. While the Eu^{2+} spins ($S = 7/2$, $L = 0$) order antiferromagnetically below 19 K at zero field, the Curie–Weiss fit of high-temperature magnetic susceptibility suggests ferromagnetic (FM) interactions between the Eu^{2+} spins. When applying a magnetic field, a metamagnetic (MM) transition was found at ~0.65 T. To further understand the intrinsic properties of this magnetically ordered material, we performed measurements of the anisotropic magnetization and magnetoresistance (MR) on single crystals of $EuFe_2As_2$. As a result, anisotropic MM transitions were uncovered. What is more, the electrical conduction of FeAs layers was found to be related to the magnetic state of Eu layers.

2. Experimental details

Single crystals of $EuFe_2As_2$ were grown using FeAs as the self-flux, similar to a previous report [18]. FeAs was presynthesized by reacting Fe powders with As shots in vacuum at 773 K

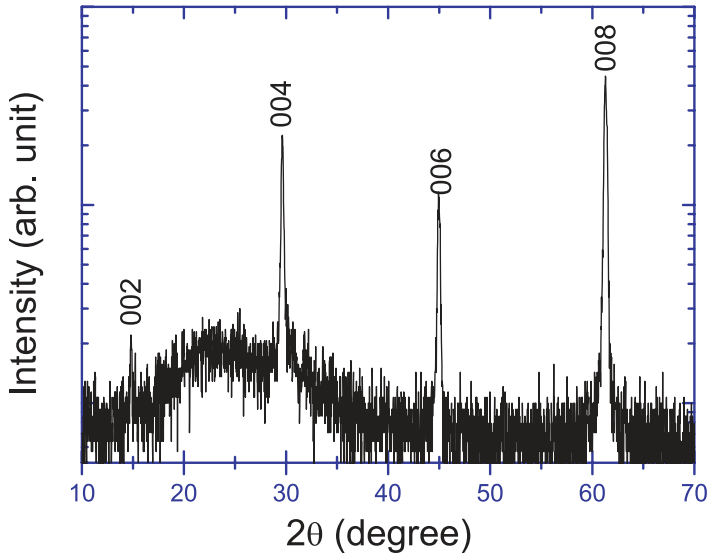

Figure 1. X-ray multiple diffraction pattern for $EuFe_2As_2$ plate-like crystals lying on the sample holder. Note that the logarithmic scale was employed for the intensity axis to verify the sample quality. The hump around $2\theta = 25^\circ$ is due to the diffractions of the glass sample holder.

for 6 h and then at 1030 K for 12 h. Fresh Eu grains and FeAs powders were thoroughly mixed in a molar ratio of 1:4. The mixture was loaded into an alumina tube which was put into a quartz ampoule. The sealed quartz ampoule was heated to 1053 K at a heating rate of 150 K h^{-1} and then held at this temperature for 10 h. Subsequently, the temperature was raised to 1398 K in 3 h and then held at this temerature for 5 h. The crystals were grown by slow cooling to 1223 K at a cooling rate of 2 K h^{-1}. Finally, the quartz ampoule was furnace-cooled to room temperature. Many shiny plate-like crystals with the typical size of $1.5 \times 1.5 \times 0.1$ mm^3 were obtained.

X-ray diffraction (XRD) was performed using a D/Max-rA diffractometer with Cu-K_α radiation and a graphite monochromator. Figure 1 shows the XRD pattern of $EuFe_2As_2$ crystals. Only (00l) reflections with even l appear, indicating that the c-axis is perpendicular to the crystal plane. The c-axis was calculated as 12.11 Å, consistent with our previous measurement using polycrystalline samples [15].

Electrical resistivity was measured using a standard four-terminal method under magnetic field up to 5 T. The dc magnetization was measured on a Quantum Design magnetic property measurement system (MPMS-5). The plate-like crystal was carefully mounted on a sample holder, so that the applied field was basically perpendicular or parallel to the crystallographic c-axis. The deviation angle was estimated to be less than 5°.

3. Results and discussion

Figure 2 shows the temperature dependence of magnetic susceptibility (χ) of $EuFe_2As_2$ crystals in two orientations of the magnetic field. At high temperatures ($T > 50$ K), there is no difference between χ_{ab} and χ_c, indicating isotropic susceptibility. In the range of $19\,\text{K} \leqslant T < 50\,\text{K}$, however, a significant anisotropy in susceptibility (e.g. $\chi_{ab}/\chi_c = 1.35$ at 19 K) shows up, suggesting an anisotropic magnetic interaction. Below 19 K, χ_{ab} decreases very sharply, while

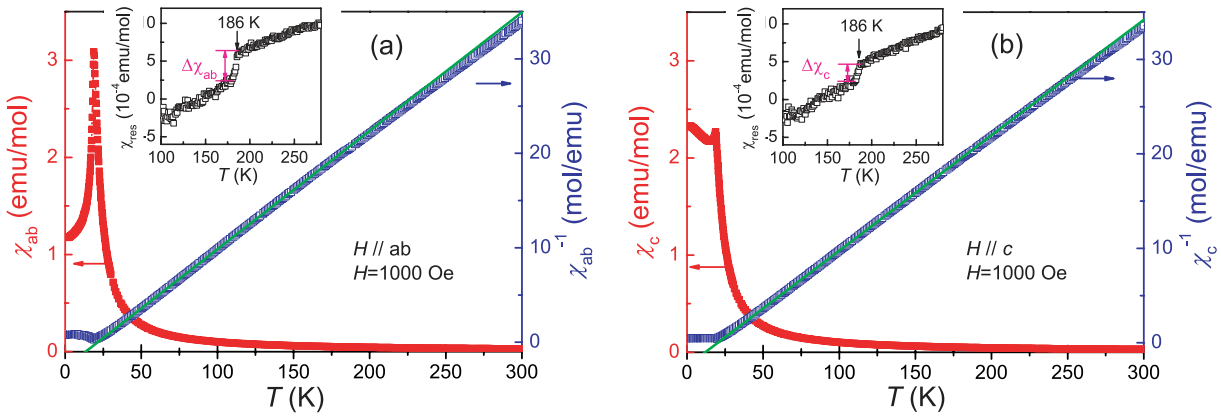

Figure 2. Temperature dependence of magnetic susceptibility of $EuFe_2As_2$ crystals with the magnetic field ($\mu_0 H = 0.1$ T) perpendicular (a) and parallel (b) to the crystallographic c-axis. The straight lines are guides to the eyes. Both the insets show a drop in χ at 186 K, after subtraction of the Curie–Weiss contribution of Eu^{2+} moments.

Table 1. Magnetic parameters from the fitting of the high-temperature (50–180 K) susceptibility data for $EuFe_2As_2$ crystals using equation (1).

Fitted parameters	$H \parallel ab$	$H \parallel c$
χ_0 (emu mol^{-1})	−0.000 22	−0.000 82
C (emu K mol^{-1})	7.99	8.31
θ (K)	−21.4	−19.7
μ_{eff} (μ_B f.u.$^{-1}$)	7.97	8.13

χ_c remains almost constant with decreasing temperature, indicating a Neel transition. This observation strongly suggests that the Eu^{2+} moments align with the ab planes, which is different from the previous proposal by the Mössbauer ^{151}Eu study [19].

The high-temperature $\chi(T)$ data follow the extended Curie–Weiss law,

$$\chi = \chi_0 + \frac{C}{T+\theta}, \tag{1}$$

where χ_0 is the temperature-independent term of the susceptibility, C the Curie constant and θ the Weiss temperature. The fitted parameters and the derived effective magnetic moments are listed in table 1. For both $H \parallel c$ and $H \parallel ab$, the experimental value of Eu^{2+} moments is close to the theoretical value of $g\sqrt{S(S+1)} = 7.94\,\mu_B$ with $S = 7/2$ and $g = 2$. The Weiss temperature is negative, indicating predominately FM interaction among Eu^{2+} spins. To reconcile the AFM ordering and the FM interaction, and considering the enhanced χ_{ab} just above the Neel temperature, the Eu^{2+} spins probably align ferromagnetically within the ab planes, but antiferromagnetically along the c-axis (see the inset of figure 5). This magnetic structure of the Eu sublattice resembles that of $LaMnO_3$, which was called A-type antiferromagnetism [20]. A more relevant example is RNi_2B_2C (R = Pr, Dy and Ho) whose magnetic structure is also A-type [21]. Further experiments such as neutron diffractions are needed to confirm this magnetic structure.

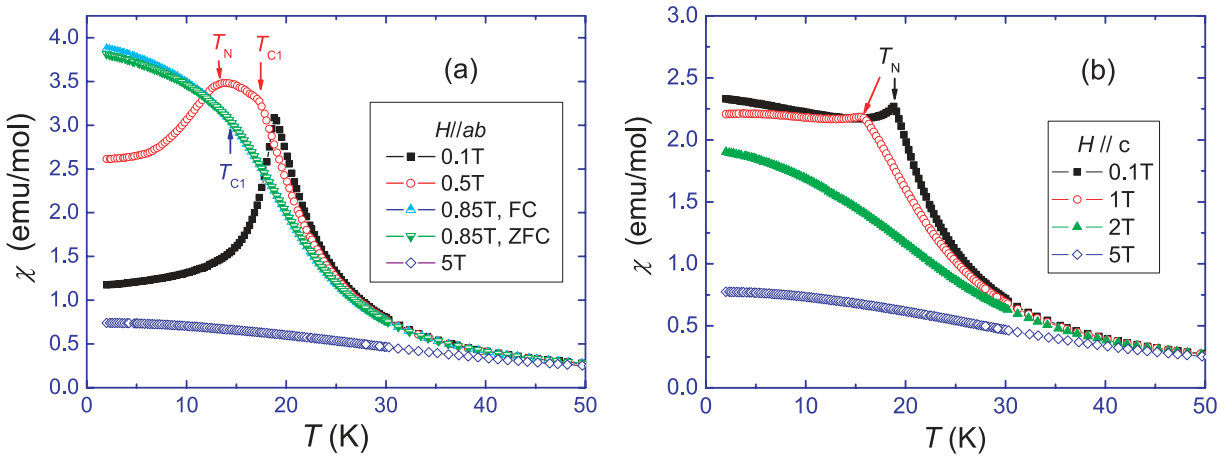

Figure 3. Temperature dependence of magnetic susceptibility of $EuFe_2As_2$ crystals under various magnetic fields. The magnetic field is perpendicular (a) and parallel (b) to the crystallographic c-axis.

After subtracting the above Curie–Weiss contribution, a small drop in χ at 186 K could be found for both field orientations. This anomaly in χ has been identified to be due to the AFM spin density wave (SDW) transition [15], although the anomaly temperature is somewhat lower than that of the polycrystalline sample. $\Delta\chi_{ab}$ is significantly larger than $\Delta\chi_c$, supporting that the Fe moments align within the ab planes in analogy with that in other related iron arsenides revealed by the neutron diffraction studies [12, 13]. In the SDW state, Fe^{2+} moments order antiferromagnetically with a collinear *stripe-like* spin structure. Thus, the coupling between Eu^{2+} and Fe^{2+} moments would be geometrically frustrated. Besides, the energy scale of AFM coupling of Fe^{2+} moments is estimated to be much higher than the AFM interlayer coupling of Eu^{2+} moments. Therefore, the magnetic coupling between Eu^{2+} and Fe^{2+} moments is negligible in the following discussion.

A-type antiferromagnetism often undergoes MM transition under a strong magnetic field because of a relatively weak interlayer AFM coupling. Figure 3 shows the $\chi(T)$ curves under various magnetic fields. At a low magnetic field of $\mu_0 H = 0.1$ T, AFM transition takes place at 19 K. For $\mu_0 H_{\|ab} = 0.5$ T, however, successive magnetic transitions were observed. First, a kink in χ appears at $T_{C1} = 17$ K. Then, χ starts to drop below $T_N = 13$ K. At lower temperatures down to 2 K, there exists impressively large residual susceptibility. When $\mu_0 H_{\|ab}$ is increased to 0.85 T, only one magnetic transition can be distinguished. The transition has small magnetic hysteresis, suggesting a kind of ferromagnetism. For $H \| c$, the Neel temperature is decreased by the applied fields for $\mu_0 H_{\|c} < 2$ T. When $\mu_0 H_{\|c} \geqslant 2$ T, the AFM transition was suppressed.

Figure 4 shows the field-dependent magnetization for $EuFe_2As_2$ crystals at various temperatures. At 50 K, which is well above the Neel temperature T_N, the $M(H)$ curve is essentially linear. When the temperature is close to T_N, a strong nonlinearity in magnetization can be seen. Below T_N, M_{ab} first increases almost linearly, then increases abruptly to a certain value (depending on temperature) and finally continues to increase to a saturated value. A small magnetic hysteresis was identified. In the case of M_c, no such step-like magnetization behaviour with magnetic hysteresis was observed. At 2 K, for example, M_c increases linearly to 7.0 μ_B f.u.$^{-1}$ at $\mu_0 H = 1.7$ T and then remains at this value for saturated Eu^{2+} moments

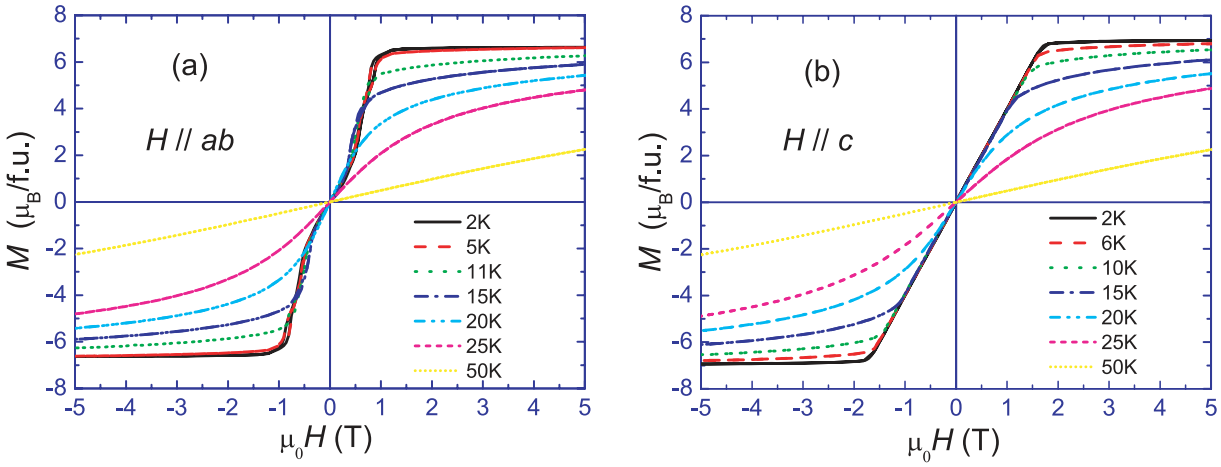

Figure 4. Magnetic field dependence of magnetization of $EuFe_2As_2$ crystals with the field perpendicular (a) and parallel (b) to the crystallographic c-axis.

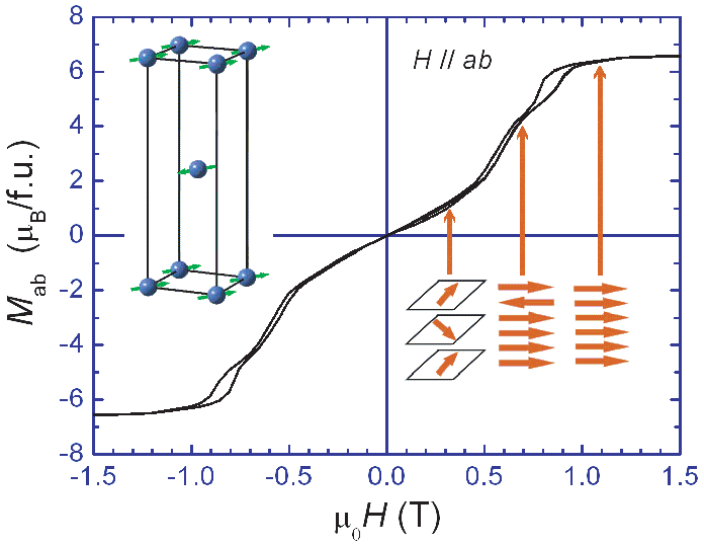

Figure 5. Expanded M–H plot for $H \parallel ab$ at 2 K. The insets give the possible magnetic structure at zero field (upper left; each ball represents a Eu atom with spin 7/2) and the configuration of magnetic polarization (lower right; each arrow represents the magnetic moment in a Eu^{2+} sheet).

($M_{\rm sat} = gS = 7.0\,\mu_{\rm B}$ f.u.$^{-1}$ for $g = 2$ and $S = 7/2$) for higher fields. The linear field dependence of M_c is consistent with spin reorientation, since the applied field rotates the moment gradually from $\perp c$ to $\parallel c$.

To analyse the complex magnetization for $H \parallel ab$, an expanded plot is shown in figure 5. The linear increase in M_{ab} below 0.45 T probably corresponds to spin reorientation. In the field range of $0.5\,{\rm T} < \mu_0 H < 0.7\,{\rm T}$, M_{ab} increases rapidly to $4.4\,\mu_{\rm B}$ f.u.$^{-1}$. Because of the small magnetic hysteresis, the rapid increase in M above 0.45 T is unlikely due to a spin–flop transition, and we ascribe it to an MM transition. For $0.7\,T < \mu_0 H < 1.0\,{\rm T}$, another FM loop can be seen. M_{ab} finally saturates to $6.6\,\mu_{\rm B}$ f.u.$^{-1}$ above 1.0 T. The saturated moment is a little

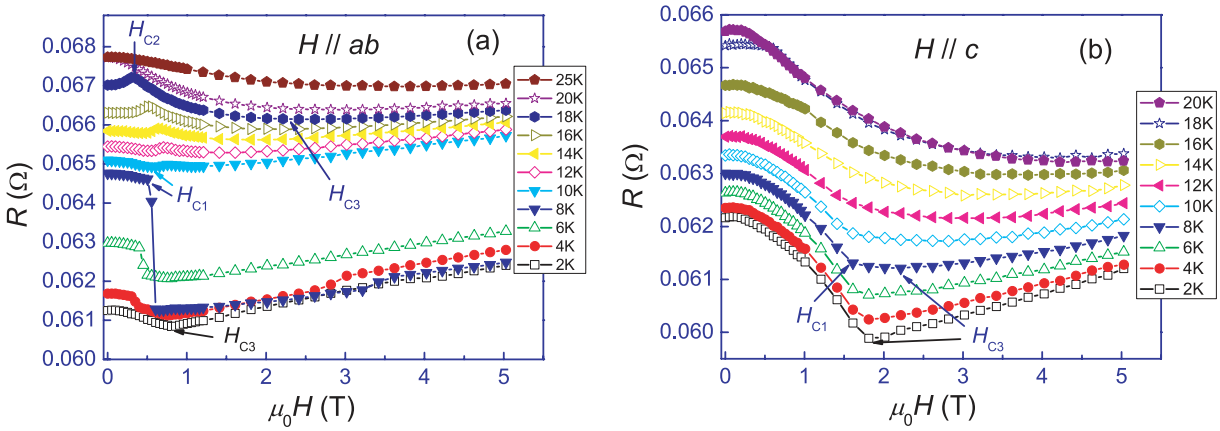

Figure 6. Isothermal in-plane resistance as a function of magnetic field for $EuFe_2As_2$ crystals. The applied field is perpendicular (a) or parallel (b) to the crystallographic c-axis.

smaller than the expected value of 7.0 μ_B f.u.$^{-1}$, which is possibly due to the crystal field effect. It is noted that the intermediate magnetization of 4.4 μ_B f.u.$^{-1}$ is just 2/3 of the saturated one. Therefore, we propose a possible configuration for the intermediate MM state: in every six sheets of Eu^{2+}, five of them have the moment parallel to the external field and the remaining one has the moment antiparallel to the applied field. We note that similar MM phases were found in the RNi_2B_2C system [22].

Figure 6 shows the isothermal in-plane resistance (R) under the applied field perpendicular or parallel to the crystallographic c-axis. At 20 K, which is very close to T_N, the resistance decreases gradually at low fields, and then remains almost unchanged under higher fields. The negative MR is ascribed to the reduction of spin disorder scattering, since the paramagnetic (PM) Eu^{2+} spins tend to align along the external magnetic field. At temperatures far below the T_N (e.g. at 2 K) in which Eu^{2+} spins order antiferromagnetically, the resistance first decreases to a minimum and then increases almost linearly. The turning point at H_{C3} corresponds to the onset of the magnetic saturation in $M(H)$ curves. The negative MR below H_{C3} suggests that the AFM-ordered Eu^{2+} spins scatter the charge transport in FeAs layers, similar to the well-known giant MR observed in magnetic multilayers [23]. The increase of MR above H_{C3} (where Eu^{2+} spins order ferromagnetically) reflects the intrinsic property of the SDW state. In fact, positive MR was observed at low temperatures for LaOFeAs, which was explained in terms of the suppression of SDW order by the external magnetic field [24].

The $R(H)$ curves with $H \parallel ab$ are shown to be more complicated. For clarity, the expanded $R(H)$ curves are presented in figure 7. At temperatures slightly higher than $T_N = 19$ K, R decreases gradually with increase in the applied field until R reaches a minimum. Since the reduction of spin-disorder scattering by external fields leads to negative MR, whereas the suppression of Fe-SDW by the fields results in positive MR, the minimum of R corresponds to the FM alignment of Eu^{2+} spins at $H = H_{C3}$.

In the temperature range of 10 K $\leqslant T \leqslant$ 18 K, $R(H)$ shows a peak below $\mu_0 H_{\parallel ab} = 1.0$ T. This high MR at H_{C2} suggests the spin disorder state (paramagnetic) of Eu^{2+} spins. Because the peak corresponds to the centre of magnetic hysteresis in the $M(H)$ curves, the increase of R below H_{C2} is probably due to the destruction of the FM-like order of Eu^{2+} spins. On the other

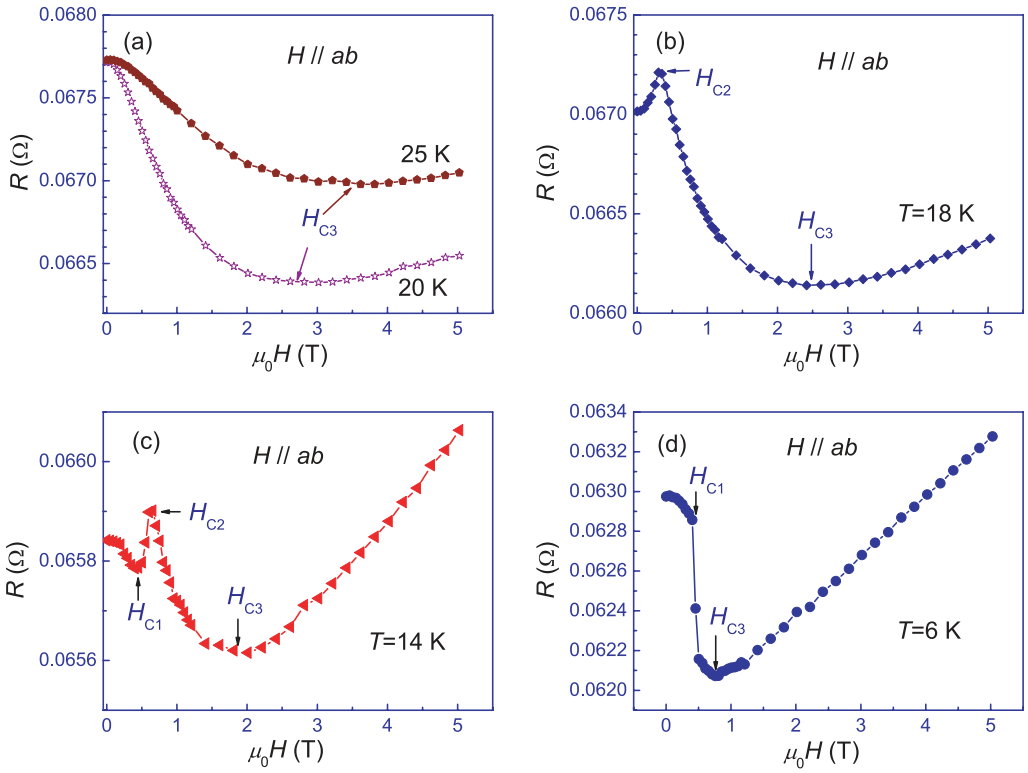

Figure 7. Expanded $R_{ab}(H)$ curves with magnetic field parallel to the ab planes at some representative temperatures for $EuFe_2As_2$ crystals.

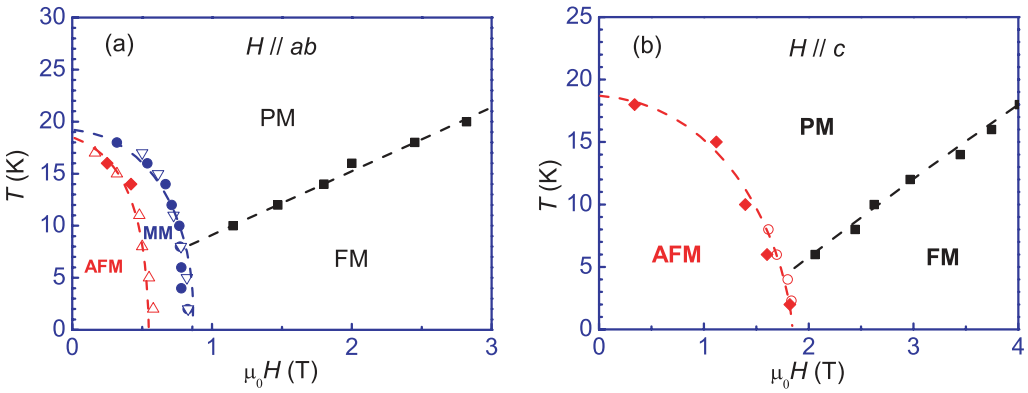

Figure 8. Magnetic phase diagrams for $EuFe_2As_2$. The applied field is perpendicular (a) or parallel (b) to the crystallographic c-axis. The open and filled symbols are from $M(H)$ and $R(H)$ measurements, respectively. The dashed lines are guides to the eyes.

hand, the spin reorientation of the AFM phase causes the decrease of R. Therefore, another minimum of R appears at H_{C1}. For $8\,\mathrm{K} \leqslant T \leqslant 4\,K$, a sharp drop in R was observed, which is due to the formation of a certain AFM configuration like the one we proposed above.

The above data allow us to draw magnetic phase diagrams, as shown in figure 8. For $H \parallel c$, one sees an AFM region at low temperatures and low fields, in which spin reorientation

dominates. Stronger fields lead to the FM state showing saturated magnetic moments. The other region is PM at elevated temperatures in which the Eu^{2+} moments are aligned to some extent by the external fields. For $H \parallel ab$, the external fields lead to spin reversal as well as spin reorientation. Apart from the AFM, FM and PM phases, there is an additional MM region.

4. Conclusion

To summarize, the property of the AFM order of Eu^{2+} spins and the evolution of the magnetic ordering under various magnetic fields were studied by the measurements of the magnetization and MR using $EuFe_2As_2$ single crystal samples. The results suggest that the magnetic structure for Eu^{2+} spins is of A type. Under external magnetic fields with $H \parallel ab$ or $H \parallel c$, the Eu^{2+} moments undergo spin-reorientation and/or spin-reversal transition depending on the relative orientations between Eu^{2+} moments and the magnetic field. The MR reflects the charge-carrier scattering by the Eu^{2+} moments. The electrical conduction of FeAs layers was found to be related to the magnetic state of Eu layers. Our preliminary result for Ni-doping [25] in $EuFe_2As_2$ suggests that the magnetic state of Eu layers even influences the appearance of superconductivity.

Acknowledgments

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