Chapter 3

Physical properties of pure and doped EuRu-1222 magneto-superconductor

Abstract

In this chapter, first section deals with synthesis, transport, and magnetic characterization of variously processed pure magneto-superconducting ruthenocuprates RuSr$_2$Eu$_{1.5}$Ce$_0.5$Cu$_2$O$_{10-\delta}$ (EuRu-1222). Magnetization measurements showed bulk magnetic ordering and superconductivity at around 100K and 30K respectively. Further the careful examination of the low field magnetic susceptibility revealed two minor magnetic transitions at around 135K and 200K in addition to the major transition at 100K. On the other hand the minor magnetic transitions are more prominent in air-annealed samples. Though the minor magnetic transitions are intrinsic to all variously processed samples, they are not clearly seen for higher O$_2$ content samples. Basically the Ru spins order antiferromagnetically (AFM) at around 200K (first minor transition), and reorient themselves at 125K (second minor transition) before finally ordering in canted ferromagnetic (FM) state or a spin-glass (SG) structure. In the next sections of the chapter we investigate the effect of Cr and Mn ions substitution at Ru site in polycrystalline EuRu-1222. Superconducting and magnetic properties of Cr and Mn doped EuRu-1222 are investigated by XRD, DC transport and DC magnetization measurements. Doping of Cr and Mn in EuRu-1222 at Ru site suppresses the superconductivity, FM components and enhances the AFM ordering of Ru spins. These results point out possible coupling between superconductivity and magnetism.
3.1 Introduction

Over a decade has passed since the synthesis [1] and subsequent observation of magneto-superconductivity in rutheno-cuprates [2, 3]. Rutheno-cuprates are derived from basic RE-123 (REBa$_2$Cu$_3$O$_7$, RE = rare earths, except Ce, Pr and Tb) with the CuO$_{1-\delta}$ chains being replaced with the RuO$_2$ sheets. Namely two compounds i.e. Ru-1212 (RuSr$_2$RECu$_2$O$_{8-\delta}$) and Ru-1222 (RuSr$_2$Eu$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10-\delta}$) are studied extensively over the years [4, 5, 6]. In these compounds Ru spins order magnetically (canted ferromagnetism) above say 150K and superconductivity is observed below 40K in CuO$_2$ planes of the same unit-cell [4, 5, 6]. Whether CuO$_2$ planes superconductivity and RuO$_2$ sheets ferromagnetism (FM) interacts electronically with each other or not is yet an unresolved question [2, 3, 4, 5, 6]. As far as the nature of Ru spins magnetic order is concerned, the same is unambiguously canted ferromagnetic in case of Ru-1212 [7, 8, 9, 10, 11], with some very recent debate related to additional Cu-AFM component [12]. On the other hand, the situation in case of Ru-1222 is quite complex [5, 6, 13, 14, 15, 16]. Basically the Ru spins order AFM at above 180K, than reorients themselves at 125K and later below 100K develops a canted FM component [17]. This is different situation than as in case of Ru-1212, where Ru spins order as canted FM in one step below around 150K [3, 4, 7, 8, 9, 10, 11]. This is interesting, because the RuO$_2$ sheets are principally same in both Ru-1212 and 1222 structures. In fact the three-step ($AFM^{180K}$-re-orientation$^{125K}$-canted $FM^{100K}$) ordering of Ru spins in Ru-1222 gives rise to a clear spin-glass (SG) transition in intermediate ranges [18], which is not seen in Ru-1212 [19]. Recently we reported the impact of varying oxygen content on magnetism and superconductivity of Ru-1212 and found that though the magnetic ordering temperature changes but the same yet remains a single step canted FM in nature [20, 21]. Seemingly the RuO$_2$ layer is robust in Ru-1212 compound. Substitutions in EuRu-1222 at the Ru site can be used to investigate both magnetic ordering and superconductivity. Some examples are the hetero-valence substitutions like Sb [22], Pb [23], Sn [24], Mo [25] and Co [26] that affects both the carrier density in the CuO$_2$ planes and the magnetic coupling between the Ru ions. As a consequence, in these substitutions, it is difficult to separate the possible genuine co-existence of superconductivity and magnetism. Cr substitution at
Ru site is very interesting, since in this case Cr has valence state $3^+$ while Ru is in $5^+$ valence state so that the changes in the carrier density are much larger than the previous examples. Similarly, Mn ion substitution for Ru [27], since Mn has valence state $4^+$ while Ru valence is close to $5^+$ therefore, changes in the carrier density should be smaller than in some of the previous examples. It has been found that the superconductivity is killed by the Cr and Mn both substitution and the magnetic moment is also drastically reduced [27]. These results could be interpreted that there may have some coupling between the superconducting (CuO$_2$) layer and magnetic (RuO$_2$) layer. However, more detailed studies on the magnetic behavior of Cr and Mn doped EuRu-1222 are certainly desirable to understand the complex interplay between superconductivity and magnetism in this hybrid system. In this chapter, we explore the magnetic behavior of (Ru$_{1-x}$TM$_x$)-1222, TM = Cr and Mn samples with $x = 0.0$-0.50, which is found to be its solubility limit at normal pressure synthesis conditions. The aim of the present study is to explore a basic question: is there an intrinsic long-range magnetic order in Ru-1222? So we carried out this investigation by studying the isomorphic (Ru$_{1-x}$TM$_x$)-1222 and series of compounds with ($0.0 \leq x \leq 0.50$).

### 3.2 Multiple magnetic ordering temperatures in pure EuRu-1222

In this section we report the magneto-superconductivity of the variously processed (air, oxygen and prolonged oxygen annealed) EuRu-1222 compound. It is found that though three-step transition ($AFM^{180K}$-re-orientation$^{125K}$-canted $FM^{100K}$) is intrinsic to all the samples, the same is more prominent in less oxygen content samples. Structural, magnetic and transport properties of variously processed EuRu-1222 are presented.

#### 3.2.1 Experimental details

The RuSr$_2$Eu$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10-\delta}$ (EuRu-1222) sample was synthesized through a solid-state reaction route from RuO$_2$, SrO$_2$, Eu$_2$O$_3$, CeO$_2$ and CuO. Calcinations were carried out on the mixed powder at 1000°C, 1020°C, 1040°C and 1060°C each for 24h with intermediate grindings. The pressed bar-shaped pellets were annealed in air and flow of oxygen at 1075°C, 600°C and 400°C for 12h each and subsequently cooled slowly over a span of another 12h down to room temperature. The former sample is
called air-annealed and later as O$_2$-annealed. One of these samples is further treated in high pressure (~3 atm.) of O$_2$ for 48h and subsequently cooled slowly to room temperature in the same atmosphere. This sample is named “HPO$_2$-treated”. X-ray diffraction (XRD) patterns were obtained at room temperature (Rigaku-Diffractrometer, Cu-\textit{K}$\alpha$ radiation). Magnetization measurements were performed on PPMS-14T. Resistivity measurements were also carried out on resistivity option of PPMS-14T in temperature range of 10 to 300K.

### 3.2.2 Results and discussion

#### 3.2.2.1 Structural studies

Figure 3.1 depicts the X-ray diffraction (XRD) patterns of air and O$_2$-annealed EuRu-1222 samples. Reitveld analysis is carried out on both samples. Reasonably good agreement can be seen in fitted (Rietveld calculated) and observed (experimental) data in Fig. 3.1. These samples crystallize in tetragonal structure with space group \textit{I}4/\textit{mmm}. All the observed diffraction peaks are from the desired structure (marked with vertical bars) except a small intensity line close to main peaks at around 30 degree. This is presumably due to presence of un-reacted SrRuO$_3$ in the matrix. Presence of SrRuO$_3$ though small in quantity, is marked (*) in both Air and O$_2$-annealed samples. Detailed Reitveld analysis is carried out on both the samples. The coordinates positions, lattice parameters and volume for these samples are tabulated in Tables 3.1 and 3.2. For O$_2$-annealed sample the lattice parameters and volume shrinks slightly in comparison to air-annealed sample. From XRD results and their Rietveld analysis we can safely conclude that our air and O$_2$-annealed RuSr$_2$Eu$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10-\delta}$ (EuRu-1222) samples are nearly single phase with only a small impurity of SrRuO$_3$ in both of them. We can safely assume that as far as the impurity contents are concerned, the presently studied samples are competitive or even better than the earlier reported Ru-1222 compounds [3, 4, 5, 6, 13, 14, 15, 16]. The lattice parameters $a$, $c$ and volume are; $a = 3.8390(3)$ Å, $c = 28.5697$ (29) Å, and $V = 421.065$ Å$^3$ for air annealed sample and $a = 3.8387(2)$ Å, $c = 28.5591(23)$ Å, and $V = 420.838$ Å$^3$ for O$_2$-annealed sample. The lattice parameters $a$, $c$ and volume for slightly oxygen-pressurized sample are $a = 3.8378(2)$ Å, $c = 28.4849(2)$ Å, and $V = 419.545$ Å$^3$ [28].
Figure 3.1: Fitted and observed X-ray diffraction patterns for air and O$_2$-annealed EuRu-1222.

Table 3.1: Rietveld refined parameters for RuSr$_2$Eu$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10-\delta}$ (air-annealed)  
Space group: I4/mmm, Lattice parameters; $a = 3.8390(3)$ Å, $c = 28.5697(29)$ Å, and cell volume is 421.065 Å$^3$.

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Table 3.2: Rietveld refined parameters for RuSr$_2$Eu$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10-\delta}$ (O$_2$-annealed)
Space group: I4/mmm, Lattice parameters; $a = 3.8387(2)$ Å, $c = 28.5591(23)$ Å, and cell volume is $420.838$ Å$^3$.

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Detailed Rietveld analysis of slightly oxygen-pressurized sample is reported earlier [29]. Decrease in lattice parameters and volume for O$_2$-annealed samples is in agreement with earlier reports [3, 4, 5, 6, 13, 14, 15, 16]. This basically happens due to an increase in oxygen content of the compound and is clearly seen in case of slightly oxygen-pressurized sample.

3.2.2.2 DC magnetization studies

The zero-field-cooled (ZFC) and field-cooled (FC) magnetic moment ($M$) versus temperature ($T$) plots for the air-annealed RuSr$_2$Eu$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10-\delta}$ (EuRu-1222) are shown in Fig. 3.2(a) in the presence of 5Oe applied field. The ZFC and FC magnetization start branching at around 200K. This transition is earlier recognized as antiferromagnetic ($AFM$) ordering temperature ($T_N$) of Ru spins [17, 22]. With decrease in temperature the Ru-spins re-orient themselves at around 125K, which is seen as a peak in ZFC and a step in FC magnetization. When the temperature is further lowered both the ZFC and FC exhibit a sharp rise in magnetization at around 100K, exhibiting a ferromagnetic ($FM$) type of ordering. Later though the FC...
magnetization exhibits a clear FM like saturation, the ZFC branch turns to a cusp like structure below say 90K. Summarily the Ru spins order AFM at 200K, re-orient themselves at 125K before exhibiting FM below say 50K. The FM component of the compound is visible from the magnetic hysteresis $M$-$H$ loop of the compound, which is being shown in inset of Fig. 3.2(a). The ZFC magnetization though touches the zero base line at 5K; hardly any meaning full diamagnetism is seen.

Figure 3.2(b) shows the $M$-$T$ plots for O$_2$-annealed RuSr$_2$Eu$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10-\delta}$ (EuRu-1222) compound. Basically, all the three magnetic ordering temperatures corresponding to the AFM (200K), FM (100K) and the intermediate spin-re-orientation (125K) are seen in the sample. Though, this is similar to that as observed for the air-annealed EuRu-1222 in Fig. 3.2(a), the extent of opening of ZFC and FC is comparatively less. Also the three characteristic Ru-spins magnetic ordering temperatures; namely the $T_N$, $T_{re-orient}$ and $T_{magnetic}$ are slightly decreased in comparison to the air-annealed EuRu-1222 sample. Further ZFC of this sample shows diamagnetic transition at around 20K, indicating towards superconductivity at this temperature. The $M$-$H$ loops for this compound at 5, 75 and 100K is shown in inset of
Figure 3.2: (b) Magnetic moment ($M$) vs. temperature ($T$) plots for $O_2$-annealed RuSr$_2$Eu$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10-\delta}$, inset shows the magnetization $M$-$H$ plots for the same at 5, 75 and 100K.

Figure 3.2: (c) Magnetic moment ($M$) vs. temperature ($T$) plots for slightly pressurized $O_2$-annealed RuSr$_2$Eu$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10-\delta}$, inset shows the magnetization $M$-$H$ plots for the same at 5, 20 and 50K.
Fig. 3.2(b). At 5K the compound is clearly ferromagnetic with nearly same saturation moment of around value of (3.0emu/g) for the air-annealed sample shown in Fig. 3.2(a). The $M-T$ of slightly pressurized (~3atm.) O$_2$-annealed EuRu-1222 sample is shown in Fig. 3.2(c). Interestingly for this sample the ZFC and FC branches opening is seen clearly only at $T_{magnetic}$ (90K) and the $T_N$ and $T_{re-orient}$ are hardly visible. Also this sample is clearly diamagnetic in ZFC below 20K. As mentioned in the introduction [17], the three magnetic ordering temperatures; namely the $T_N$, $T_{re-orient}$ and $T_{magnetic}$ are identified clearly in literature for various studied Ru-1222 compounds. Interestingly besides the main transition $T_{magnetic}$ (90K), the other two i.e., $T_N$ and $T_{re-orient}$ are hardly visible in magnetization of oxygen annealed samples. Detailed characterization of this sample is reported earlier [29]. On the other hand these two transitions can be clearly marked in the magnetic susceptibility of air-annealed or presumably less oxygen content samples. Further though the O$_2$-annealed sample show diamagnetism below 20K, the air-annealed exhibits hardly any diamagnetism down to 5K.

3.2.2.3 DC transport studies

The $R$ vs. $T$ plots of the, air, O$_2$ and slightly pressurized O$_2$-annealed samples showed them to be non-superconducting in case of air and superconducting at 18K and 23K respectively in case of O$_2$-annealed samples. The $R-T$ lots of O$_2$-annealed and slightly O$_2$-pressurized EuRu-1222 samples are depicted in Fig. 3.3(a) and 3.3(b). The $R-T$ of air-annealed sample is of highly semiconducting nature and superconductivity is not observed down to 2K, plot not shown. For O$_2$-annealed sample the $R-T$ plot is semiconducting like, and $T_c$ ($R = 0$) is seen at 18K, Fig. 3.3(a). For the O$_2$-pressurized EuRu-1222 sample, the $R-T$ behavior is slightly metallic and $T_c$ ($R = 0$) is seen at 23K, Fig. 3.3(b), for more details see ref. [29]. The results of magnetization and transport measurements can be summarized as follows;

(i). We have synthesized a nearly single-phase EuRu-1222 compound. Post annealing of as formed Ru-1222 in air, O$_2$ or slightly pressurized O$_2$ does not alter parent tetragonal $I4/mmm$ phase of the EuRu-1222 structure.

(ii). Three known characteristic magnetic ordering temperatures of EuRu-1222,
namely the $T_N$, $T_{re-orient}$ and $T_{magnetic}$ for Ru spins are although seen for all the air, O$_2$ and pressurized O$_2$-annealed samples.

Figure 3.3: (a) Resistance vs. temperature plot for O$_2$-annealed EuRu-1222 sample.

Figure 3.3: (b) Resistance vs. temperature plot for slightly pressurized O$_2$-annealed EuRu-1222 sample.
Though in case of Ru-1212 compound a single magnetic transition at $T_{AFM}$ (140-150K) is seen with a canted $FM$ at low temperature in case of Ru-1222 three magnetic ordering steps are known to be present mainly at $T_N$, $T_{re-orient}$ and $T_{magnetic}$ for Ru spins [17, 21]. Our present results exhibited that three characteristic ordering temperatures of Ru-1222 can be seen more prominently in oxygen deficient samples. It is reported earlier by some of us that though in Ru-1212 the Ru stays mainly in Ru$^{5+}$ state, in Ru-1222 the same has around 10-20% proportion of Ru$^{4+}$ as well [30]. Also the oxygen stability of the Ru-1212 is more than the Ru-1222 [31]. The competitive ordering of Ru$^{4+}$ and Ru$^{5+}$ spins can be the reason behind multiple magnetic transitions of $T_N$ (180K), $T_{re-orient}$ (125K) and $T_{magnetic}$ (100K) before low temperature $FM$ of Ru spins in Ru-1222. The proportion of Ru$^{4+}$ is more in oxygen deficient samples and hence the multiple magnetic transitions are seen more prominently in them [30]. An increase in oxygen content due to annealing in oxygen (indicated in present case by decrease in volume) is to increase both the content of Ru$^{5+}$ and the effective Cu valence in superconducting CuO$_2$ planes. The former (increase in Ru$^{5+}$ amount) results in merging of multiple magnetic transitions [$T_N$ (180K), $T_{re-orient}$ (125K) and $T_{magnetic}$ (100K)] to a single transition [$T_{magnetic}$ (100K), Fig. 3.2(c)] and the second (increase in Cu valence) induces the superconductivity in Ru-1222 system. This explains the multiple transitions and appearance/disappearance of superconductivity in Ru-1222 system.

### 3.3 Effect of Cr substitution on the superconducting and magnetic properties of EuRu-1222

In this section we explore the magnetic behavior of (Ru$_{1-x}$Cr$_x$)-1222, with x = 0.0-0.40, which is found to be its solubility limit at normal pressure synthesis conditions. Aim of the present study is to explore a basic question: is there an intrinsic long-range magnetic order in Ru-1222? So we carried out this investigation by studying the isomorphic (Ru$_{1-x}$Cr$_x$)-1222 series of compounds with (0.0 ≤ x ≤ 0.40).

### 3.3.1 Experimental details

Detailed procedure of samples synthesis and measurements is given in section
3.2.1 of this chapter. Briefly, Polycrystalline samples of the series Ru$_{1-x}$Cr$_x$-1222 (0.0 $\leq x \leq 0.40$) were synthesized by standard solid state reaction route.

### 3.3.2 Results and discussion

#### 3.3.2.1 DC transport studies

![Figure 3.4: Variation of normalized resistance ($R_n$) with temperature for Ru$_{1-x}$Cr$_x$-1222 (0.00 $\leq x \leq 0.40$).](image)

Figure 3.4 shows the temperature dependence of the normalized resistance for samples Ru$_{1-x}$Cr$_x$-1222 ($x = 0.0$, 0.10, 0.20, 0.30 & 0.40). The superconducting transition is observed only for pure sample and rest all samples are semiconductor like down to 10K. Also, superconductivity vanishes with Cr doping. As Cr$^{3+}$ substitutes Ru$^{5+}$, the hole concentration in the CuO$_2$ planes should increase. Hence disappearance of superconductivity may be due to the disorder-induced localization. There may exist magnetic trapping or scattering of holes [32] due to distortion of RuO$_6$ octahedra. Cr doping could introduce more distortion of the RuO$_6$ octahedra, and lead to more magnetic trapping or scattering of holes. Both the scattering and magnetic trapping hamper the movement of carriers and results in the hole localization. Consequently,
though Cr doping increases the hole concentration, the same creates enough disorder, which results in the hole localization to exceed the effect of increased hole concentration.

3.3.2.2 DC magnetization studies

Figure 3.5: Field cooled (FC) and zero-field cooled (ZFC) temperature dependencies of magnetization at 10Oe for EuRu-1222.

Figure 3.5 shows the temperature dependencies of both field cooled (FC) & zero-field cooled (ZFC) DC magnetization measured at 10Oe. There is a sharp rise of both the ZFC and FC curves at Curie temperature $T_C = 106$K shows a PM to FM transition. At temperature close to $T_C$, the ZFC and FC curves branch out, and now the system enters into a new state, called glassy-state. The ZFC branch indicates a prominent peak at $T_p = 92.5$K, just below the temperature where ZFC and FC curves separate, while the FC branch increases with decreasing temperature.

Figure 3.6 depicts the ZFC and FC behavior of samples Ru$_{1-x}$Cr$_x$-1222 for $x = 0.10-0.40$. Doping of Cr in place of long-range magnetically ordered Ru spins break the FM order and induces AFM ordering. It was also observed that the net magnetic moment decreases drastically with Cr doping, though without any monotonic trend.

~ 89 ~
Figure 3.6: FC and ZFC temperature dependences of the magnetization of Ru$_{1-x}$Cr$_x$-1222 ($x = 0.10, 0.20, 0.30$ and $0.40$) at $H = 100$Oe.

3.4 Effect of Mn substitution at Ru site in EuRu-1222 magneto-superconductor

We explore the magnetic behavior of Ru$_{1-x}$Mn$_x$Sr$_2$Eu$_{1.4}$Ce$_{0.6}$Cu$_2$O$_{10-\delta}$ samples with Mn substitution at Ru site up to $x = 0.50$, which is found to be its solubility limit at normal pressure synthesis conditions. The aim of the present study is to explore a basic question: is there an intrinsic long-range magnetic order in Ru-1222? So we carried out this investigation by studying the isomorphic (Ru$_{1-x}$Mn$_x$)-1222 series of compounds with ($0.0 \leq x \leq 0.50$).

3.4.1 Experimental details

Detailed procedure of samples synthesis and measurements is given in section 3.2.1 of this chapter. Briefly, polycrystalline samples of the series Ru$_{1-x}$Mn$_x$-1222 ($0.0 \leq x \leq 0.50$) were synthesized by conventional solid state reaction route.
3.4.2 Results and discussion

3.4.2.1 Structural studies

Figure 3.7: Observed (solids circles) and calculated (solid lines) XRD patterns of Ru$_{1-x}$Mn$_x$Sr$_2$Eu$_{1.4}$Ce$_{0.6}$Cu$_2$O$_{10-\delta}$ ($x = 0.0, 0.02 & 0.30$) compound at room temperature. Solid lines at the bottom of each panel are the difference between the observed and calculated patterns. Vertical lines at the bottom of each curve show the position of allowed Bragg peaks.

The main intensity lines of the patterns i.e., the low angle high intensity with $hkl$ [107] and high angle low intensity with [110], corresponding to tetragonal structure with space group $I4/mmm$ are visible for all samples. Observed (open circle) and fitted (solid lines) X-ray patterns for the compounds Ru$_{1-x}$Mn$_x$Sr$_2$Eu$_{1.4}$Ce$_{0.6}$Cu$_2$O$_{10-\delta}$ ($x = 0.0, 0.02 & 0.30$) are shown in Fig. 3.7. For $x > 0.30$, XRD indicates multiphase nature of the system and complete substitution of Ru by Mn is not possible as it leads to the formation of Sr$_3$Mn$_2$O$_7$ as a major phase and impurity phases SrCuO$_2$, CeO$_2$ and CuO. XRD plots of multiphase $x = 0.50$ sample is not shown here. The structural analysis was performed using the Rietveld refinement analysis by employing the FullProf Program. The Rietveld analysis confirms a single phase formation in $I4/mmm$ space.
group for all the Mn doped samples. The lattice parameters $a$ and $c$ decreases continuously as the Mn% concentration increases. The decrease in lattice parameters with the Mn content is due to the smaller ionic radii of Mn (0.53 Å) in comparison to the Ru (0.62 Å) in hexagonal coordination state. All the Rietveld refined structural parameters (atomic coordinates and site occupancy) of Mn doped Ru-1222 are shown in the Table 3.3.

Table 3.3: Atomic coordinates and site occupancy of Ru$_{1-x}$Mn$_x$Sr$_2$Eu$_{1.4}$Ce$_{0.6}$Cu$_2$O$_{10-\delta}$ ($x = 0.0, 0.01$ and $0.30$): Space group: $I4/nmm$, Lattice parameters; $a = 3.849(4)$ Å, $c = 28.568(4)$ Å ($x = 0.00$), $a = 3.845(4)$ Å, $c = 28.555(4)$ Å ($x = 0.02$), and $a = 3.840(4)$ Å, $c = 28.537(4)$ Å ($x = 0.30$).

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<td>0.2500</td>
</tr>
</tbody>
</table>

3.4.2.2 DC magnetization studies

The temperature dependent DC magnetic susceptibility for all the Mn doped samples is shown in Fig. 3.8(a) and (b). Samples were cooled in zero magnetic fields down to the lowest accessible temperature (2K). After temperature stabilization a DC magnetic field of 10Oe is applied and the magnetization is recorded as the temperature being raised (ZFC curve) up to 175K. Then the measurement continued while the temperature was again decreased back to 2K (FC curve), keeping the same DC magnetic field. For all samples the ZFC curves show a smaller intensity than the FC ones, as indicated in Fig. 3.8(a) for the undoped ($x = 0$) sample. The results of
lightly and heavily doped samples are presented in different panels (Fig. 3.8(a) and Fig. 3.8(b), respectively). For substitution of 1%, 2%, 5%, 10% and 20% of Ru atoms by Mn (x= 0.01, 0.02, 0.05, 0.10 and 0.20), we observed that the overall shape of magnetization curve is similar to the result obtained for the undoped sample, but with spin-glass (SG) [21] transition (~90K) being shifted towards the lower temperature, see Fig. 3.8(a). For undoped and the lightly doped (x up to 0.10) samples diamagnetic signal is also observed and low temperatures and the ZFC curve is turned negative. This is signature of low temperature superconductivity in these samples. Superconductivity in these samples is also seen as small reduction of the magnetization in the FC curve at low temperatures.

The superconducting transition temperature being observed at low temperatures for pure and lightly doped samples decreases continuously as the Mn% content increases. The superconducting transition temperature ($T_c$) and spin-glass (SG) transition decreases with increase in Mn content. Superconductivity being observed...
for samples with Mn content of up to 10% and 20% samples is just at the boundary of non superconductivity. Dramatic changes are observed for the heavily doped non superconducting samples with $x \geq 0.30$, see Fig. 3.8 (b). For those samples, the $SG$ peak in the $ZFC$ curve is not present; indicating that the glassy transition [18] is completely suppressed. Also there is a dramatic reduction in the magnetic moment associated with the Ru sublattice. Curiously, as mentioned before the superconducting diamagnetic signal becomes weaker with the Mn content, for $(x = 0.0-0.20)$, indicating a smaller superconducting fraction. For $x \leq 0.20$ the superposition of the magnetic and superconducting responses makes it difficult to calculate the change in the superconducting fraction from $DC$ magnetization. The reduction in the superconducting fraction and $T_c$ with the increase of manganese (Mn) content for $x \leq 0.2$ can be explained by the charge in the carrier transfer to the CuO$_2$ planes with doping. But the most striking feature of the magnetization curves presented in Fig. 3.8(a) and (b), is that there is a critical doping level $(x = 0.2)$ up to which spin-glass or cluster glass like transition and high magnetic moments appears, while for $x \geq 0.3$ this transition is completely suppressed and the total magnetic moment becomes smaller by about two order of magnitude. Considering only the changes in the carrier density we would expect $T_c$ (and the superconducting fraction) to be maximum for $x = 0.0$, and to decrease with the increase in Mn concentration up to $x = 0.2$. However, much higher magnetic moments occurring for the samples with $x \leq 0.2$ act as Cooper pair-breakers, thus reducing $T_c$ as well as the superconducting fraction. Our results confirm the conclusions presented in [32] where Mo-doped Ru-1222 samples were studied. In the case of Mo$^{6+}$ doping, the changes in $T_c$ were significantly more prominent than in the present Mn doping case, due to the larger change in the carrier density. The presence of pair-breaking effect was also identified for Mo doping and modeled using the Abrikosov-Gorkov theory for magnetic impurities [32].

The substitution of ruthenium (Ru) by manganese (Mn) also induces significant changes in the low temperature ($T = 5K$) magnetic hysteresis loop, as shown in Fig. 3.9. The loops for samples $x = 0.0$ and $x = 0.01$ in low applied field range are similar, differing basically only by the magnitude of the magnetization (see Fig. 3.9). In fact, if these two curves are normalized by the corresponding magnetization at 1000Oe,
they collapse in a single curve (not shown here). Increasing the Mn content to \( x = 0.02 \) causes a significant change in the shape of the hysteresis loop, particularly the
coercive field is increased (see Fig. 3.10). Further increases in the Mn concentration also affect the hysteresis loops (see Fig. 3.11).

The coercive field ($H_c$) and remanent magnetization ($M_r$) calculated from the hysteresis loop for all the samples, are plotted in Fig. 3.12. As the content of Mn in the samples increases, $H_c$ increases up to the $x = 0.3$ and later decreases. The remnant magnetization ($M_r$), decreases continuously with the content of Mn. However, the most striking features presented in Fig. 3.12 is the anomalous increase in $H_c$ as the Mn content increases from $x = 0.1$ to 0.2. The maximum value of $H_c$ is observed for $x = 0.3$. It is important to notice that the samples for $x \geq 0.2$ do not show the spin-glass transition. Therefore, one could analyze the magnetization loops to be a result of two separate contributions. One of them (dominant for $x < 0.2$) could be associated with the canted antiferromagnetic phase. The second contribution comes from the cluster glass phase. This contribution (dominant for $x > 0.2$) increases the magnetization at high magnetic fields and is very sensitive to the Mn doping. Therefore, the observed loops provide evidence for the existence of different regions in the sample, which present essentially independent magnetic behaviors. The interpretation has recently been proposed to explain complex magnetic response of EuRu-1222 [33, 34, 35, 36].

**Figure 3.11:** Magnetic hysteresis loops for Mn doped $x = 0.30-0.50$, measured at 5K.
According to [36], the presence of oxygen vacancies may favor the ruthenium ions around it to assume valence $4^+$, instead of the usual $5^+$. This would lead to the formation of Ru$^{4+}$ rich clusters, which would present different magnetic interaction compared to the rest of the matrix. Therefore the strong suppression of the cluster-glass transition with Mn substitution may come from an increase in the overall oxygen content in heavily Mn-substituted samples. This is also consistent of our previous results that showed an increase in the blocking temperature of the glassy transition, when the oxygen content of the samples was reduced [37]. The Mn substitution could provide some dilution effect in the Ru sublattice as well, since AFM components of Ru spin enhances and the FM components decreases so the octahedral RuO$_6$ cause the frustration of magnetic ordering and leading to the glassy behavior.

### 3.5 Conclusion

Summarily, we have synthesized nearly single phase Ru-1222 compound. Further with various post annealing of air, O$_2$ and pressurized O$_2$ the nature of multiple magnetic transitions and appearance/disappearance of superconductivity in
Ru-1222 system are presented. Our results demonstrate that magnetic transitions i.e.,
$T_N$ (180K), $T_{re-orient}$ (125K) and $T_{magnetic}$ (100K) before low temperature $FM$ of Ru
spins in Ru-1222 are intrinsic in nature and not due to embedded impurities. These
results are clear substantiation of an earlier report, where we demonstrated that the
opening of $ZFC$ and $FC$ irreversibility of magnetization in Ru-1222 is dependent on
the oxygen content and not driven by the impurities [37]. Doping of Cr in EuRu-1222
at Ru site enhances the $AFM$ of Ru spin and suppresses the $FM$ components. This may
cause the frustration of magnetic ordering of Ru ions, leading to a glassy behavior in
this compound. It was observed that Mn substitution strongly reduces the spin-glass
transition temperature. By increasing the Mn content the superconducting transition
also decreases. We explain this behavior through a decrease in carrier density, caused
by the increase of Mn doping, combined with a pair-breaking effect of the strong
magnetic moments presents in the samples with $x = 0.0$ to 0.1. As the Mn
concentration increases the $SG$ phase is strongly suppressed and disappeared
completely for $x \geq 0.3$. We also observed that doping of Mn in EuRu-1222 at Ru site
enhance the $AFM$ of Ru spin and suppress the $FM$ components.
3.6 References


