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Spin dynamics, short-range order and superparamagnetism in superconducting ferromagnet $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$

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ABSTRACT

We report structural, detailed DC and linear/non-linear AC, isothermal and thermoremanent magnetization study of the rutheno-cuprate superconducting ferromagnet $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ (GdRu-1222). Structural analysis, by employing Rietveld refinement of X-ray diffraction pattern, reveals that GdRu-1222 crystallizes in tetragonal phase with *I4/mmm* space group. GdRu-1222 is a reported superconducting ferromagnet with Ru spins magnetic ordering at around 110 K and superconductivity below 40 K in Cu–O_2 planes. Detailed linear/non-linear first and higher order harmonic of AC susceptibility studies unveiled the complex magnetism of GdRu-1222. A frequency dependent cusp is observed in AC susceptibility (χ_{ac}) vs. T measurements. The change in cusp position with applied frequency followed the well known *Vogel–Fulcher law*, which is a feature to describe a spin-glass (SG) system with possibility of embedded homogeneous/non-homogeneous magnetically interacting/non-interacting ferromagnetic clusters. Such an interpretation is also supported by thermoremanent magnetization (TRM) study at T=60 K. Detailed interpretation of AC magnetization results revealed the formation of magnetic (ferromagnetic) homogenous/non-homogenous clusters of different sizes embedded in spin-glass (SG) matrix. The magnetization vs. applied field loops do not saturate, even at high applied fields (50 kOe), resulting in the short-range magnetic ordering in the system, which causes the formation of clusters that freeze at low temperatures. Temperature variation of first- and third-order susceptibility harmonics show good agreement with the Wohlfarth's model (WM), leading to the superparamagnetism (SPM) state. Detailed magnetization (DC and AC both) results and their analysis helped in explaining the temperature dependent magnetism of the GdRu-1222 system.

1. Introduction

Discovery of co-existing superconductivity (SC) and weak ferromagnetic order (W-FM) in the hybrid rutheno-cuperate systems $RuSr_2(Eu,Gd,Sm)_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ (Ru-1222) and $RuSr_2$(Eu, Gd,Sm)$Cu_2O_{8-\delta}$ (Ru-1212) are particularly interesting because the magnetic ordering temperature or Curie temperature (T_C) is much higher than the superconducting transition temperature (T_c) [1–5]. Despite extensive research on these materials, some unanswered questions remain unsolved. In particular, the possibility of magnetic ordering of the weak ferromagnetic (W-FM) [1] or ferromagnetic type [6], as originally reported based on bulk magnetization measurements, generated additional excitement with some agnosticism. The reason behind that the dipolar and exchange fields generated by a FM or W-FM Ru-O_2 layer in close vicinity to the Cu–O_2 layers could act as pair breakers or stop singlet-pair formation altogether. The Density functional theory [7] concluded some of these concerns by showing that these dipolar and exchange fields are weak enough in Ru-1222 and hence singlet pairing can still survive in the Cu–O_2 layers with a modulated superconducting (SC) order parameter. This depends on whether the Ru magnetization is parallel or perpendicular to the Ru–O_2 layers. One of the most controversial question is the exact type of magnetic ordering in Ru-1222 family. Both Ru-1212 and Ru-1222 possess two Cu–O_2 planes and one Ru–O_2 layer in a tetragonal unit cell with space group *P4/mmm* and *I4/mmm* respectively. The structure of Ru-1212 is related to the structure of well known $CuBa_2YCu_2O_{7-\delta}$ (Cu-1212) such that the Ba ion is replaced by Sr ion and Cu–$O_{1-\delta}$ chain is replaced by $RuO_{2-\delta}$ sheet. While in case of Ru-1222 a fluorite type block (R,Ce)$O_{2-\delta}$ (R=Eu and Gd) is inserted between two Ru-1212 unit cells and each unit cell of Ru-1212 is shifted by (a/2, a/2) coordinate positions [8,9]. Studies of DC magnetization [10], muon-spin rotation (μSR) [11], as well as Mössbauer spectroscopy [12] indicated a double magnetic transition, which has been explained as due to the presence of

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some Ru-1212 impurity phase in Ru-1222. Further, granularity and clustering in the system had been considered to lead to various phenomena with the contradictory explanations. Phase separation into ferromagnetic (FM) clusters and paramagnetic matrix followed by an antiferromagnetic (AFM) transition has been assumed to establish long-range order in the system [13]. In contrast to this, neutron diffraction data [14,15] did not show any long-range order, which is further contradicted by McLaughlin et al. [16] who observed clear magnetic scattering in their neutron-diffraction measurements on $RuSr_2Y_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ (YRu-1222), indicating antiferromagnetic alignment of Ru spin (Ru moments along the *c*-axis). On the other hand the proposed magnetically frustrated spin-glass (SG) [17–19] opposed the claims of long-range magnetic order in the system. The neutron diffraction data could not be modeled with a simple G-type AFM structure and arguments were put in favor of both FM and AFM Ru–Ru coupling being simultaneously present along the *c*-axis [16]. Neutron diffraction study also failed to observe a net FM component in Ru-1222 compounds, with an upper limit of $\sim 3\,\mu_B$/Ru as calculated from magnetization measurements. Recently, it was proposed, in $Nb_{1-x}Ru_x$-1222 system, that there are interacting clusters at the $Ru–O_2$ planes without any long-range magnetic order [20]. On the other hand, the slow spin dynamics [13] suggested that the FM clusters in Ru-1222 could exhibit superparamagnetism (SPM). Whereas, observation of the frequency dependent peak shift of the AC susceptibility as a function of temperature along with thermoremanent magnetization (TRM) measurements [21] have indicated spin-glass (SG) behavior in $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$, which also contradicts the existence of long-range order in the system. The magnetic behavior in Ru-1222 is more challenging and complex as compared to Ru-1212. One of the drawbacks with the rutheno-cuperate based superconductors is that the most effective technique for studying magnetism i.e., neutron diffraction, is not suitable. This is because both Ru-1212 and Ru-1222 systems forms with only Eu, Gd and Sm, which are high neutron absorbers. Hence, the non-linear susceptibility is the most effective tool to investigate the complex magnetic behavior of Eu, Gd, and Sm based rutheno-cuprates. In particular, strong evidences of spin-glass (SG) behavior was observed in $Gd_{1.5}Ce_{0.5}$Ru-1222 [21].

Superparamagnetism is nothing but an ensemble of nano particles, in which the inter-particle magnetic interactions are sufficiently weak. When the inter-particle interactions are non-negligible, the system eventually shows collective behavior, which overcomes the individual anisotropy properties of the particles. On the other hand at sufficiently strong interactions a magnetic nanoparticle ensemble can exhibit super spin-glass (SSG), which is similar to the spin-glass (SG) systems in bulk materials. In the typical superparamagnetic state, below the temperature called the blocking temperature (T_B), the anisotropy energy is greater than the thermal energy so that easy axis of magnetization in clusters orient in same direction. The spin-glass (SG) state [22,23] is a low temperature phenomenon that occurs due to the disorder and frustration in the system. Frustration is created due to the competing ferromagnetic and antiferromagnetic interactions between the neighboring spins. At a particular temperature, called freezing temperature (T_f), all spins freeze in a random direction, in order to minimize the total energy of the system. Non-linear AC susceptibility is a very effective tool to investigate the spin-glass (SG) and superparamagnetism (SPM) states in the material. Because the measurements can be performed at very low applied AC fields, hence any small change in the magnetic susceptibility due to the phase transition can be observed. Otherwise these small changes in AC magnetic susceptibility could have been masked by the high applied field. Non-linear complex AC susceptibility in presence of an excitation field H_{ac} can be interpreted as

$$M = M_0 + \chi_1 H_{ac} + \chi_2 H_{ac}^2 + \chi_3 H_{ac}^3 + \ldots \quad (1)$$

where χ_1, χ_2 and χ_3 are the first-, second- and third-order harmonic susceptibilities respectively [22,23].

In this paper we extend our investigation [18] of the complex magnetic behavior in rutheno-cuprate systems. The temperature dependent DC, linear/non-linear AC magnetization (frequency and field dependence) and thermoremanant magnetization (TRM) of $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ (GdRu-1222) sample are studied in detail to understand the spin-glass (SG) with ferromagnetic clusters (FM) and superparamagnetism (SPM) states. Specially first and third-order harmonic of AC susceptibility are discussed in detail to probe the superparamagnetism (SPM) state in this compound. A temperature dependent scenario of the complex magnetism of GdRu-1222 is presented. In present MS we reported the existence of spin-glass (SG) phase with homogeneous/non-homogeneous ferromagnetic clusters by using the AC susceptibility as tool. This work may provide better understanding of the system about how the spin-glass phase exists with the ferromagnetic clusters in between the ferromagnetic and the superconductivity transition temperatures of the system.

2. Experimental details

Polycrystalline bulk sample of $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ (GdRu-1222) was synthesized through solid state reaction route from stoichiometric powders of purity 99.9% RuO_2, $SrCO_3$, Gd_2O_3, CeO_2 and CuO. These mixtures were ground together in an agate and calcined in air at 1020 °C, 1040 °C and 1060 °C each for 24 h with intermediate grindings. The pressed bar shaped pellet of the sample was annealed in Oxygen atmosphere at 850 °C, 650 °C and 450 °C each for 24 h, and subsequently cooled down slowly over a span of 12 h to the room temperature. X-ray diffraction (XRD) was performed at room temperature in the scattering angular (2θ) range of 20°–80° in equal 2θ step of 0.02° using *Rigaku Diffractrometer* with *Cu* K_α ($\lambda = 1.54$ Å) radiation. Rietveld analysis was performed using the standard *FullProf* program. Sample is crystallized in tetragonal structure with $I4/mmm$ space group. Detailed DC and AC (linear and non-linear) magnetization were performed on Physical Property Measurements System (PPMS-14T, Quantum Design-USA) as a function of both temperature and applied magnetic field. Linear and non-linear AC susceptibilities as a function of temperature (i) in the frequency range 33–9999 Hz and, (ii) in the AC drive magnetic field amplitude variation 1–17 Oe, with zero external DC magnetic fields were also measured on PPMS-14T. Resistivity measurement was performed in zero magnetic fields on a close cycle refrigerator (CCR), in temperature range 12–300 K, designed by Advanced Research System (ARS), USA.

3. Results and discussion

Phase purity of complex Rutheno-cuperates GdRu-1222 is very important for a meaningful scientific discussion, because impurities like $SrRuO_3$ (SRO) and Sr_2RuGdO_6 ($211O_6$) phase tend to form readily in the host GdRu-1222 matrix. Small impurity of these compounds can alter the net outcome magnetization of GdRu-1222. It is clear that main peaks corresponding to SRO and $211O_6$ phases are not observed within the XRD limit. Observed (open circle) and fitted (solid lines) X-ray patterns for the studied compound $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ (GdRu-1222) are shown in Fig. 1. The structural analysis was performed using the Rietveld refinement analysis by employing the *FullProf* Program.