The electronic phase diagrams of the
Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ superconductor

Vinh Hung Tran$^1$, Zbigniew Bukowski, Lan Maria Tran and Andrzej J Zaleski

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 1410, 50-422 Wroclaw, Poland
E-mail: V.H.Tran@int.pan.wroc.pl

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Abstract. The magnetic and superconducting properties of an Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ single crystal are investigated by means of ac magnetic susceptibility, dc magnetization, specific heat, transverse resistivity and Hall effect measurements in magnetic fields up to 9 T, applied parallel and perpendicular to the $c$-axis. The compound exhibits the coexistence of magnetism and superconductivity (SC), characterized by structural distortion (SD) and/or spin-density-wave (SDW) ordering at $T_{\text{SD/SDW}} = 78 \pm 4$ K, canted-antiferromagnetic (C-AF) ordering at the Néel temperature $T_N = 16.5 \pm 0.5$ K and SC at the critical temperature $T_c = 5.3 \pm 0.2$ K at zero field. Upon applying fields both the C-AF and SC states evolve in an unconventional manner. Magnetic field distinctly affects the spin canting, resulting in separation of the C-AF into two new phases: the C-AF and ferromagnetic (F) ones. The unusual behavior of the SC state produces field-induced SC in the $H \perp c$ configuration as an outcome of the weakening orbital pair-breaking effect. From the experimental data we derive the field-temperature phase diagrams for Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$. A comparison of experimental results is made with theory developed for type II superconductors and then some important thermodynamic parameters characteristic of the superconducting state of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ are deduced such as the specific heat jump at $T_c$, $\Delta C_p(T_c)/\gamma_n T_c$, the electron–phonon coupling constant $\lambda_{\text{e-ph}}$, the upper critical field $H_{c2}$, coherence length $\xi$, the Fermi wave-vector $k_F$, effective mass $m^*$, Hall mobility $\mu_H$, magnetic penetration depth $\lambda$ and the Ginzburg–Landau parameter $\kappa$.

$^1$ Author to whom any correspondence should be addressed.
1. Introduction

The superconducting properties of solid solutions Eu(Fe$_{1-x}$Co$_x$)$_2$As$_2$, crystallizing in a tetragonal ThCr$_2$Si$_2$-type structure (space group I4/mmm), have been studied through the measurement of ac magnetic susceptibility, dc magnetization, electron transport, electron spin resonance and $^{57}$Fe Mössbauer properties in several works [1–8]. According to Ying et al [3], superconductivity (SC) exists in a narrow concentration range of $x \sim 0.1$–0.2 and onset of SC takes place when the spin-density-wave (SDW) ordering of Fe ions lying at the $z = 0.25$ layers vanishes. The authors found a maximum critical temperature $T_{\text{onset}}^c = 24.5$ K at the optimally doped Co concentration $x \sim 0.142$. However, it should be recalled that the signature of the SC was regarded as a resistivity drop, in spite of the fact that the resistivity does not attain zero value at all. Nonzero resistance in Eu(Fe$_{1-x}$Co$_x$)$_2$As$_2$ superconductors has also been reported by Jiang et al [2] and Niclas et al [4]. On the other hand, electron transport measurements by Matusiak et al [5] revealed SC in two samples with $x = 0.15$ and 0.20. The first sample with $T_{\text{onset}}^c = 20.5$ K undergoes SDW ordering below $T_{\text{SDW}} = 131$ K, and the other sample without SDW shows SC below $T_{\text{onset}}^c = 8.5$ K. Furthermore, in the sample showing both SC and SDW, zero resistance appears just below $T_{\text{c}}^{\text{zero}} = 2$ K, whereas in the sample without SDW, $T_{\text{c}}^{\text{zero}}$ sets in at 4.5 K. The absence of zero resistance [2–4], a large difference between $T_{\text{onset}}^c$ and $T_{\text{c}}^{\text{zero}}$ [5] and the lack of a diamagnetic signal in the magnetization of Eu(Fe$_{1-x}$Co$_x$)$_2$As$_2$ superconductors [4, 8] have been ascribed to a competition between SC and magnetic Eu$^{2+}$ moments. In addition to the SC and SDW phenomena occurring in Eu(Fe$_{1-x}$Co$_x$)$_2$As$_2$, notably an antiferromagnetic (AF) order exists in the Eu$^{2+}$ sublattice. The antiferromagnetism (AFM) manifests itself through anomalies in the temperature dependence of electrical resistivity, magnetization and Mössbauer spectra [2–8]. It was found that the Néel temperature $T_N$ is hardly influenced by Co doping; $T_N$ amounts to about 17 K in the optimally doped concentration, compared to $T_N = 19$ K in the parent EuFe$_2$As$_2$ compound. However, Co doping dramatically changes the arrangement of the Eu$^{2+}$ moments. While the AF structure of EuFe$_2$As$_2$ is collinear with Eu$^{2+}$ moments situated in the $z = 0$ layers aligned along the $a$-axis (in the orthorhombic-distorted notation of the space group Fmmm) [9], the magnetic structure of superconducting Eu(Fe$_{1-x}$Co$_x$)$_2$As$_2$ compounds is more complicated. A helimagnetic ordering of the Eu$^{2+}$ moments was considered by Jiang

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et al [2] or a canting of the Eu$^{2+}$ moments from the $c$-axis was suggested by Guguchia et al [6] and Blachowski et al [7]. It is worth mentioning that Jiang et al [2], Niclas et al [4] and Guguchia et al [6] found a spin reorientation from an AF to a ferromagnetic (F) arrangement upon application of external magnetic fields or hydrostatic pressure. The only two reports of field–temperature $H$–$T$ magnetic phase diagrams that we are aware of are those obtained for superconducting Eu(Fe$_{0.88}$Co$_{0.11}$)$_2$As$_2$ [2] and nonsuperconducting Eu(Fe$_{0.9}$Co$_{0.1}$)$_2$As$_2$ [6] crystals. The diagram of Eu(Fe$_{0.88}$Co$_{0.11}$)$_2$As$_2$ is complex, not only due to as many as five different types of phase regimes: paramagnetism, SC, F ordering and coexistence of SC and AF or F states, but also due to magnetocrystalline anisotropy. For magnetic fields parallel to the $ab$-plane, SC and F states coexist in a wide temperature range. On the other hand, for magnetic fields parallel to the $c$-axis, SC and AF states coexist in a wide range of magnetic fields. In this paper, we investigate $H$–$T$ magnetic phase diagrams of other superconducting Eu-based superconductors, i.e. Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$. The compound exhibits multiple phase transitions, from paramagnetic (P) through structural distortion (SD) or SDW ordering at $T_{SD/SDW} = 80$ K to a canted-antiferromagnetic (C-AF) state at $T_N = 16.5 \pm 0.5$ K and finally to SC at $T_c = 5.15 \pm 0.05$ K at zero field. As in the published data for Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ [2] and for Eu(Fe$_{0.8}$Co$_{0.1}$)$_2$As$_2$ [6], we found a separation of the C-AF phase into two new phases: the AF and F phases by the external magnetic field. However, the main point of our work is to show the field effect on superconducting properties of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$, namely an applied field in the $H \perp c$ configuration can induce SC. Moreover, based on the measurements of the temperature and magnetic field dependences of ac susceptibility, dc magnetization, specific heat, ac electrical resistivity, magnetoresistance and Hall effect, we determine the most important thermodynamic parameters characteristic of the superconducting state of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$.

2. Sample preparation and characterization

Single crystals of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ were grown using tin as a flux. A mixture of high-purity elements (Eu : 3N, Fe, Co, Sn : 4N and As : 5N) with the atomic ratio Eu : Fe : Co : As : Sn = 1 : 1.65 : 0.5 : 2 : 30 was placed in an alumina crucible and sealed at a pressure of 0.3 bar under a purified Ar atmosphere in a quartz ampule. The ampule was heated to 1050°C, kept at this temperature for 12 h to ensure the complete dissolving of all components in molten Sn and then, slowly cooled (2–3°C h$^{-1}$) down to 600°C. Finally, the liquid Sn flux was decanted and the remaining Sn was etched away with hydrochloric acid. The obtained single crystals are in the form of irregular platelets with the crystallographic $c$-axis perpendicular to their surface.

In order to examine the quality of the grown crystals, transmission and scanning electron microscopy (TEM and SEM) were performed with a Philips CM-20 Super Twin microscope operating at 200 kV and a FEI Nova NanoSEM 230, respectively. Figure 1 shows the SEM picture of the largest grown crystal, which has dimensions of $0.7 \times 2.5 \times 3.5$ mm$^3$. The average chemical composition of grown crystals was determined by collecting EDX spectra at selected points of the surface, corresponding to the chemical formula Eu(Fe$_{0.81\pm0.02}$Co$_{0.19\pm0.02}$)$_2$As$_2$. No impurity elements, e.g. Sn, are observed in the EDX spectra (see figure 2). X-ray powder diffraction of powdered small crystals was performed at room temperature using an X’Pert PRO x-ray diffractometer with monochromatized CuK$_\alpha$ radiation. All the observed Bragg lines on the x-ray diffraction (XRD) pattern could be indexed on the basis of the tetragonal ThCr$_2$Si$_2$-type structure (space group I4/mmm) with the lattice parameters $a = 0.391$ 15(4) nm.
Figure 1. SEM picture of a grown Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ single crystal. Sheet-type structure is visible. The chemical composition was calculated from energy dispersive x-ray (EDX) spectra collected on the denoted points.

Figure 2. The EDX spectrum of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ is shown as a plot of x-ray counts versus energy. Energy peaks corresponding to various elements in the sample are indicated.

and $c = 1.208\ 05(2)$ nm (see figure 3). The absence of un-indexed peaks indicates an upper limit of the impurity phases of less than 3 wt%. The unit cell volume of our sample is slightly larger (about 0.2%) than that reported for Eu(Fe$_{0.8}$Co$_{0.2}$)$_2$As$_2$ [5].

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3. Experimental techniques

Measurements of ac magnetic susceptibility $\chi_{ac}$ were made using an Oxford Instruments susceptometer at external fields up to 9 T. An ac field with an amplitude of 10 Oe and a frequency of 1 kHz was applied. Dc magnetization $M$ measurements were carried out with a Quantum Design magnetic property measurement system MPMS-5 SQUID magnetometer in the temperature range of 1.8–400 K and at magnetic fields up to 5.5 T. The strength of the low fields was controlled by an Applied Physics Systems fluxgate model 150-6325 magnetometer. The ac-susceptibility and magnetization data were collected in the zero-field-cooled sample mode with field applied parallel and perpendicular to the $c$-axis. Specific heat data were obtained on a Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ crystal of 2.5 mg by the 2-$\tau$-thermal relaxation method in a Quantum Design physical property measurement system 9 T-PPMS platform. The data were collected twice at each temperature in the temperature range of 1.8–300 K and at fields up to 9 T. The specific heat of an addendum with a small amount of Apiezon N grease was determined previously. Measurements of the transverse resistivity and Hall effect were carried out simultaneously using a standard six-wire ac technique with a frequency of 47 Hz and a current $j = 5$ mA parallel to the $ab$-plane. The electron transport data were collected on two samples by employing a Quantum Design horizontal rotator in a Quantum Design PPMS platform. Sample 1 ($0.7 \times 1.5 \times 2.5$ mm$^3$) and sample 2 ($0.4 \times 0.6 \times 1$ mm$^3$) were cut from two different crystals originating from the same batch. The gold-wire contacts were mounted using DuPont silver conductive paint and the contact resistances were less than 0.8 $\Omega$. The transverse resistivity ($H \perp j$) and the Hall coefficient $R_H$ were measured rotating the sample by 90$^\circ$ and 180$^\circ$, respectively. The 0$^\circ$ and 90$^\circ$ resistivity data correspond to the $H \parallel c$ and $H \perp c$ data, respectively. The 0$^\circ$ and 180$^\circ$ $R_H$ data were used to determine the Hall coefficient $R_H = \frac{1}{2}(R_{H,0^\circ} - R_{H,180^\circ})$. A magnetic field strength up to 9 T was applied perpendicular to the current direction.

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4. Experimental results

4.1. Magnetic susceptibility and magnetization

The inset of figure 4 shows the temperature dependence of dc-magnetic susceptibility $\chi(T) \equiv M/H$ of the Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ single crystal at a low magnetic field of 1 mT, applied parallel and perpendicular to the C-AF ordering of the Eu$^{2+}$ moments. It is seen that $\chi_{H//c}(T)$ flattens off below $T_N$, whereas $\chi_{H\perp c}(T)$ is more temperature dependent. Such anisotropic behavior of the dc-$\chi(T)$ curves suggests that the magnetic easy axis is close to the $ab$-plane. Similar anisotropic behavior of the dc-magnetic susceptibility was reported for Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ [2] and Eu(Fe$_{0.9}$Co$_{0.1}$)$_2$As$_2$ [6]. However, in contrast to Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ and Eu(Fe$_{0.9}$Co$_{0.1}$)$_2$As$_2$, in which no further anomaly was detected in the magnetic state, the investigated Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ sample additionally exhibits a clear drop in $\chi(T)$ around 5 K. Taking into account the ac magnetic susceptibility and electrical resistivity data (see below), we ascribe the drop in $\chi(T)$ curves to the onset of SC. For $T > 25$ K the $\chi_{H\perp c}(T)$ and $\chi_{H//c}(T)$ data are of approximately the same magnitude. We show in figure 4 the inverse susceptibility $\chi^{-1}_{H\perp c}(T)$ measured up to 400 K at a field of 5 T. The same behaviour of susceptibility at temperatures above 80 K was obtained at a field of 0.5 T. Our data can be fitted well with the Curie–Weiss law with an effective moment $\mu_{\text{eff}} = 8.05(3)\mu_B$ $\text{lu}^{-1}$ and a paramagnetic Curie temperature $\Theta_p = 25.3(4)$ K. We also obtain $\mu_{\text{eff}} = 7.90(3)\mu_B$ $\text{lu}^{-1}$ and $\Theta_p = 25.5(6)$ K for the $\chi^{-1}_{H//c}(T)$ data. A similar difference between the effective moments for $H \parallel c$ and $H \perp c$ was previously observed for EuFe$_2$As$_2$ and Eu(Fe$_{0.8}$Co$_{0.1}$)$_2$As$_2$ [6].

Figure 4. Temperature dependence of the inverse dc-magnetic susceptibility of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ single crystal at a magnetic field of 5 T applied perpendicular to the $c$-axis. The Curie–Weiss behavior in the temperature range of 80–400 K is shown by the solid line. The inset shows the low-temperature data collected at a field of 1 mT parallel and perpendicular to the $c$-axis. The anomaly at 16.8 K indicated by the solid arrow is due to a C-AF ordering of Eu$^{2+}$ moments, while the drop at low temperatures is ascribed to SC.
Figure 5. Isothermal magnetization of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ in fields applied parallel to the $c$-axis. The inset shows the second field derivative of the magnetization $d^2M/dH^2$ at 2 K. The arrows indicate the field runs with increasing and decreasing fields.

Figure 6. Isothermal magnetization of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ in fields applied perpendicular to the $c$-axis. The inset shows the second field derivative of the magnetization $d^2M/dH^2$ at 2 K. The arrows indicate the field runs with increasing and decreasing fields.

Figures 5 and 6 depict the field dependence of the magnetization of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ measured in fields parallel $M_{H//c}$ and perpendicular $M_{H \perp c}$ to the $c$-axis, respectively. The measurements were carried out with increasing and decreasing field strengths. No clear hysteresis of the magnetization is observed, although for each $M(H)$ curve below $T_N$ we can determine a crossover field $H_{cr}$ at which the second field derivative
of the magnetization \( d^2M/dH^2 \) reaches a minimum. As an example, the derivative \( d^2M/dH^2 \) versus \( H \) at 2 K is shown in the insets of figures 5 and 6. It is found that the value of \( H_c \) decreases as the temperature increases. The temperature dependence of \( H_c(T) \) for \( H \parallel c \) and \( H \perp c \) is gathered in the \( H–T \) phase diagrams (see below). To describe the physical meaning of \( H_c \) we consider the field dependence of \( M(H) \) below and above \( H_c \). For \( H < H_c \) the magnetization increases linearly with increasing field, whereas for \( H > H_c \) the magnetization saturates. The linearity of \( M(H) \) in the low-field regime indicates that the ground state of \( \text{Eu(Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2 \) must be AF. On the other hand, the saturation at high fields points to a field-induced ferromagnetic (FI-F) state. Therefore, \( H_c \) may denote the field at which the \( \text{Eu}^{2+} \) moments start flipping. It is worth noting the large values of the slopes \( dM_{H\parallel c}/dH \) and \( dM_{H\perp c}/H \) and the distinct difference between them. This feature may signify a canting of the \( \text{Eu}^{2+} \) moments. For \( \text{Eu(Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2 \) a faster increase of \( M \) versus \( H \) with field is observed for \( H \perp c \), corresponding to a larger susceptibility \( \chi_{H\perp c} \) than \( \chi_{H\parallel c} \). In fact, at 2 K, \( \chi_{H\perp c} \) amounts to 10.7 cm\(^3\) mol\(^{-1}\) compared to \( \chi_{H\parallel c} = 7.5 \text{ cm}^3\text{ mol}^{-1} \). The tilt angle from the \( c \)-axis can be estimated using the relation \( \theta = \arctan(\frac{\mu_{H\perp c}}{\mu_{H\parallel c}}) \). The experimental value is \( \theta = 54.8^\circ \) for \( \text{Eu(Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2 \), being consistent with those deduced from the Mössbauer experiment of \( \theta = 37 \pm 5^\circ \) for \( \text{Eu(Fe}_{0.81}\text{Co}_{0.185})_2\text{As}_2 \) and \( \theta = 60 \pm 8^\circ \) for \( \text{Eu(Fe}_{0.805}\text{Co}_{0.195})_2\text{As}_2 \) [7]. The magnetic sublattice of the \( \text{Eu}^{2+} \) moments in \( \text{Eu(Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2 \) is shown schematically in figure 7, where spins at the \( \text{Eu} \) position are shown to be canted with respect to the \( c \)-axis.

Let us now discuss the origin of the spin-canting and spin-flip transitions upon applied fields. We first evaluate interatomic distances in the \( \text{Eu(Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2 \) unit cell, assuming atomic positions in this compound to be the same as those in the parent \( \text{EuFe}_2\text{As}_2 \) compound [9]. In the \( \text{Eu}^{2+} \) layers, each magnetic ion is surrounded by four nearest neighbors at 0.391 nm and two next-nearest neighbors at 0.551 nm. The magnetic interactions between them can be described using two respective exchange integrals \( J_{ab1} \) and \( J_{ab2} \), shown by dash-dotted lines in figure 7. Along the \( c \)-axis, the \( \text{Eu}^{2+} \) ions are separated by a very long distance of 0.638 nm; thus the magnetic coupling \( J_c \), between the \( \text{Eu}^{2+} \) ions located on different layers will no longer be direct. There are three possibilities of magnetic exchange over long distances between magnetic ions: via the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction [10–12], via a superexchange path \( \text{Eu–As–Eu} \) or \( \text{Eu–Fe/Co–Eu} \) and finally via the Fert–Levy interaction [13]. These interactions may be expressed as the respective exchange constants \( J_{RKKY}, J_{\text{superex}} \) and \( J_{\text{FL}} \). According to the neutron diffraction experiment on \( \text{EuFe}_2\text{As}_2 \) [10], both \( J_{ab1} \) and \( J_{ab2} \) are ferromagnetic, whereas the coupling \( J_c \) is AF, and thus we can expect that all the coupling integrals \( J_{RKKY}, J_{\text{superex}} \) and \( J_{\text{FL}} \) in \( \text{Eu(Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2 \) are AF.

In order to explain long-range AF ordering in \( \text{EuFe}_2\text{As}_2 \) and its Co-doped \( \text{Eu(Fe}_{1-x}\text{Co}_x)_2\text{As}_2 \) alloys, one takes into account the conduction-electron-mediated RKKY interaction. However, the RKKY interaction alone seems to be an insufficient factor for the spin-canting in \( \text{Eu(Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2 \). Generally, spin-canting can arise from two different sources. The first one is due to the Dzyaloshinskii–Moriya (DM) interaction [14, 15]. The second one is due to the magnetocrystalline anisotropy because of different preferential directions for the magnetic moments located on different sublattices. The crystal structure of \( \text{Eu(Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2 \) is characterized by only one atomic position for the \( \text{Eu}^{2+} \) ions and therefore only the DM interaction will be considered. Classically speaking, the DM interaction describes an antisymmetric, anisotropic exchange coupling between two magnetic moments on a lattice bond \( ij \). Due to a relativistic spin–orbit coupling the DM Hamiltonian has the form: \( H \propto \hat{D}_{ij} \cdot (\hat{S}_i \times \hat{S}_j) \), where \( \hat{D}_{ij} \) is the so-called Dzyaloshinskii–Moriya coupling constant.
Figure 7. Schematic structure of $\text{Eu}(\text{Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2$. The magnetic sublattice of the Eu$^{2+}$ moments is shown. Magnetic moments are ferromagnetically coupled within the $ab$-plane but antiferromagnetically coupled between adjacent planes. Direct ferromagnetic couplings between the Eu$^{2+}$ spins in the $ab$-plane are represented by the exchange constants $J_{ab1}$ and $J_{ab2}$. The indirect exchange paths between the two Eu$^{2+}$ spins, Eu···As···Eu and Eu···(Fe/Co)···Eu, are shown by dotted and dashed lines, respectively.

Clearly, the Hamiltonian depends on the direction of spins $i$ and $j$, which in fact leans on the exchange path $S_i \cdots S_j$. An inspection of the unit cell of $\text{Eu}(\text{Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2$ shows that angles of the bonds Eu–As–Eu or Eu–(Fe/Co)–Eu are always 180°. Moreover, the position of As or (Fe/Co) located inside the exchange path excludes the inversion center of the $S_i \cdots S_j$ bonds. The paths of indirect exchange between two Eu$^{2+}$ spins, Eu···As···Eu and Eu···(Fe/Co)···Eu, furnishing the exchange constant $J_c$ are pictured in figure 7 by dotted and dashed lines, respectively. This observation suggests that the crystal structure of both $\text{EuFe}_2\text{As}_2$ and $\text{Eu}(\text{Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2$ is favorable for spin-canting. After all, within the DM interaction picture it is difficult to comprehend why there is absence of spin-canting in the Co-undoped $\text{EuFe}_2\text{As}_2$. Thus, in order to interpret the spin canting in $\text{Eu}(\text{Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2$ and other Co-doped $\text{Eu}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ alloys, we need to take into account the role of nonmagnetic Co atoms and hence invoke the model developed by Fert and Levy [14]. The authors have investigated the indirect interaction between two localized spins $S_i$ and $S_j$ mediated by spin $s$ of a conduction electron. According to Fert and Levy, the enhancement of the anisotropy field may arise from an additional term in the RKKY interaction, which is of the DM type and is due to spin–orbit scattering of the conduction electrons by the nonmagnetic impurities. The role of nonmagnetic Co ions here is to cause such interactions. The doped Co atoms introduce such a spin–orbit scattering and basically break the inversion symmetry with respect to the midpoint.
between the two spin sites, allowing the realization of a DM-type interaction. In our opinion, the substitution of magnetic Fe ions by nonmagnetic Co ions permits the realization of the Fert–Levy interaction and this might explain why the spin-canting occurs at low temperatures in the Co-doped Eu(Fe$_{1-x}$Co$_x$)$_2$As$_2$ alloys and not in EuFe$_2$As$_2$.

In figures 8(a) and (b), we compare the field dependence of magnetization $M_{H\|c}$ and $M_{H\perp c}$ in the form of an Arrott plot. It is seen that there is no spontaneous magnetization at low fields, corroborating the AF ordering. Below $T_N$, the $M^2 (H/M)$ curves are distinguished by a jump at $H/M = 0.077 \, \mu_0^{-1}$ for $H \parallel c$ and at $0.055 \, \mu_0^{-1}$ for $H \perp c$. The jump in the $M^2 (H/M)$ curves is due to the spin-flip of the Eu$^{2+}$ moments. The high-field data at 2 K furnish an estimate of ordered moments $M_{\text{ord}}$ in the FI-F state. We obtained $M_{\text{ord}, H\|c} = 7.14 \, \mu_B$ and $M_{\text{ord}, H\perp c} = 7.36 \, \mu_B$ at 5 T, which are larger than the theoretical value of $gS = 7 \, \mu_B$ per Eu atom. This finding suggests that the Fe moments possibly give some contribution to the observed $M_{\text{ord}}$ values. Remarkably, we found that $M_{\text{ord}, H\perp c} > M_{\text{ord}, H\|c}$; thus we suspect that the Fe moments are aligned within the $ab$-plane. A similar difference between $M_{\text{ord}, H\perp c}$ and $M_{\text{ord}, H\|c}$ was reported for the parent EuFe$_2$As$_2$ compound [9].

The results of the ac magnetic susceptibility measurements at several dc magnetic fields are presented in figures 9 and 10. At zero dc field the ac susceptibility displays a pronounced maximum in its real part $\chi'(T)$ at the Néel temperature $T_N = 16.5 \, \text{K}$, followed by a change in the slope $d\chi'(T)/dT$ at the superconducting phase transition $T_c \sim 5 \, \text{K}$. The occurrence of SC and AF ordering of a canted type is supported by maxima presented at the respective temperatures in the imaginary component of the ac magnetic susceptibility $\chi''(T)$. Besides, the $\chi''(T)$ curves show an additional maximum inside the superconducting state. Usually, the $\chi''(T)$ maximum at $T_c$ corresponds to intragrain dissipation in the material and the maximum at a lower temperature coincides with the temperature where weak links between grains or Josephson-type junctions start carrying super-currents. The sheet-type structure of the investigated crystals (see figure 1) seems to be the main source of the weak link behavior.

Figure 8. Comparison of the field dependence of magnetization (a) $M_{H\|c}$ and (b) $M_{H\perp c}$ in the form of an Arrott plot.
Figure 9. Temperature dependence of the real $\chi'(T)$ and imaginary $\chi''(T)$ components of ac magnetic susceptibility of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ measured at several magnetic fields parallel to the $c$-axis. The superconducting transition temperature $T_c$ is denoted by solid arrows, the Néel temperature by dashed arrows and the Curie temperature $T_C$ by dotted arrows.

Applied magnetic fields parallel or perpendicular to the $c$-axis significantly affect the magnetic Eu$^{2+}$ sublattice. As can be seen in figures 9 and 10, the $\chi'(T)$-maximum at $T_N$ splits into two anomalies upon application of magnetic fields; one shifts down to lower temperatures and the other shifts upwards to higher temperatures. We attribute this behavior to a change in the C-AF structure. The field dependence of the low and high temperature maxima corresponds to a change of AF and F components, respectively. Previously, such a change in the magnetic ground state from AFM to ferromagnetism (FM) under applied magnetic fields was found in Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ [2] and in Eu(Fe$_{0.9}$Co$_{0.1}$)$_2$As$_2$ [6]. A conspicuous influence of external magnetic fields on the observed physical properties emerges in the vicinity of $T_c$. The applied field reduces the value of $\chi'(T)$ and finally the real component of the ac susceptibility starts showing a diamagnetic signal at fields above 0.6 T. We may recall that naked diamagnetism was not observed previously in either Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ [2] and Eu(Fe$_{0.8}$Co$_{0.2}$)$_2$As$_2$ [8]. This may indicate that SC in our samples is more robust. A comparison of the field dependence of $T_c(H)$ for $H \parallel c$ and $H \perp c$ reveals a distinct difference between them. When applying the external magnetic field parallel to the $c$-axis (figure 9), the superconducting transition temperature is found to decrease with increasing field, as can be expected for a type II superconductor. At a field above 2 T, SC vanishes. On the other hand, for the magnetic field applied perpendicular to the
Figure 10. Temperature dependence of the real $\chi'(T)$ and imaginary $\chi''(T)$ components of ac magnetic susceptibility of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ measured at several external magnetic fields perpendicular to the $c$-axis. The superconducting transition temperature $T_c$ is denoted by solid arrows, the Néel temperature by dashed arrows and the Curie temperature $T_C$ by dotted arrows.

$c$-axis, after an initial decrease, $T_c$ shifts upwards to higher temperatures, as high as 7.2 K at 0.6 T. With further increasing field $T_c$ decreases, i.e. the $T_c$ versus $H$ dependence recovers the behavior of an ordinary type-II superconductor. The anisotropic properties of the superconducting state are evidenced by the difference in magnitude of $H_{c2}(T)$ for $H \parallel c$ and $H \perp c$. As is visible in figure 10, the diamagnetism still persists strongly at a field of 2 T. This fact means that the upper critical field for fields applied perpendicular to the $c$-axis $H_{c2}^{\perp}$ is much larger than that for fields applied parallel $H_{c2}^{\parallel}$. Therefore, our observation of the diamagnetic signal provides evidence that magnetism and SC have a close relationship.

4.2. Specific heat

The temperature dependences of specific heat divided by the temperature of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ measured at 0 and 9 T are shown in figure 11. These data overlap each another above 100 K, indicating a dominating lattice contribution to the specific heat. Assuming that the specific heat is additive we analyze the high-temperature $C_p(T)$ as the sum of the lattice $C_{ph}$ and the conduction electron $C_{el}$ contributions. The latter was taken as linearly temperature dependent $C_{el} = \gamma_{HT} T$. At room temperature (RT), the specific heat
Figure 11. Specific heat divided by the temperature of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ measured at 0 and 9 T as a function of temperature. The dashed line indicates the sum of the electronic and lattice contributions to the total specific heat.

amounts to about 134 J mol K$^{-1}$. The difference between the RT-$C_p$ and the Dulong–Petit value of 124.7 J mol K$^{-1}$ implies that the coefficient of the high-temperature electronic specific heat $\gamma_{HT}$ is approximately 0.03 J mol K$^{-2}$. Assuming all phonon modes are acoustic, $C_{ph}$ of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ can be modeled by the Debye function [16]:

$$C_{ph}(T) = 9RN_D(T/\Theta_D)^3 \int_0^{\Theta_D/T} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx,$$

(1)

where $R$ is the molar gas constant, $n_D$ is the number of Debye vibrators and $\Theta_D$ is the Debye temperature. For $T > 100$ K, fixing $\gamma_{HT} = 30$ mJ mol K$^{-2}$ we are able to fit the $C_p(T)$ data (dashed line) with $\Theta_D = 330 \pm 10$ K. This value is quite large compared to those found in AFe$_2$As$_2$ (A = Ca, Sr and Ba) compounds ($\Theta_D = 292$ K [17] and 267 K [18] for CaFe$_2$As$_2$, 245 K [19] and 248 K [20] for SrFe$_2$As$_2$ and 134 K [21], 186 K [22] and 230 K [23] for BaFe$_2$As$_2$). We must note that the definitive Debye temperature of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ would be obtained under a more rigorous analysis of the $C_p$ data, including the well-defined phonon spectrum, e.g. from inelastic neutron scattering data, and another possible contribution such as a Schottky-like anomaly. The Debye temperature $\Theta_D$ appears to be linked to the electron–phonon coupling constant $\lambda_{e-ph}$ via the McMillan equation [24]

$$\lambda = \frac{1.04 + \mu^* \ln(\Theta_D/1.45T_c)}{(1 - 0.62\mu^*) \ln(\Theta_D/1.45T_c) - 1.04},$$

(2)

where $\mu^*$ is the Coulomb pseudopotential, so one can estimate the $\lambda_{e-ph}$ value for Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$. Putting $T_c = 5.15$ K, $\Theta_D = 330$ K and typical values of $\mu^* = 0.1$–0.15 [24, 25] into equation (2) we obtained $\lambda_{e-ph} = 0.6$–0.7, being appreciably enhanced above the usual Bardeen–Cooper–Schrieffer (BCS) weak-coupling value of 0.4. Low-temperature $C_p/T$ data at zero field (open circles) are dominated by a pronounced $\lambda$-type anomaly at 16.8 K, corroborating the Néel temperature of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$. As we have noted above, the Néel temperature of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ is comparable in magnitude to that
Figure 12. (a) Temperature dependence of the difference $C_p(T, 0\, T) - C_p(T, 9\, T)$ divided by temperature. The dashed line is used to determine the specific heat jump at $T_c$. (b) The field dependence of the Sommerfeld ratio at 2 K.

of the parent compound EuFe$_2$As$_2$ ($T_N = 19\, K$), but the nature of the AF ordering in those compounds is essentially different. Besides the difference in spin arrangements, we may point out also a disparity in the entropy $S$ at $T_N$. For Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ we found the $S$ at $T_N$ to amount to only $\sim 14.7\, J\,(\text{mol K})^{-1}$, corresponding to 85% of $R\ln 8$ expected for $J = 7/2$, which was observed in EuFe$_2$As$_2$ [26, 27]. The evidence for a superconducting phase transition in the zero-field specific heat of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ is not clear-cut. As can be seen from figure 11 the $C_p/T$ curve does not show any discontinuity but only a knee around $T_c$. In a BCS-type conventional superconductor, a sharp discontinuity at $T_c$ is generally observed in the $C_p(T)$ curve. This difference in $C_p(T)$ behavior between the Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ and BCS-type superconductors may be for several possible reasons: (i) a dominating magnetic contribution, (ii) the possibility of gapless SC or (iii) unconventional $C_p(T)$ dependence. On the other hand, the absence of naked specific jump $\Delta C_p(T)/T_c$ is not surprising if we remember the similar behavior of specific heat found in other FeAs-based superconductors. We recall the data reported by Budko et al [28]. According to the authors the magnitude of $\Delta C_p(T)/T_c$ at $T_c$ is strongly dependent on the $T_c$ value as $\Delta C_p(T)/T_c \propto T_c^2$. If we assume that the specific heat of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ also follows the scaling behavior (see figure 3 of [28]), we may expect the ratio $\Delta C_p(T)/T_c$ to amount to 1.6 J mol K$^{-2}$. Such a small change in the specific heat, especially in magnetic materials such as Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$, is not easy to observe in the raw data. Since we have no reasonable way of determining $\Delta C_p(T)/T_c$ from the zero-field $C_p$ data, we will try to evaluate $\Delta C_p(T)/T_c$ by combining the 0 T and 9 T data (open diamonds). Because an applied field of 9 T suppresses the AF order down to temperatures below 2 K and pushes the F phase transition to temperatures higher than 35 K, the magnon contribution to the 9T $C_p$ at around $T_c$ should be considerably quenched. Therefore, we may use the 9T $C_p$ data as the reference in the first approximation. In figure 12(a), we show the temperature dependence of the difference $C_p(T, 0\, T) - C_p(T, 9\, T)$ divided by temperature. Apparently, the $\Delta C_p(T)/T_c$ at $T_c$ ratio shows an anomaly around $T_c$. Clearly, this anomaly must be associated with the superconducting phase transition and may
prove the bulk effect of SC. By extrapolating the two branches of the \( C_p/T \) versus \( T \) curve below and above \( T_c \) (see figure 12(a)) we evaluate the \( \Delta C_p(T)/T_c \) at \( T_c \) ratio to be about 0.18 J mol K\(^{-2}\). The Sommerfeld ratio \( \gamma_n \) in the normal state of Eu(Fe\(_{0.81}\)Co\(_{0.19}\))\(_2\)As\(_2\) amounts to 0.35 J mol K\(^{-2}\), corresponding to the ratio \( \Delta C_p(T)/\langle \gamma_n T_c \rangle = 0.5 \), considerably smaller than the BCS weak coupling limit of 1.43. Usually, the deviation of the specific heat jump from the BCS theory might mean a nonconventional SC. However, one should take care in the case of Eu(Fe\(_{0.81}\)Co\(_{0.19}\))\(_2\)As\(_2\), since the phonon and magnetic contributions to the total specific heat are not yet well defined. In figure 12(b), the Sommerfeld ratio \( C_p(T)/T \) at 2 K in magnetic fields up to 9 T is shown. \( C_p(T)/T \) at 2 K amounts to 0.477 J mol K\(^{-2}\) at zero field. With increasing magnetic field, \( C_p(T)/T \) decreases to lower values, and at 9 T the 2 K \( C_p(T)/T \) arrives at a value of 44 J mol K\(^{-2}\). A large decrease in \( C_p(T)/T \) at 2 K under magnetic fields implies that the magnon contribution to the specific heat is considerably suppressed by applied fields.

4.3. Electron transport properties

Figure 13 displays the temperature dependence of the ac-electrical resistivity during cooling for the single-crystalline Eu(Fe\(_{0.81}\)Co\(_{0.19}\))\(_2\)As\(_2\) (sample 1) at zero field. The investigated sample exhibits three successive phase transitions, more clearly evidenced by respective anomalies.
Figure 14. The temperature dependence of ac electrical resistivity of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ measured with a current of 5 mA in fields (a) parallel and (b) perpendicular to the c-axis. Joined symbols are the data of sample 1, while the solid line in panels (a) and (b) represents the resistivity of sample 2 at zero field and at 0.4 T, respectively.

in the temperature derivative of the $\rho(T)$ curve shown in the lower inset of figure 13. The high-temperature anomaly at $T_{SD/SDW}$ is attributed to an SD and/or SDW transition, while two anomalies at lower temperatures $T_N = 16.5$ K and $T_c = 5.15$ K correspond to AF and SC transitions, respectively. We note that the SD/SDW phase transition temperature $T_{SD/SDW}$ depends on the thermal history of the sample. During the cooling cycle $T_{SD/SDW}$ is equal to 82 K, while in the heating cycle it amounts to 87 K (see the upper inset). The SD/SDW transition and its thermal history are confirmed once by the resistivity measurements on sample 2, for which we obtain $T_{SD/SDW} = 74$ and 85 K during cooling and heating cycles, respectively. The onset of SC in our samples sets in at 8 K, being consistent with the published critical temperature $T_c$ for the samples Eu(Fe$_{1-x}$Co$_x$)$_2$As$_2$ with a similar stoichiometry, i.e. of 9.5 and 7.5 K for $x = 0.185$ and 0.195, respectively [7]. Moreover, a comparison of the overall temperature dependence of $\rho(T)$ reveals a systematic change in $T_{SD/SDW}$ with a change of the Co concentration. If Eu(Fe$_{0.815}$Co$_{0.185}$)$_2$As$_2$ shows the SD/SDW transition at 100 K and Eu(Fe$_{0.8}$Co$_2$)$_2$As$_2$ shows no SDW transition, our samples with $x = 0.81$ exhibit an SD/SDW transition at $T_{SD/SDW}$ with an average value 78 ± 4 K from the two samples.

In order to investigate the nature of the superconducting transition, the resistivity around the superconducting transition was measured in more detail. The obtained data are presented in figures 14(a) and (b) for magnetic fields applied parallel and perpendicular to the c-axis, respectively. The critical transition $T_c$ is defined as the midpoint of the resistivity jump of the resistivity curve. At zero field, sample 1 exhibits the superconducting phase transition at $T_c = 5.15$ K, while sample 2 has a higher $T_c$ value of 5.51 K, yielding an average value $T_c = 5.3 \pm 0.2$ K. We must note here that the superconducting phase transition $T_c$ is affected differently by applied fields $H \parallel c$ or $H \perp c$. For $H \parallel c$, the value of $T_c$ of both Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ samples decreases as the applied field strength increases. The field
dependence of $T_c$ for Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ measured upon applying fields perpendicular to the $c$-axis is complex. After an initial decrease of $T_c$ with increasing fields up to 0.15 T, $T_c$ undoubtedly increases with further increasing fields and at 0.4 T $T_c$ attains a value of 6.59 K in sample 1 or 6.64 K in sample 2. Thus, the magnetic field in the $H \perp c$ configuration acts very strongly on SC, resulting in increasing $T_c$ up to at least 27%. This unusual FI-SC is an intrinsic property of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ since it is observed in both ac magnetic susceptibility and electrical resistivity measurements.

It is worth noting that there exist a close relationship between the field dependences of $T_c(H)$ and superconducting transition width $\Delta T_c(H)$. The width $\Delta T_c(H)$ is defined as $\Delta T_c = T_{90\%} - T_{10\%}$, where $T_{90\%}$ and $T_{10\%}$ are the temperatures corresponding to 90 and 10% of the resistivity jump. At zero field, $\Delta T_c(H)$ amounts to 2.96 K. For $H \parallel c$, $\Delta T_c(H)$ decreases smoothly and at $\mu_0 H = 1$ T the relative decrease of $\Delta T_c(H)$ is 42%. On the other hand, for $H \perp c$, $\Delta T_c(H)$ rapidly decreases below $T_c$ and levels off at a value of 1.07 K at higher fields. The relative decrease of $\Delta T_c(H)$ for this field configuration is equal to 64%, and is substantially larger than that for $H \parallel c$. Very recently, we pointed out that the drop in $\Delta T_c(H)$ of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ is associated with a weakness of the orbital pair-breaking effect [30]. We suggested that this phenomenon would account for FI-SC in Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$. We may add that such FI-SC behavior was not observed in the closely stoichiometric Eu(Fe$_{0.8}$Co$_{0.2}$)$_2$As$_2$ compound [8]. Instead, an external field applied parallel to the $c$-axis causes re-entrance of the superconducting state. The authors have interpreted the unusual behavior to be a weakening of the vortex pining induced by rotation of the Eu magnetic moments.

In figure 15(a), we show the temperature dependence of the Hall coefficient $R_H$ of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ at 5 and 9 T. $R_H(T)$ amounts to $0.76 \times 10^{-9}$ m$^2$ C$^{-1}$ at room temperature and is comparable to that of Eu(Fe$_{0.8}$Co$_{0.2}$)$_2$As$_2$ measured at 13 T [6]. However, there exists a difference in $R_H$ value at low temperatures between two samples, $x = 0.19$ and 0.2. At 1.8 K, the $R_H$ of our sample ($x = 0.19$) at 5 T reaches a value of $-2.3 \times 10^{-9}$ m$^2$ C$^{-1}$. The application of a larger field of 9 T results in an increase in $R_H(T)$, and at 1.8 K the 9 T $R_H(T)$ attains a value of $-1.92 \times 10^{-9}$ m$^3$ C$^{-1}$. This value is still smaller than that of Eu(Fe$_{0.8}$Co$_{0.2}$)$_2$As$_2$ measured at 13 T [5] and that of the parent EuFe$_2$As$_2$ compound at 8 T [26], both the latter compounds have the same value of $R_H$ of $\sim 1 \times 10^{-9}$ m$^3$ C$^{-1}$ at 2 K. Except for the visible field effect below 30 K, $R_H$ of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ shows an anomaly at $T_{SD/SDW} = 86$ K. This behavior may be attributed to a change in the Hall mobility $\mu_H(T)$. Neglecting the temperature dependence of the magnetic contribution to the total Hall coefficient, the Hall mobility can be evaluated by calculating the ratio $\mu_H(T) = |R_H(T)|/\rho(T)$. Our data reveal that $\mu_H(T)$ remarkably increases with decreasing temperature. In the three temperature intervals 300 K–$T_{SD/SDW}$, $T_{SD/SDW}$–$T_N$, and $T_N$–1.8 K, $\mu_H(T)$ changes with the respective rates $\Delta \mu_H(T)/\Delta T = 9$, 24 and 26%. Based on the proportionality $\mu_H = \tau/m^*$ and due to the close relationship between the effective mass of quasi-particles $m^*$ and the electron correlation strength, one would expect an increase in the scattering time of quasi-particles $\tau$ with decreasing temperature.

The temperature and field dependences of $R_H(T)$ shown in figure 15 imply that in addition to the ordinary contribution to the Hall effect $R_0$, which corresponds to the effect of the Lorentz force on the motion of the free carriers, there exists also an anomalous contribution to the Hall effect $R_S$ arising from the spin–orbit coupling between localized moments and itinerant electrons. The Hall coefficient of such a magnetic material can be written as [29]

$$R_H(T) = R_0 + R_s \frac{M(T)}{\mu_0 H},$$

(3)
The Hall coefficient $R_H$ of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ as a function of (a) temperature at 5 and 9 T and (b) magnetic field at 1.8 K. Magnetic field is applied parallel to the $c$-axis. The solid lines are fits of equation (3) to the $R_H$ data.

where $\chi(T) = \frac{M(T)}{\mu_0 H}$ is the volume susceptibility. Taking the volume susceptibility $\chi(T)$ at 5 T, we have fitted the Hall data. The agreement between theoretical calculations and experimental data, presented as solid lines in figure 15(a), indicates that equation (3) holds for Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ in the temperature range 200–300 K. The values of $R_0$ and $R_s$ were obtained as $3.08 \times 10^{-10}$ and $-3.55 \times 10^{-8}$ m$^3$C$^{-1}$, respectively. A large ratio $R_s/R_0$ of the order of 100 implies that the high-temperature $R_H(T)$ is dominated by spin–orbit coupling.

The charge-carrier concentration $n$ estimated in a one-band model from $R_0$ is $2.13 \times 10^{28}$ m$^{-3}$ or 1.97 electrons per Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ formula unit. The field dependence of the Hall coefficient $R_H$ of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ at 1.8 K is shown in figure 15(b). It is apparent that $R_H$ weakly increases with increasing field. In figure 15(b), we also show the fit of equation (3) to the Hall data. The best fit for data below 5 T was obtained with $R_0 = -(1.80 \pm 0.05) \times 10^{-9}$ m$^3$C$^{-1}$ and $R_s = -(2.56 \pm 0.06) \times 10^{-9}$ m$^3$C$^{-1}$. The $R_0$ value corresponds to the number of carriers in simple one-band approximation, $n = 3.47 \times 10^{27}$ m$^{-3}$ or 0.16 electron per Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ formula unit. We may access quantitatively the Hall mobility using the formula: $\mu_H = R_0/\rho$. For the 5 T data at 1.8 and 300 K, we find that $\mu_H = 38.8$ and 2.7 cm$^2$V$^{-1}$s$^{-1}$, respectively. These values are of the same order of magnitude as those found...
Figure 16. Magnetic $H$–$T$ phase diagrams of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ in fields (a) parallel and (b) perpendicular to the $c$-axis. All abbreviations are explained in the text. The empty and closed symbols are the magnetic and electron transport data, respectively.

in heavy-fermion systems CeCu$_2$ and CePd$_3$ [31]. This means that the charge carriers in Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ may have enhanced the effective masses $m^*$.

5. Magnetic phase diagrams and estimation of thermodynamic parameters

The field dependences of $T_c$, $T_N$ and $T_C$ are summarized in the temperature versus magnetic field phase diagrams shown in figures 16(a) and (b) for $H \parallel c$ and $H \perp c$, respectively.

At zero field, Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ undergoes three successive phase transitions: from a paramagnetic phase (phase I), to a C-AF phase (phase II) and finally to an unconventional superconducting phase. In the latter phase, in fact, the SC coexists with the C-AF, i.e. SC+C-AF, (phase III). Under applied fields both the C-AF and SC phases evolve unusually. In addition to the C-AF phase, there appears a new FI-F phase (phase IV). This phase originated from the Eu$^{2+}$ spin-canting and exists above the spin-flop field $H_{cr}$. The boundary lines between C-AF and FI-F phases are determined by the ac-susceptibility (empty diamonds) and dc-magnetization (empty squares) data. As $T \to 0$ the critical field $\mu_0 H \parallel c \geq 0.55$ T and $\mu_0 H \perp c \geq 0.45$ T. Because SC remains in the new FI-F state, we may designate this phase as SC+FI-F (phase V). We recognize that phase VI, i.e. FI-SC, exists for $H \perp c$ only. An interesting point of comparison to the $H$–$T$ phase diagram of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ is given by the Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ superconductor [2]. Our Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ sample exhibits SC coexisting only with magnetism, in contrast to Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$, where for some range of $H$–$T$ SC exists alone, i.e. without magnetism. Another difference between the two superconductors is that FI-SC occurs in Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ upon $H \perp c$. In the following, we shall concentrate on estimation of some thermodynamic parameters of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$. An examination of the $H_{c2}(T)$ in the vicinity of $T_c$ reveals a linearity between $H$ and $T_c$,
and thus one can estimate the initial slope of the \( \frac{d\mu_0 H}{dT} \bigg|_{T=T_c} = -0.49 \text{T} \) and \(-0.33 \text{T/K} \) for \( H \parallel c \) and \( H \perp c \), respectively. Using the Werthamer–Helfand–Hohenberg formula [32]: \( \mu_0 H_{c2}^{\text{orb}} \simeq -0.7 T_c \frac{d\mu_0 H_{c2}^{\text{orb}}}{dT} \bigg|_{T=T_c}, \) we evaluated the orbital pair-breaking fields \( \mu_0 H_{c2}^{\text{orb}, c} = 1.8 \text{T} \) and \( \mu_0 H_{c2}^{\text{orb}, \perp c} = 1.2 \text{T} \) in the absence of any paramagnetic limitation. On the other hand, Clogston has shown that the paramagnetically limited upper critical field should be given by [33]: \( \mu_0 H_{po} = 1.84 T_c \). Taking \( T_c = 5.15 \text{ K} \) we estimated \( \mu_0 H_{po} \) to be \( 9.5 \text{ T} \). An extrapolation of \( T_c(H) \) to \( T = 0 \) yields the value of the upper critical field \( \mu_0 H_{c2}(0) \sim 2.7 \text{T} \) for \( H \parallel c \) and \( 6.5 \text{T} \) for \( H \perp c \). A comparison of these upper critical fields implies that the \( T_c(H) \) curve in the \( H \parallel c \) configuration is mainly governed by the orbital pair-breaking effect, but a dominating paramagnetic effect is taken down for \( H \perp c \). The absence of the orbital limit for high field strength \( H \perp c \) is consistent with the behavior of \( \Delta T_c(H) \) considered above. Using \( H_{c2}(0) \), a few thermodynamic parameters related to the superconducting state of \( \text{Eu(Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2 \) can be derived. Using the formula [34]:

\[
H_{c2}(0)^{\parallel c} = \frac{\Phi_0}{2\pi \xi_{ab}^2}, \\
H_{c2}(0)^{\perp c} = \frac{\Phi_0}{2\pi \xi_{ab}\xi_c},
\]

where \( \Phi_0 = 2.0679 \times 10^{-15} \text{Wb} \) is the flux quantum and \( \xi_{ab} \) and \( \xi_c \) are the coherence lengths in the \( ab \)-plane and along the \( c \)-axis, respectively and taking \( \mu_0 H_{c2}(0)^{\parallel c} = 2.7 \text{T} \) and \( \mu_0 H_{c2}(0)^{\perp c} = 6.5 \text{T} \), we derive the values of \( \xi_{ab} = 11.0 \text{ nm} \) and \( \xi_c = 4.6 \text{ nm} \). The anisotropy ratio of the coherence lengths determined by the following equation:

\[
\Gamma = \frac{H_{c2}(0)^{\perp c}}{H_{c2}(0)^{\parallel c}} = \frac{\xi_{ab}}{\xi_c}
\]

amounts to 2.4, noticeably smaller than those of high-\(T_c\) cuprate superconductors (~10). The Fermi wave vector \( k_F = (3\pi^2 n)^{1/3} \) depends on the carrier concentration \( n \). From the Hall coefficient measurements, \( n \) was deduced to be \( 3.47 \times 10^{27} \text{ m}^{-3} \) at 1.8 K. Taking into account the number of electron pairs, the superconducting carrier \( n_s \) is equal to \( n/2 \) and we derive the value of \( k_F = 3.72 \times 10^9 \text{ m}^{-1} \). Knowledge of the Fermi wave vector \( k_F \) and the electronic specific heat coefficient \( \gamma_V = 1.581 \times 10^3 \text{ J m}^{-3} \text{ K}^2 \) (assuming the space group to be Fmrm at low temperatures) allows us to evaluate the effective mass of quasi-particles \( m^* = 3h^2 \gamma_V / (k_B^2 k_F) = 81.7 \text{ m}_e \), where \( m_e \) is the mass of the free electron. Employing the formulæ given in [35, 36] and taking into account the values of \( \rho_n, \gamma_V, k_F \) and \( T_c \), we calculated the values of BCS coherence length \( \xi_0 = 1.35 \text{ nm} \) and mean free path \( l_c = 18.3 \text{ nm} \) for \( \text{Eu(Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2 \). The relation \( l_c > \xi_0 \) suggests that \( \text{Eu(Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2 \) can be considered as a clean superconductor. We now estimate the magnetic penetration depth \( \lambda \), using the London formula:

\[
\lambda = \sqrt{\frac{\varepsilon_0 m^* c^2}{4\pi n_s e^2}} \times \left( 1 + \frac{\xi_0}{l} \right),
\]

where \( \varepsilon_0 \) is the vacuum permittivity, \( c \) is the light velocity and \( e \) is the electron charge. Using equation (6), we obtain \( \lambda = 350 \text{ nm} \), which corresponds to the Ginzburg–Landau parameter \( \kappa = \lambda/\xi = 31.8 \), confirming the type II SC in \( \text{Eu(Fe}_{0.81}\text{Co}_{0.19})_2\text{As}_2 \). Further direct measurements, however, will be needed to refine the \( \lambda \) value more precisely.

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Table 1. Several thermodynamic parameters of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ deduced from electron transport and specific heat measurements.

| Parameter | Along the c-axis | In the ab-plane |
|-----------|-----------------|-----------------|
| $T_c$ (K) | 5.3 ± 0.2        | 5.3 ± 0.2       |
| $\gamma$ (mJ mol K$^{-2}$) | 44             | 44             |
| $\mu_0 H_{c2}(0)$ (T) | 2.7            | 6.5            |
| $k_F (\times 10^9$ m$^{-1}$) | –              | 3.72           |
| $\mu_H$ (cm$^2$ V s$^{-1}$) | –              | 37.5           |
| $m^*(m_e)$ | –              | 81.7           |
| $\xi_0$ (nm) | –              | 1.35           |
| $l_e$ (nm) | –              | 18.3           |
| $\xi$ (nm) | 4.6            | 11             |
| $\lambda$ (nm) | –              | 350            |
| $\kappa$ (–) | –              | 31.8           |

6. Summary

We have synthesized single-crystalline Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ adopting the tetragonal ThCr$_2$Si$_2$-type structure at room temperature. The measurements of the ac magnetic susceptibility, dc-magnetization, specific heat, magnetoresistivity and Hall coefficient reveal that the compound undergoes multiple phase transitions, from paramagnetism via SD and/or SDW ordering at $T_{SD/SDW} = 78 ± 4$ K, to C-AF at $T_N = 16.5 ± 0.5$ K and finally to SC at $T_c = 5.3 ± 0.2$ K at zero field. From the field dependence of $T_N$, $T_c$ and $T_c$ we propose the magnetic phase diagrams and compare to the literature data for other compositions of the Eu(Fe$_{1-x}$Co$_x$)$_2$As$_2$ solid solutions. We found an FI separation of the C-AF phase into two new phases: C-AF and F. We have discussed the spin-canting in Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ and in other Co-doped in the framework of the Fert–Levy model, which includes RKKY interaction and spin–orbit coupling between conduction electrons and nonmagnetic ions. We discovered that the external field applied perpendicular to the c-axis may increase $T_c$ significantly, at least up to 27%. Since the SC is intimately associated with the observed magnetic phase transitions of the Eu$^{2+}$ moments, we may interpret the phenomenon by a weakening of the orbital-breaking effect as a result of the alignment of magnetic Eu$^{2+}$ moments within the ab-plane. Because of the fact that the SC is basically related to Fe ions, further investigation of possible effects of small magnetic fields on the magnetic Fe moments and/or their fluctuations affecting the FI-SC is highly desirable. Finally, some physical parameters characteristic of the superconducting state of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$, such as the specific heat jump at $T_c$, $\Delta C_p(T_c)/\gamma_n T_c$, the electron–phonon coupling constant $\lambda_{e-ph}$, the upper critical field $H_{c2}$, effective mass $m^*$, Hall mobility $\mu_H$, the penetration depth $\lambda$, coherence length $\xi$ and the Ginzburg–Landau parameter $\kappa$ were determined. The evaluated thermodynamic parameters of Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ are listed in table 1. The notable information in the table is that Eu(Fe$_{0.81}$Co$_{0.19}$)$_2$As$_2$ exhibits small values of $\xi$ and $\mu_H$ but large values of $\lambda$ and $m^*$. This finding is indicative of a metal with heavily renormalized electrons and may call for further studies in order to explore the mechanism leading to the coexistence of magnetism and heavy-fermion SC in Eu(Fe$_{1-x}$Co$_x$)$_2$As$_2$ superconductors.
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