Chapter 6

Spin-glass, cluster ferromagnetism, superparamagnetism in YRu-1222 and magnetic, thermal properties of YRu-1212

Abstract

In this chapter, First part deals with the structural, DC magnetization, detailed linear/non-linear AC susceptibility, isothermal and thermoremanent magnetization (TRM) behavior for RuSr$_2$Y$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10}$ (YRu-1222) magneto-superconductor to understand its complex magnetism. Variation of cusp position with applied AC frequency follows the famous Vogel-Fulcher law, which is commonly accepted feature for spin-glass (SG) system with homogeneous/non-homogeneous ferromagnetic clusters embedded in spin-glass (SG) matrix. Above the freezing temperature ($T_f$), first and third harmonics AC susceptibility analysis indicated possibility of the co-existence of spin cluster ferromagnetism with superparamagnetism (SPM). The $M$-$H$ loops at low temperature exhibit the ferromagnetic behavior with rather small coercive field ($H_c$) and remnant magnetization ($M_r$). In second part, structural, magnetic and thermal property details of Ru$_{0.9}$Sr$_2$YCu$_{2.1}$O$_{7.9}$ (YRu-1212) are presented. Clear diamagnetic transitions are seen in both zero field cooled (ZFC) and field cooled (FC) magnetic susceptibility measurements and exhibiting superconductivity below 50K. Both the thermoelectric power ($S$) and thermal conductivity ($\kappa$) measurements show superconductivity onset below 50K with $S = 0$ at 30K and a broad hump in heat capacity $C_p(T)$ below 30K. The appearance of a hump in $C_p(T)$, instead of a clear transition, is indicative of short-range magnetic correlations. Both studied samples are synthesized through the novel solid state High Pressure (6GPa) High Temperature (1400-1450°C) (HPHT) technique.
6.1 Introduction

Superconductivity (SC) and ferromagnetism (FM) are two antagonistic states of matter that tend to avoid each other. The mutual co-existence of these two states below their magnetic ordering temperature ($T_m$) and superconducting transition temperature ($T_c$) are matters of fundamental interest. This antagonistic nature between superconductivity and ferromagnetism has long been recognized. In 1959 it was proposed [1] that co-existence can occur simultaneously, while the ferromagnetic state can adjust itself with a non-uniform structure to accommodate superconductivity. Some non-uniform ferromagnetic states have been observed to co-exist with the superconducting state, which are called ferromagnetic superconductors [2]. These compounds become superconducting below $T_c$ and ferromagnetic at further lower temperature $T_m$, such as ErRh$_4$B$_4$, HoMo$_6$S$_8$ and HoMo$_6$Se$_8$. There are only a few compounds where $T_m$ is higher than $T_c$ and both states do co-exist below superconducting transition temperature ($T_c$). I. Felner and his colleagues [3] reported the co-existence of weak ferromagnetism ($T_m < 100K$) with superconductivity ($T_c \sim 45K$) in the high $T_c$ rutheno-cuprates and coined the term ‘superconducting ferromagnets’ ($T_m > T_c$), in contrast to ferromagnetic superconductors ($T_m < T_c$). The discovery of co-existence of weak ferromagnetism (W-FM) and superconductivity (SC) in RuSr$_2$Ln$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10-\delta}$ (Ru-1222) and RuSr$_2$LnCu$_2$O$_{8-\delta}$ (Ru-1212) with Ln = Eu, Gd, Sm and Y attracted a lot of attention from scientific community [3, 4, 5, 6]. These systems show weak ferromagnetic ordering below the 100-135K and superconductivity at a lower critical temperature of about 15-40K, depending on the synthesis and annealing conditions. It seems that the pair breaking phenomenon due to magnetic interactions does not play a role in this system. Unit cell of rutheno-cuprates consists of alternating layers of RuO$_2$ and CuO$_2$ planes. RuO$_2$ layer is responsible for weak ferromagnetism and carrier creation mechanism, while superconductivity resides in CuO$_2$ planes below a certain temperature and both of the phenomena are seemingly decoupled from each other. Muon-spin rotation (ZF-$\mu$SR) for Ru-1222, concluded the possibility of phase separation [7, 8] in terms of various magnetic domains, but supported the idea concerning the coexistence of bulk magnetism and superconductivity in this system. The ZF-$\mu$SR could detect the
different magnetization domains in the bulk material and as result proposed phase separation. Our detailed magnetization results do not go against the phase separation scenario, but rather support the same. We talk of magnetic phase separation here and not the structural phase impurities. Recently, efforts have been devoted to the understanding of phase purity, lattice distortions and true nature of magnetism in Ru-1222 structure [9]. Phase purity, in particular ruling out the presence of SrRuO₃ magnetic impurity is crucial. In order to support confirmations of microscopic uniform co-existence of superconductivity and magnetism, the presence of impurity phases, in particular the magnetic one need to be rules out. Lattice distortions such as rotations of RuO₆ octahedra can also affect the magnetic structure via spin-orbit coupling (Dzyaloshinsky-Moriya interactions) anti-symmetric exchange interactions or single-ion anisotropy [10, 11].

Some unsolved questions still remains about the exact type of magnetic ordering in these systems. Various experimental techniques being used to understand the exact type of magnetic ordering for this system are muon-spin rotation ($\mu$SR) [7, 8], magnetic resonance (MR) [12], neutron powder diffraction (NPD) [13, 14], magnetization [15, 16] and nuclear magnetic resonance (NMR) [17]. Interestingly, as far as exact magnetic order is concerned, all these techniques are not in full agreement with each other [7, 12, 13, 14, 15, 16, 17]. The only commonality was that all the techniques indicated the presence of canted antiferromagnetic ordering being embedded in ferromagnetic matrix. Though, some earlier neutron diffraction data [18, 19] did not reveal long-range antiferromagnetic (AFM) order, more recent works had clearly exhibited the evidence of the long-range AFM ordering of Ru spins in Ru-1222 phase [20, 21, 22]. In fact it is known by now that there is antiferromagnetism (or most likely weak ferromagnetism) in this material down to 2K [20, 21, 22]. Neutron scattering is more authentic tool to determine magnetic structure than the bulk magnetization. Also, it was purposed that in Ru site Nb substituted Ru-1222 compounds there are interacting clusters in the Ru-O₂ layers, without any long-range magnetic order [23]. Furthermore, the slow spin dynamics [24] suggested that FM clusters in Ru-1222 could exhibit superparamagnetism (SPM). On the other hand, detailed observations of the frequency and field dependent peak of the AC
susceptibility as a function of temperature along with isothermal magnetization measurements at low and high fields [25, 26] indicated spin-glass (SG) and cluster ferromagnetism behavior in Ru-1222. As reported for EuRu-1222 system [27], though clear peak shift is seen with frequency in real part of AC susceptibility, the characteristic frequency based upon Arrhenius fit is found to be unrealistic i.e., $10^{130}\text{Hz}$. However, Vogel-Fulcher fit suggested SG state with $f_o = 10^{12}\text{Hz}$, which is acceptable. The only question remains is the small deviation of Vogel-Fulcher fit at lower side of temperature range [27]. It is well known that frequency dependence of the peak and isothermal magnetization are characteristics features of both spin-glass (SG) and superparamagnetism (SPM), yet the physics behind them is different. Hence, a more careful investigation of the Ru-1222 is required to probe the exact nature of these two states. AC susceptibility and its various harmonics study is very important tool to exactly probe the complex magnetization of such systems. The magnetization measured in presence of excitation AC field can be represents as power law [28, 29],

$$M = M_0 + \chi_1 H^1 + \chi_2 H^2 + \chi_3 H^3 + \chi_4 H^4 + \ldots \quad (6.1)$$

where $\chi_1$, $\chi_2$, $\chi_3$ are the first-, second-, third-order harmonics of AC susceptibility respectively, which provides useful information about the existing complex magnetism of the studied system.

Such co-existence implies, moreover, that both states develop in one thermodynamic phase, therefore a strict spatial chemical and structural uniformity of the samples is a key question for the study of such hybrid system. Various explanations were put forward to understand the phenomenon, viz., accommodation of superconductivity in spiral like magnetic structure [30]. YRu-1212 has an oxygen-deficient triple perovskite structure similar to that of YBa$_2$Cu$_3$O$_7$ (YBCO), where Ba is formally replaced by Sr and Cu in the charge reservoir by RuO$_6$ octahedra. Actually, the ground state is considered to be antiferromagnetic with a ferromagnetic component in the $ab$ plane due to the lack of symmetry caused by canting of the RuO$_6$ octahedra. Magnetism and superconductivity can co-exist because they supposed to act in different layers, namely the first one in the layer containing Ru, and the second one in the Cu layer. Structures of both RuSr$_2$RECu$_2$O$_8$ and RuSr$_2$(RE,Ce)$_2$Cu$_2$O$_{10}$ are derived from that of $REBa_2Cu_3O_7$ with Cu in the charge reservoir layer substituted by
Ru to generate RuO$_2$ sheet for the CuO chain.

6.2 Spin-glass, cluster ferromagnetism and superparamagnetism in HPHT synthesized YRu-1222

The part of present YRu-1222 was reported earlier but the $AC$ susceptibility measurements were done only in narrow range of frequency (165-1465Hz) [31], which could not detect the peak shift with frequency and hence excluded the $SG$ state. We believe the extended frequency range $AC$ susceptibility measurements were warranted on YRu-1222. Hence in the present chapter, the temperature dependence of the $DC$ magnetization, linear and nonlinear $AC$ susceptibility with first and higher harmonics and isothermal magnetization at high magnetic field of RuSr$_2$Y$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10}$ (YRu-1222) sample are investigated in detail to understand the spin-glass ($SG$), ferromagnetic clusters and superparamagnetism ($SPM$) behavior in the system. First, some $DC$ magnetization and linear $AC$ susceptibility with frequency is performed, which confirmed the spin-glass ($SG$) state. Second, it will be shown that YRu-1222 is better described as a spin-glass ($SG$) with magnetic clusters as a result of the formation of homogenous/non-homogenous ferromagnetic clusters in spin-glass ($SG$) matrix. Third, fitting of first and third harmonics of $AC$ susceptibility with Wohlfarth’s model ($WM$) suggests the superparamagnetism ($SPM$) state in YRu-1222. Summarily, complex magnetism of superconducting ferromagnet YRu-1222 is unearthed. Note that the lower case subscript notation is for the superconducting transition temperature ($T_c$), and the upper case subscript notation for Curie temperature ($T_C$), whereas the magnetic ordering transition is marked by $T_m$.

6.2.1 Experimental details

Polycrystalline sample of chemical composition RuSr$_2$Y$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10}$ and was synthesized through High Pressure High Temperature ($HPHT$) solid state reaction route under optimized 6GPa pressure and 1450°C temperature. For the $HPHT$ synthesis the ratio of the ingredients used are (RuO$_2$) + 2(SrO$_2$) + 3/4(Y$_2$O$_3$) + 1/2(CeO$_2$) + 3/4(Cu$_2$O) + 1/2(Cu) resulting in RuSr$_2$Y$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10}$ (YRu-1222). The ingredients were mixed in an agate mortar with pestle in a Glove Box to obtain starting material for high pressure synthesis. Later on, around 300mg of the raw
mixture was sealed in a high purity gold capsule and allow to heat in a flat belt type HPHT apparatus at 6GPa and 1450°C for 3h. After the heat treatment, the sample was quenched to room temperature, and the pressure was slowly released [32]. To confirm the exact oxygen content in the synthesized samples, the weight of the capsule was measured before and after the high pressure reaction. No reasonable change was observed in the weight, warranting the fixed nominal oxygen content in the synthesized samples. The surface of the sintered high-pressure samples was polished with sand paper; the inner clean black sintered material was used for characterization.

The structure and phase purity of HPHT synthesized samples was confirmed by X-ray diffraction (XRD) measured at room temperature in the scattering angular (2θ) range of 20°-80° in equal steps of 0.02° using Rigaku Diffractometer with Cu-Kα (λ = 1.54 Å) radiation. Detailed Rietveld analysis was performed using the FullProf program. Detailed DC and AC (linear and non-linear) susceptibility data were measured on physical property measurements system (PPMS-14T, Quantum Design-USA) in temperature range 1.9 – 200K. The isothermal magnetization (M-H) loops at different temperatures with applied magnetic field up to ± 5kOe were also measured using the same PPMS. Detailed linear and non-linear AC susceptibility as a function of temperature T, in (i) in the frequency ranges of 33-9999Hz and (ii) in the AC drive field amplitude 1-17Oe in the zero external DC magnetic fields, were also measured on physical property measurements system (PPMS-14T, Quantum Design-USA).

6.2.2 Results and discussion

6.2.2.1 Structural studies

After several optimizations through HPHT method we obtained the phase pure YRu-1222 compound [32]. The sample is HPHT synthesized and despite various trials minute amount of impurity of perovskite Sr2RuYO6 (211O6) phase is seen.

Figure 6.1 depicts the room temperature observed and calculated X-ray diffraction (XRD) patterns of studied RuSr2Y1.5Ce0.5Cu2O10 (YRu-1222). The structural analysis was performed using the Rietveld refinements with help of FullProf software. Rietveld analysis confirmed the single phase formation of studied
Figure 6.1: Observed (solids circles) and calculated (solid lines) XRD patterns of RuSr$_2$Y$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10}$ compound at room temperature. Solid lines at the bottom are the difference between the observed and calculated patterns. Vertical lines at the bottom show the position of allowed Bragg peaks.

Table 6.1: Atomic coordinates and site occupancy of RuSr$_2$Y$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10}$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
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<tr>
<td>Ru</td>
<td>2b</td>
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<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Sr</td>
<td>2h</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.4211 (5)</td>
</tr>
<tr>
<td>Y/Ce</td>
<td>1c</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.2932 (8)</td>
</tr>
<tr>
<td>Cu</td>
<td>4e</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.1451 (3)</td>
</tr>
<tr>
<td>O(1)</td>
<td>8j</td>
<td>0.8228 (3)</td>
<td>0.5000</td>
<td>0.0000</td>
</tr>
<tr>
<td>O(2)</td>
<td>4e</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0719 (5)</td>
</tr>
<tr>
<td>O(3)</td>
<td>8g</td>
<td>0.0000</td>
<td>0.5000</td>
<td>0.1460 (6)</td>
</tr>
<tr>
<td>O(4)</td>
<td>4d</td>
<td>0.0000</td>
<td>0.5000</td>
<td>0.2500</td>
</tr>
</tbody>
</table>
YRu-1222 compound in space group I4/mmm. All Rietveld refined parameters (Lattice parameters, Wyckoff position and site occupancy) of studied YRu-1222 compound are shown in Table 6.1.

6.2.2.2 DC magnetization studies

Figure 6.2 depicts the DC magnetization ($M-T$) of HPHT synthesized RuSr$_2$Y$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10}$ (YRu-1222) compound in zero-field-cooled (ZFC) and field-cooled (FC) situations measured at 200e. The compound exhibits complex magnetic behavior. We define the $T_C$ (Curie temperature), simply a paramagnetic (PM) to ferromagnetic (FM) transition, as the temperature corresponding to common tangent on ZFC and FC curve cutting the temperature x-axis. The $T_C$ (Curie temperature) of YRu-1222 is around 110K as marked in Fig. 6.2. In fact the branching of FC and ZFC starts with a dip before $T_C$ (110K) at around 120K ($T_N$). This is consistent with an earlier report on YRu-1222 where it is shown that before canted ferromagnetism the Ru spins order antiferromagnetically (AFM) [33]. Interestingly the AFM persists down to 2K as evidenced from NPD [20-22]. Below the $T_C$ (Curie temperature) at around 90K, the ZFC and FC curves branch out. This temperature, where ZFC and FC curves branch out called the freezing temperature below which the system enters into a new state called glassy state. Below the freezing temperature ($T_f$) the magnetic moment corresponding to ZFC curve decreases and FC curve increases with decreasing the temperature. The system enters into a superconducting state below the superconducting transition temperature $T_c = 28$K (a kink observed in both ZFC and FC curves shown in Fig. 6.2) and finally a diamagnetic transition at $T_d = 21$K. Despite a clear diamagnetic transition in ZFC at $T_c$, the FC branch shows a paramagnetic Meissner effect (PME) like situation. The PME is often seen in some superconductors [34]. For more detailed description, please see Refs. [25, 35, 36]. The strong irreversibility between the ZFC and FC curve exhibits in the $M-T$, typical of a superparamagnetism (SPM) relaxation phenomenon of a spin-glass/cluster glass system [37, 38, 39]. Several features, which are shown here, support the likely occurrence of a spin-glass/cluster glass in RuSr$_2$Eu$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10-\delta}$ (EuRu-1222) sample, and are similar to the results for some other compositions of this system as being reported by other authors [40]. The freezing temperature ($T_f$) is also observed in
Figure 6.2: ZFC and FC DC magnetization plots for RuSr$_2$Y$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10}$, measured in the applied magnetic field, $H = 20$Oe. Inset shows the $M$ vs. $H$ plot at temperature 5 and 20K in the range of $-3000$Oe $\leq H \leq +3000$Oe.

$AC$ susceptibility measurements, which will be discussed in later sections. $M$-$H$ loops for studied YRu-1222 at 5 and 20K are shown for an applied field range ($-3000$Oe $\leq H \leq +3000$Oe) in the inset of Fig. 6.2. The compound exhibits clear ferromagnetic magnetization loops below the Curie and superconducting transition temperatures with a reasonable coercive field ($H_c$) and remnant magnetization ($M_r$). The value of $M_r$ and $H_c$ decreases monotonically as the temperature increases.

Figure 6.3 shows the typical isothermal magnetization of $HPHT$ synthesized YRu-1222 compound at various temperatures (5, 20, 50, 75, 100, 125, 150 and 200K) for applied magnetic field range (-50kOe $\leq H \leq +50$kOe). At low temperatures the $M$-$H$ loop exhibits the S-type shape with reasonable coercive field ($H_c$) and remnant magnetization ($M_r$), which are the characteristics features of the spin-glass ($SG$) system. The opening of $M$-$H$ loop at low temperature resembles the ferromagnetic nature in the system. Seemingly the system shows the co-existence of spin-glass ($SG$) and ferromagnetism. The magnetization becomes a nonlinear function of applied field and shows ferromagnetic behavior with hysteresis loop at low field range. The isothermal magnetization as a function of applied field at 5K may be viewed as: $M(H)$
Figure 6.3: Typical magnetization loops as a function of applied magnetic field measured at different temperatures (5, 20, 50, 75, 100, 125, 150 and 200K) in the range - 50kOe to + 50kOe.

\[ \chi H + \sigma_s(H) \]

where \( \chi H \) is the linear contribution from the antiferromagnetic (\( T_C \)) Ru spins and \( \sigma_s(H) \) represents the ferromagnetic component of Ru. The appearance of ferromagnetic component at low temperature within antiferromagnetic/spin-glass Ru spins is possibly due to the slight canting of Ru spins as seen from neutron diffraction for Ru-1212 [19]. As the temperature increases this \( S \) type shape of \( M-H \) loop transforms to the linear paramagnetic (\( PM \)) shape. At 200K the \( M-H \) is like a straight line, resembling the \( PM \) nature of compound at that temperature. It is also observed that these \( M-H \) loops do not saturate even at 50kOe applied magnetic field. Both, the absence of magnetization saturation at high field and the existence of hysteresis loop at low temperatures and low field-regions, are the characteristics of spin-glass (\( SG \)) [41, 42] phase with possibly co-existing ferromagnetic clusters. This co-existence of spin-glass (\( SG \)) and ferromagnetic clusters will be discussed in later sections in details.

A complementary test is shown in Fig. 6.4 where an Arrott plot, [43] \( M^2 \) vs. \( H/M \) is performed for the same set of isothermal magnetization curves. In this standard experimental method the occurrence of \( FM \) order is predicted to occur when
straight line $M^2 \propto H/M$ are obtained in the plots. Further, it defines the Curie temperature ($T_c$) of the isotherm whose linear extrapolation intercepts the vertical axis at zero. In our case we find $T_c \sim 100K$ for the studied YRu-1222 sample, which is in agreement with the $T_c = 110K$ observed from the $M-T$ curve (Fig. 6.2). No sign of spontaneous magnetization are observed in Arrott plots instead of that there is strong curvature towards $H/M$ axis and some intercept on $M^2$ axis. Absence of spontaneous magnetization confirms the short-range magnetic ordering [44], which is also a feature of spin-glass ($SG$) with homogenous/non-homogenous ferromagnetic clusters.

Figure 6.4: Arrott plots ($H/M$ vs. $M^2$) using DC magnetization vs. applied field data observed at different fixed temperatures (5, 20, 50, 75, 100 and 125K).

A further investigation of spin-glass/cluster-glass behavior is also done by thermo-remnant magnetization ($TRM$) measurements. The time response of $DC$ magnetization is important to reveal the spin dynamics for spin-glass ($SG$) system [28, 29]. The behavior of a spin-glass ($SG$) below $T_f$ is irreversible and complicated by the aging process, so it is necessary to employ a well-defined $H-T$ procedure to obtain a meaningful data. The sample was field-cooled ($FC$) in the presence of 5000Oe field from 200 to 60K and after certain waiting times ($t_w = 100s$ and 500s), the field was reduced to zero and the corresponding decay of magnetization was recorded as a
function of elapsed time. The result for the studied YRu-1222 is shown in Fig. 6.5. The observed behavior of TRM is strictly the same as those of site-disordered spin-glasses system [45]. Longer the hold time $t_w$, the slower the decay of the TRM. The system has become “stiffer” with time. The changes observed in $M(t)$ measured for different values $t_w$ shows the occurrence of aging effects, which means that the system is in meta-stable spin-glass (SG) state. The situation will be clearer in next sections.

![Figure 6.5: Thermoremanent magnetization (TRM) relaxation for $T = 60K$ and for waiting time $t_w = 100s$ and $500s$.](image)

6.2.2.3 AC magnetization studies

The AC susceptibility (linear and non-linear) technique is a powerful method, which has been used to study the spin-glass/cluster spin-glass/superparamagnetism type systems. Both real and imaginary parts exhibit sharp frequency dependent cusp according to the desired phenomena (spin-glass/cluster-glass/superparamagnetism). It is well known that a small external DC magnetic field as low as few m-Oe can change the cusp nature. The main panels of Fig. 6.6(a) and 6.6(b) show the temperature dependence of real part $\chi'$ (dispersion) and the imaginary part $\chi''$ (absorption) of the
Figure 6.6: (a) Temperature dependence of the real part of AC susceptibility, measured at different frequency with zero external DC magnetic fields. Inset shows the enlarged view of the real part of the first harmonic AC susceptibility.

Figure 6.6: (b) Temperature dependence of the imaginary part of AC susceptibility, measured at different frequency with zero external DC magnetic fields. Inset shows the enlarged view of the imaginary part of the first harmonic AC susceptibility.
first harmonics of AC susceptibility $\chi_{ac}$, in the presence of applied frequency (33, 333, 666, 999, 3333, 6666 and 9999Hz) at zero external DC field. Before major magnetic transitions ($SG/FM$ peak in magnetization), the $AFM$ correlations related Neel temperature $T_N$ is seen clearly in both Figs. 6.6(a) and 6.6(b) at around 120K, again consistent with an earlier report on this system [33]. Further as mentioned earlier, this $AFM$ order is reported persistent down to 2K as evidenced from NPD results [20, 21, 22]. Neel temperature ($T_N$) does not shift with the frequency of applied AC field. Inset of Figs. 6.6 (a) and 6.6 (b) show the enlarge view of real $\chi'$ and imaginary $\chi''$ part of AC susceptibility respectively. Real ($\chi'$) and imaginary ($\chi''$) both part show the clear peak around the spin-glass ($SG$) transition or peak temperature ($T_p$) or freezing temperature ($T_f$). $T_p$ is an average blocking temperature where the clusters moments begin to freeze, and $T_f$ is the freezing temperature where this thermally activated process reaches a maximum. Possibly the clusters consists of $FM$ or $FM$-like islands in an $AFM$ matrix [46, 47]. This would be consistent with the fact that $T_p$ and $T_f$ are always smaller than $T_C$ for studied system. This peak temperature corresponds to the peak in the ZFC curve with a slight change in peak temperature because of the difference in the response of the system to DC and AC fields. Inset of Fig. 6.6(a) shows that height of the peak corresponding to the freezing temperature ($T_f$) decreases and also the peak shifted towards higher temperature with increasing the frequency ($f$). Similarly, for imaginary part ($\chi''$) the height of the peak decreases and shifted towards the higher temperature (see inset of Fig. 6.6(b)). However, the qualitative effect is same but the exact shift is larger for imaginary part ($\chi''$) than the real one ($\chi'$). It is observed there is a change in freezing temperature ($T_f$) with applied frequency. The change in freezing temperature $T_f(\chi')(T_f = 89.8K$ at $f = 33Hz$ and $T_f = 90.7K$ at $f = 9999Hz$) with applied frequency is the characteristics of spin-glass ($SG$) behavior. At primary stage it is estimated from the quantity $k = \Delta T_f/T_f$ $\Delta(\log_{10}f)$, where $\Delta$ represents the change in the corresponding quantity. It is known this quantity ($k$) varies in the range of 0.004-0.018 for spin-glass ($SG$) system, however for superparamagnetic systems it is of the order of 0.3-0.5 [27]. $T_f$ is as assumed the temperature corresponding to the maximum value of the $\chi'$ curve or the inflection point from the $\chi''$ curves. Here we obtained $k = 6.6 \times 10^{-3}$ or 0.0066, which is in good agreement with the typical spin-glass ($SG$) system values, e.g., $2.0 \times 10^{-2}$, $1.8 \times 10^{-2}$
\[ \omega = \omega_o \exp\left[-\frac{E_a}{k_B(T_f - T_o)}\right] \]  

where, \( E_a \) is the activation energy or the potential barrier separating two nearby clusters, \( \omega_o \) is the characteristics individual frequency of clusters, \( T_f \) the freezing temperature and \( T_o \) is the \textit{Vogel-Fulcher} temperature, which gives inter-clusters interaction strength. When \( T_o = 0 \) means there is no inter-clusters interaction (isolated clusters).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{The variation of the freezing temperature \( T_f \) with the frequency of the AC field, at different characteristics frequency, in a Vogel-Fulcher plot. The solid lines are the best fit of equation.}
\end{figure}
clusters or superparamagnetism state) takes place then the Vogel-Fulcher law transforms into the well known Arrhenius law [28, 29], which is useful to determine the relaxation process of non-interacting magnetic clusters,

$$\omega = \omega_0 \exp\left[-\frac{E_a}{k_B T_f}\right]$$

(6.3)

The Vogel-Fulcher law fits with experimental data of studied YRu-1222 for various characteristics frequency ($\omega_0/2\pi$) ranging $10^{10}-10^{13}$Hz (shown Fig. 6.7). Figure 6.7 depicts a linear fit between the freezing temperature $T_f$ and $1/(\ln(f_0/f))$. Two parameters (Activation energy $E_a$ and Vogel-Fulcher temperature $T_o$) are calculated for corresponding to each chosen characteristic frequency. The value of the inverse of slope $E_a/k_B$, Vogel-Fulcher temperature $T_o$ and the parameter $t* = (T_f - T_o)/T_f$ corresponding to each characteristic frequency ranging from $10^{10}$-$10^{13}$Hz are listed in Table 6.2. The values of the Vogel-Fulcher temperature $T_o = 88.34, 87.93, 87.82,$ and $87.52$K corresponding to the each characteristic frequency $10^{10}, 10^{11}, 10^{12},$ and $10^{13}$Hz respectively, are in good agreement with the value of freezing temperature $T_f = 90.70$K, obtained from the AC susceptibility measurements. Also, for spin-glass (SG) system, the parameter $t* = (T_f - T_o)/T_f$ must be $< 0.10$ and $t* \geq 0.5$ for a cluster spin-glass (CSG) system [27, 34]. In our case $t*$ is of the order of 0.026-0.035, qualifying for a pure spin-glass (SG) system. Hence the fitted experimental data of Vogel-Fulcher law and parameter $t*$ indicate the presence of spin-glass state in the studied YRu-1222 system.

To further verify the spin-glass (SG) state with ferromagnetic clusters, we performed the linear AC susceptibility measurements on studied YRu-1222 system.

<table>
<thead>
<tr>
<th>Characteristic frequency (Hz)</th>
<th>Inverse of slope $E_a/k_B$ (K)</th>
<th>Vogel-Fulcher temperature $T_o$ (K)</th>
<th>Parameter $t* = (T_f - T_o)/T_f$</th>
</tr>
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<tbody>
<tr>
<td>$f_0 = 10^{10}$</td>
<td>34.60</td>
<td>88.34</td>
<td>0.026</td>
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<tr>
<td>$f_0 = 10^{11}$</td>
<td>48.31</td>
<td>87.93</td>
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<tr>
<td>$f_0 = 10^{12}$</td>
<td>57.80</td>
<td>87.82</td>
<td>0.032</td>
</tr>
<tr>
<td>$f_0 = 10^{13}$</td>
<td>68.97</td>
<td>87.52</td>
<td>0.035</td>
</tr>
</tbody>
</table>
Figure 6.8: (a) Temperature dependence of the real part of AC susceptibility measured at different amplitude with zero external DC magnetic fields.

Figure 6.8: (b) Temperature dependence of the imaginary part of AC susceptibility, measured at different amplitude with zero external DC magnetic fields.

with varying AC drive field and a fixed frequency of 333Hz. Figure 6.8(a) and 6.8(b) revels the real ($\chi'$) and imaginary part ($\chi''$) part of the first harmonic of AC
susceptibility respectively. Both real ($\chi'$) and imaginary part ($\chi''$) are measured as a function of temperature from range 200 to 2K range with zero external DC field bias. Both parts (real and imaginary) are measured with varying AC drive amplitude from 1 to 17Oe and at a fix frequency 333Hz. It is observed from Figs. 6.8(a) and 6.8(b) that the peak temperature corresponding to $\chi'$ and $\chi''$ shifts slightly towards the lower temperature and the height of the peak increases with increasing the AC drive amplitude of field. This is a contradictory behavior, because it was observed and well known earlier that the height of the peak decreases with increasing amplitude of the AC drive field for atypical spin-glass (SG) system [29, 30]. When the amplitude of the AC drive field increases, the magnetic energy associated with external AC field is large enough to compare with the thermodynamic energy of the magnetic dipole inside the system. In present situation (Figs. 6.8(a) and 6.8(b)), because there is no freezing of magnetic moments taking place in the direction of applied magnetic field, hence the studied system YRu-1222 is not a pure spin-glass (SG) system. Instead of it has pure spin-glass (SG) state along with some non-interacting homogeneous/non-homogeneous magnetic clusters component. On the basis of above discussed results there may be a possibility of superparamagnetism state in the studied YRu-1222 system, which will be discussed in details in next section.

6.2.2.4 Superparamagnetism studies

To confirm the existence of superparamagnetism (SPM) state in the studied YRu-1222 system, we analyzed our AC susceptibility data by using Wohlfarth’s model [52]. According to the Wohlfarth’s superparamagnetic blocking model, real part of the first harmonic of AC susceptibility ($\chi'$) above the blocking temperature ($T_B$) should follow the Curie-Weiss law, while it is independent below the $T_B$.

\[
\chi'_1 = \frac{\varepsilon M_{sat}^2 V}{3k_B T} = \frac{P_1}{T} \text{ or } \chi'_1 \propto \frac{1}{T} \ldots (6.4)
\]

\[
\chi'_3 = -\frac{\varepsilon M_{sat}}{45} \left( \frac{M_{sat} V}{k_B T} \right)^3 = -\frac{P_3}{T^3} \text{ or } \chi'_3 \propto \frac{1}{T^3} \ldots (6.5)
\]
Here $\varepsilon$ is the volume fraction occupied by the magnetic particles, $T$ is absolute temperature, $M_{sat}$ is saturation magnetization, $k_B$ is Boltzmann constant and $V$ is the volume of magnetic particles. $P_1$ and $P_2$ are two temperature-independent constants.

Figure 6.9: (a) First order harmonics of AC susceptibility is fitted to Wohlfarth’s model above the freezing temperature ($T_f$) for studied YRu-1222. The solid red line shows $T^{-1}$ fit to $\chi'$. Figure 6.9(a) and 6.9(b) depicts the first-order harmonic ($\chi'_1$) and third-order harmonic ($\chi'_3$) of AC susceptibilities as a function of $T^{-1}$ and $T^{-3}$ respectively. Also the solid lines are best fit of equation (6.4) and (6.5) to be the experimental data respectively. The $T^{-3}$ temperature dependence of third harmonic ($\chi'_3$) can be reasonably fit with the temperature interval between 88.5 and 102K. A similar fit has been obtained over narrower temperature range around 10K in a study of SPM in polycrystalline $\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}$ compound [53]. On the basis of above mentioned fitting analysis, the range of the fitting the equations is typically around 10K above $T_B$. Above this temperature the spin correlation within a particle vanishes. Generally, for a conventional SPM system the spin freezing temperature or particle’s spin correlation temperature is much higher than $T_B$. For example in superparamagnetic clusters of magnetite $\text{Fe}_3\text{O}_4$, the Curie temperature of bulk magnetite is around 850K while the
blocking temperature is observed around 20K [54]. Hence in principle, one can measure the superparamagnetic (SPM) state above $T_B$, covering a large temperature range. But in our case, the blocking temperature and spin freezing temperature are very near to each other, and hence fitting is done in limited range (88.5 to 102K).

Figure 6.10 depicts a plot between $1/\chi_{ac}$ vs. $T$ for studied YRu-1222 system, which clearly shows two distinct slopes. Hence it is clear that a superparamagnetic state is developed over a narrow temperature range $T_C \geq T \geq T_f$. It concludes that superparamagnetic (SPM) state co-exists with the spin-glass (SG) state in studied YRu-1222 system.

The value of $H_c$ and $M_{rem}$ are almost zero within the temperature range $T_C \geq T \geq T_f$ but the $M_{sat}$ has definite value (0.30$\mu_B$) as shown in Fig. 6.11. The reason is that just below $T_C$ the FM order lying within the clusters, leading to a non-zero value of $M_{sat}$. On the other hand magnetocrystalline energy become of the order of thermal activation energy of the clusters, resulting the random orientation of the clusters with respect to each other. This random orientation of clusters reduces $H_c$ and $M_{rem}$ to zero.
Figure 6.10: The inverse of first-order AC susceptibility ($\chi$) plotted with temperature indicating two distinct slopes corresponding to paramagnetic and superparamagnetic phase.

Figure 6.11: Saturation magnetization ($M_{sat}$), remanent magnetization ($M_{rem}$) and coercive field ($H_c$) as a function of temperature.

A same feature is observed for superparamagnetic (SPM) particles [29, 55].
Fitting of Wohlfarth’s model (WM) of SPM to the AC susceptibility data of YRu-1222 in the range of $T_C \geq T \geq T_f$ suggests that in a particular range of temperature, spin-glass (SG) state with ferromagnetic clusters giving rise to the SPM state. Thus YRu-1222 has different FM phases below the $T_C$.

6.3 Magnetic and thermal properties of HPHT synthesized YRu-1212

The magnetism of Ru-1212 phase though more or less is understood in terms of canted ferromagnetism (FM) arising from the antiferromagnetic (AFM) spins [56, 57], the same is more complicated in case of Ru-1222 for which a spin glass structure is proposed [58]. An intriguing question regarding rutheno-cuprates is the origin of anti/ferro magnetism in RuO$_2$ sheets. Detailed electron-microscopic works have revealed a super-structure along the $a$-$b$ plane due to tilting of RuO$_6$ octahedra [59, 60, 61]. Also reported is the possible intermixing of Ru and Cu in RuO$_2$ and thus resulting superstructure in Ru-1212 phase in particular [62]. The observation of superstructures in these systems has direct implication to the observed magnetism due to the rotation of RuO$_6$ octahedra. In case of rutheno-cuprates the micro-structural studies reported so far are only for the samples synthesized under normal pressure conditions [59, 60, 61, 62]. It is worth noting that both Ru-1212 and Ru-1222 can be synthesized at ambient conditions only for RE = Gd, Sm and Eu [58, 59, 60, 61, 62]. In case of lighter rare-earths, however, one needs to employ high-pressure high-temperature (HPHT) process to achieve the required phase [57, 63, 64]. Though the HPHT synthesized Ru-1212 are reported to be having higher superconductivity volume fraction [57, 63] and better phase purity. Thermoelectric Power (TEP) measurements can provide both information of the type and the characteristic energy of charge carriers and therefore are a complementary tool to the resistivity measurements for transport properties. Since TEP is a measure of the heat per carrier over temperature, we can thus view it as a measure of the entropy per carrier. Both La$_{1.85}$Sr$_{0.15}$CuO$_{4-\delta}$ and YBa$_2$Cu$_3$O$_{7-\delta}$ show a field independent of TEP up to 30 Tesla, indicating retaining no spin degree of freedom in the CuO$_2$ layers [65]. Here we present the temperature dependence of thermal properties of thermo-power [$S(T)$], thermal conductivity [$\kappa(T)$] and specific heat [$C_p(T)$]. Magnetization data on the HPHT synthesized YRu-1212 material are also presented.
6.3.1 Experimental details

Starting precursor materials used for high-pressure synthesis of Ru$_{0.9}$Sr$_2$YCu$_{2.1}$O$_{7.9}$ (YRu-1212) were RuO$_2$ (99.9%), SrO$_2$, SrCuO$_2$, Y$_2$O$_3$ (99.9%) and CuO (99.9%). These materials were mixed in an agate mortar to serve as the starting mixtures for high-pressure synthesis. High-purity sample was obtained with the ‘Ru-poor’ starting composition of Ru$_{0.9}$Sr$_2$YCu$_{2.1}$O$_{7.9}$. XRD patterns are taken on a Rigaku MiniFlex machine with Cu-K$_\alpha$ ($\lambda = 1.54\,\text{Å}$) radiation. The Rietveld analysis was performed using the FullProf program. The magnetization measurements were carried out on Quantum Design PPMS-14T system. Thermal conductivity ($\kappa$) in the range 10-300K, Thermoelectric power ($S$) and Heat capacity ($C_p$) was also carried out PPMS-14T system with TTO assembly. Sample was cut to a rectangular parallelepiped shape with typical sizes $1.5 \times 1.5 \times 5.0\,\text{mm}^3$. More experimental details about the thermal conductivity, thermoelectric power and heat capacity measurements are provided in chapter 2.

6.3.2 Results and discussion

6.3.2.1 Structural studies

It would be worthwhile mentioning here that the Ru-deficient Ru$_{0.9}$Sr$_2$YCu$_{2.1}$O$_{7.9}$ material considered in the present study was optimized for its phase purity earlier after several trials [65]. The compound crystallizes in the single-phase form in space group $P4/mmm$. Observed (solid circles) and calculated (solid lines) X-ray patterns for the compound is shown in Fig. 6.12. The structure analysis was performed using the Rietveld refinement analysis by employing the FullProf Program. The Rietveld analysis confirms a single phase formation in $P4/mmm$ space group. There is no impurity of SrRuO$_3$ and Sr$_2$YRuO$_6$ in the studied YRu-1212 sample. All the Rietveld refined structural parameters (lattice parameters, atomic coordinates and site occupancy) of compound are shown in Table 6.3.
Figure 6.12: Observed (solid circles) and calculated (solid lines) XRD patterns of Ru$_{0.9}$Sr$_2$YCu$_{2.1}$O$_{7.9}$ 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 curve show the position of allowed Bragg peaks.

Table 6.3: Atomic coordinates and site occupancy of Ru$_{0.9}$Sr$_2$YCu$_{2.1}$O$_{7.9}$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
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<th>$y$</th>
<th>$z$</th>
</tr>
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<tr>
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<td>0.0000</td>
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</tr>
<tr>
<td>Sr</td>
<td>2h</td>
<td>0.5000</td>
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</tr>
<tr>
<td>Y</td>
<td>1c</td>
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<td>0.5000</td>
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</tr>
<tr>
<td>Cu</td>
<td>2g</td>
<td>0.0000</td>
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</tr>
<tr>
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<td>0.1020</td>
<td>0.5000</td>
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</tr>
</tbody>
</table>
6.3.2.2 DC magnetization studies

The temperature dependent DC magnetic susceptibility of the presently studied YRu-1212 compound is shown in Fig. 6.13. The sample was cooled in zero magnetic field down to the lowest accessible temperature (2K). After temperature stabilization, a DC magnetic field of 20Oe is applied and the magnetization is recorded as the temperature being raised (ZFC curve) up to 300K. Then the measurement continued while the temperature was again decreased back to 2K (FC curve), keeping the same DC magnetic field. Both the ZFC and FC magnetization curves depict a significant branching at around 145K, which is indicative of the magnetic ordering temperature ($T_{mag}$) of Ru moments. Neutron diffraction studies have earlier shown that Ru moments order antiferromagnetically at around 133K for GdRu-1212 compound [56]. For the HPHT synthesized YRu-1212 compound, $T_m$ of around 150K was observed [57], which is in close agreement to the present measurements. Both the ZFC and FC magnetic susceptibility data exhibit clear magnetic transitions at 50K and below. The diamagnetic signal onset temperature (FC curve) is described as the superconducting

![Figure 6.13](image-url)
transition temperature ($T_c$) of the material. Summarily, the studied YRu-1212 compound is magnetic below 145K, and superconducting below 50K. In other words the compound is magneto-superconducting below 50K. To further elucidate the magnetic nature of the compound at low temperatures, field dependence of magnetization $M-H$ at 5K (in the magneto-superconducting region) of the compound was also carried out. The inset of Fig. 6.13 clearly demonstrates that the compound indeed is in the ferromagnetic state. Interestingly, in HPHT synthesized YRu-1212 material superconductivity transition is noticed at high temperature (~50K) and that also of bulk nature, which is generally scanty in FC magnetization of earlier reports on the normal-pressure synthesized samples [56, 66, 67].

In order to further probe the magneto-superconducting character of the HPHT synthesized YRu-1212 magneto-superconductor and its bulk superconductivity, we have investigated the thermal properties, using the TTO (Thermal Transport Option) on PPMS-14T, like thermal conductivity ($\kappa$), thermoelectric power ($S$) and specific heat ($C_p$) of the material as well.

### 6.3.2.3 Thermal conductivity ($\kappa$)

![Temperature dependences of the thermal conductivity $\kappa(T)$ of studied HPHT synthesized YRu-1212.](image)

**Figure 6.14:** Temperature dependences of the thermal conductivity $\kappa(T)$ of studied HPHT synthesized YRu-1212.
Figure 6.14 shows the temperature dependence of the thermal conductivity $\kappa(T)$ of the YRu-1212 sample with the room temperature (300K) value of $\kappa$ being 52mW/cm-K. Thermal conductivity $\kappa$ decreases slightly with temperature down to ~55K, and later starts dropping like a transition with a value of 20mW/cm-K at 4.2K. Interestingly, the transition-like drop in $\kappa(T)$ occurs at same temperature, where the $S(T)$ goes through the superconducting transition.

### 6.3.2.4 Thermoelectric power ($S$)

Figure 6.15 depicts the thermoelectric power $S(T)$ behaviors for the YRu-1212 compound. The sign of $S(T)$ is positive with the room temperature value of 60$\mu$V/K, which is reminiscent of a $p$-type under-doped material. $S(T)$ increases slightly with decreasing temperature down to ~170K and later decreases considerably with temperature down to 55K, giving rise to a general hump type shape. Hump temperature for the present sample coincides with the magnetic ordering temperature $(T_m)$ of Ru. $S(T)$ goes through a superconducting-like transition below ~ 55K and becomes zero at 33K, establishing superconducting state of the sample below 33K. It is clear from Figs. 6.14 and 6.15; both $\kappa(T)$ and $S(T)$ measurements establish the...
appearance of superconductivity in the present YRu-1212 sample below \( \sim 50 \text{K} \), which coincides with the magnetization measurements (see Fig. 6.13).

### 6.3.2.5 Heat capacity studies

Figure 6.16 depicts the temperature dependence of the specific heat \( C_p(T) \) of the YRu-1212 sample with the room temperature (300K) \( C_p \) value of 350J/mole-K. While no clear transition is observed in \( C_p(T) \) around \( T_{mag} \) (~145K), only a slope change is noticed at \( \sim 150 \text{K} \). However, an anomaly can be seen in \( C_p(T) \) at temperature below 30K, which could be attributed to the bulk superconductivity of the sample. To further elucidate on the \( T_m \), the higher temperature part is plotted as \( C_p/T \) vs. \( T \) (inset of Fig. 6.16) which clearly shows a change in slope at \( \sim 145 \text{K} \). There are studies available [68] on \( C_p \) of rutheno-cuprates, which corroborate the observed result. In fact \( T_m \) of Ru in rutheno-cuprates does not correspond to a long-range order but with a short-range SG order and hence cannot be seen distinctly in the \( C_p(T) \) measurements. \( C_p(T) \) results on the present YRu-1212 material are in general agreement with reported data on normal-pressure synthesized rutheno-cuprates, except for the distinct

![Figure 6.16: Temperature dependence of the specific heat \( C_p \) (J/mol-K) and the inset shows \( C_p/T \) (J/mol-K\(^2\)) as a function of temperature.](image_url)
anomaly exhibited at the superconducting transition.

**Figure 6.17:** Variation of $C_p/T$ (J-mol/K$^2$) with square of the temperature $T^2$ (K$^2$).

**Figure 6.18:** Specific heat variations with temperature for the Ru$_{0.9}$Sr$_2$YCu$_{2.1}$O$_{7.9}$. Inset: $\Delta C_p$ variation with temperature.
To further, elucidate upon the low temperature superconductivity anomaly in $C_p(T)$ of YRu-1212, we plot the $C_p/T$ vs. $T^2$ in Fig. 6.17. The straight linear intercept of the plot on $y$-axis is at 0.4J/mole-K$^2$, which corresponds to the Sommerfeld–Gruneisen constant $\gamma$ and is in agreement with reported $C_p(T)$ data on superconducting rutheno-cuprates [67 and refs therein]. Deviation from the linear plot is clearly seen at $\sim$22K, establishing the occurrence of superconductivity in the material below this temperature. $\Delta C_p$ as a function of temperature is also plotted in the inset of Fig. 6.18. $\Delta C_p$ is obtained by subtracting the background specific heat data. Specific heat jump noticed at $\sim$ 140K indicates a clear magnetic transition. Excess entropy ($\Delta S$) can be evaluated by integrating the area under $\Delta C_p$ vs. $T$ curve (inset of Fig. 6.18). The value of $\Delta S$ is seen to be higher (3.8) than the theoretical value of Rln2 (2.503), indicating magnetic in homogeneity possibly linked to the polycrystalline nature of the material. As far as the change in entropy below $T_c$ is concerned we believe that it is not due to the superconductivity alone, but is also mixed with the $FM$ of the material.

6.4 Conclusion

We have reported detailed results and analysis of structural, DC/linear and non-linear AC magnetization, isothermal magnetization and thermoremanent magnetization (TRM) on HPHT synthesized RuSr$_2$Y$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10}$ (YRu-1222) magneto-superconductor. The YRu-1222 has a rich verity of magnetic phenomena. A paramagnetic (PM) to antiferromagnetic (AFM) transition at 120K, canted ferromagnetic (FM) transition at around 110K, spin-glass (SG) transition temperature ($T_f$) at around 88.5K, formation of homogeneous/non-homogeneous ferromagnetic non-interacting clusters just below the spin-glass (SG) temperature and also the possible presence of superparamagnetic state in the compound (SPM). The DC and AC susceptibility studied presented in this paper shows that SG state coexist with some homogeneous/non-homogeneous ferromagnetic non-interacting clusters followed by possible SPM state. The cluster ferromagnetism could be originated from the canting of reported long- range AFM order in this system. The temperature variation of first and third-order harmonic AC susceptibility is fitting well to Wohlfarth’s model (WM) of superparamagnetism in a narrow temperature range. A FM cluster and spin-glass (SG) state have been seen to co-exist just below the $T_f$. The
superparamagnetism (SPM) and spin-glass (SG) state coexist between the temperature range $T_C \geq T \geq T_f$. Superconductivity is not affected by various co-existing magnetic phenomena. In last, our results support the presence of spin-glass (SG) state with non-homogeneous ferromagnetic clusters followed by SPM state in YRu-1222 system. Possible random distribution of Ru$^{5+}$-Ru$^{5+}$, Ru$^{4+}$-Ru$^{5+}$ and Ru$^{4+}$-Ru$^{4+}$ exchange interactions may be responsible for observed spin-glass (SG) with ferromagnetic clusters (FM) followed by superparamagnetism (SPM) complex magnetic state. The magnetic and thermal properties of a single-phase high pressure high temperature (HPHT) synthesized YRu-1212 compound establish it a bulk magneto-superconductor with magnetic ordering of Ru spins below 145K and superconductivity in CuO$_2$ planes at $\sim$30K. The bulk superconductivity is also established through the specific anomaly noticed in $C_p(T)$. 
6.5 References


