Impact of rare earth magnetic moment on ordering of Ru in \( \text{Sr}_2\text{RuREO}_6 \) (RE = Gd and Eu)

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We report synthesis and magnetization of \( \text{Sr}_2\text{RuREO}_6 \) (RE/Ru-211O\(_6\)) with RE = Gd and Eu. Both Gd,Eu/Ru-211O\(_6\) are formed in distorted perovskite-type single phase with monoclinic \( P2_1/n \) space group. Magnetization \((M/T)\) measurements exhibited antiferromagnetic ordering of Ru moments for both Gd and Eu compounds at \( T_N \) of around 30 K due to super-exchange Ru-O-O-Ru interaction. Interestingly enough, detailed \( M/H \) plots of Gd/Ru-211O\(_6\) exhibited, the development of a ferromagnetic \((FM)\) component at 20 K. Further at below 10 K, the \( FM \) component disappears and rather an spin freezing field \((H_{SF})\) of around 1000 Oe is seen at 5 K. In case of Eu/Ru-211O\(_6\), the basic antiferromagnetic ordering of Ru moments remains invariant down to 5 K, and the appearance of \( FM \) component is not seen. It seems that the high magnetic moment of \( 8\mu_B \) for Gd\(^{3+}\) influences the \( AFM \) ordering of Ru in case of Gd/Ru-211O\(_6\).

Key Words: Ruthenates, Antiferromagnetism, Ferromagnetism, and Spin Freezing

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I. INTRODUCTION

The double perovskite \( \text{Sr}_2\text{RuREO}_6 \) (\( \text{RE} = \text{rare earth} \)) are studied extensively over the years [1,2]. Basically they are derived from \( \text{SrRuO}_3 \) with replacement of alternate Ru atoms by \( \text{RE} \) in the unit cell [3]. Alternate replacement of \( \text{Sr}^{2+}/\text{RE}^{3+} \) results in two interesting effects i.e., increase of Ru valence from +4 to +5 and the change of ferromagnetic (FM) order (150 K) to anti-ferromagnetic (AFM) below 30 K. The ionic size difference between six fold coordinated \( \text{Ru}^{5+} \) (0.565 Å) and various rare earths for example \( \text{Eu}^{3+} \) (0.947 Å) is quite large and hence the AFM temperature (30 K) and exact ordered perovskite structure is not guaranteed for all the cases. In fact the AFM temperature seems to scale with RE/unit cell size [4]. Further it was reported earlier that the nature of AFM order for Ru in \( \text{Sr}_2\text{RuREO}_6 \) is not the same for all the RE, for example in case of Er some phase separation is reported with in AFM structure [3]. Despite the fact that well documented neutron scattering experiments are available, the influence of RE on Ru AFM order in \( \text{Sr}_2\text{RuREO}_6 \) is not yet studied in detail [3]. In this direction a very recent study on \( \text{Sr}_2\text{RuGdO}_6 \) reported an FM component below AFM ordering due to possible Ru-O-Gd interactions [4].

Furthermore the possible influence of RE moment on Ru magnetic ordering in rutheno-cuprate magneto-superconductors \( \text{RuSr}_2\text{GdCu}_2\text{O}_8 \) and \( \text{RuSr}_2(\text{Gd,Ce})\text{Cu}_2\text{O}_10 \) [5,6] has increased the interest in various ruthenates containing RE. Keeping in mind the very recent report on \( \text{Sr}_2\text{RuGdO}_6 \) [4] and our continuous interest on various rare earths containing rutheno-cuprates [7], we studied the magnetization of both magnetic RE containing \( \text{Sr}_2\text{RuGdO}_6 \) and non-magnetic RE based \( \text{Sr}_2\text{EuGdO}_6 \). Our choice of Eu and Gd guarantees the closest possible neighbors in terms of their ionic size [3]. These compounds are formed in an essentially single-phase form, without any trace of FM (150 K) phase of \( \text{SrRuO}_3 \). It is concluded on the basis of
detailed magnetization measurements, that RE magnetic moment influences the nature of Ru magnetic ordering by Ru-O-RE interactions.

II. EXPERIMENTAL DETAILS

Samples of composition Sr$_2$RuREO$_6$ with RE = Gd and Eu were synthesized through a solid-state reaction route. Calcinations were carried out on the mixed powder at 1000, 1100, 1200 and 1350 °C each for 24 hours with intermediate grindings. The pressed bar-shaped pellets were annealed in a flow of oxygen at 1000 °C for 40 hours and subsequently cooled slowly over a span of another 20 hours down to room temperature X-ray powder diffraction patterns were obtained by a diffractometer with Cu K$_\alpha$ radiation. DC susceptibility data were collected by a SQUID magnetometer (Quantum Design, MPMS).

III. RESULTS AND DISCUSSION

The X-ray diffraction patterns of the Sr$_2$RuREO$_6$ with RE = Gd and Eu are depicted in Fig. 1. The powder diffraction pattern resembles that of other iso-structural compounds reported in the literature [1,3,4]. The entire pattern can be indexed on the basis of a distorted perovskite-type crystal structure in monoclinic $P2_1/n$ space group. Within the sensitivity limit (~3%) of the X-ray machine, the phase purity of the studied compounds is assured. In particular the parent $FM$ SrRuO$_3$ phase is not available in these samples. The lattice parameters are $a = 5.793(2)$ Å, $b = 5.832(1)$ Å, $c = 8.2134 (7)$ Å and $\beta = 90.31(1)$ for Gd and $a = 5.811(4)$ Å, $b = 5.846(3)$ Å, $c = 8.2269(4)$ Å and $\beta = 90.35(1)$ for Eu, which is in good agreement with earlier reports [3,4].
Fig. 2 depicts the magnetization ($M$) versus temperature ($T$) plot for Sr$_2$RuGdO$_6$ sample in field-cooled (FC) situation under an applied field of 1000 Oe. As is evident from this figure, the sample is paramagnetic down to around 32 K with a small saturation/down turn in $M/T$ near this temperature, with a further shoot up and a clear $FM$ like saturation between 25 K and 10 K. Below 10 K, there is a further shoot up in the magnetization down to 5 K. Though $M/T$ measurements generally do not lend to exact magnetic structure of a compound, they certainly provide an indication for the same. It seems from the plot in Fig. 2, that Sr$_2$RuGdO$_6$ undergoes an $AFM$ like transition at 32 K and develops a $FM$ component below 25 K to 10 K, with a further super-paramagnetic like behavior down to 5 K. As the ordering temperatures discussed above seem too high for the ordering of Gd moments, the ordering above 5 K is mainly due to Ru moments. In general the $M/T$ behavior of presently studied Sr$_2$RuGdO$_6$ sample is in accordance with a very recent report on this compound [4]. The only difference is that our sample exhibited clear $FM$ like saturation of the moments in $M/T$ between 25 K and 10 K. We also carried out low field FC and ZFC (zero-field-cooled) $M/T$ measurements (plots not shown) to check the presence of SrRuO$_3$, which is ferromagnetic at above 150 K. In our sample the FC and ZFC branching is not observed at higher $T$ above 32 K, hence we conclude that our sample is free of SrRuO$_3$ impurity.

For comparison with non magnetic RE ion containing Sr$_2$RuREO$_6$ system, in inset of Fig. 2 we show the $M/T$ behavior of RE = Eu compound in field-cooled (FC) situation under an applied field of 1000 Oe. Interestingly Sr$_2$RuEuO$_6$ sample exhibits only the $AFM$ ordering at around 28 K and no further FM or paramagnetic like situation is observed down to 5 K. It seems in case of non-magnetic RE ion Eu, the AFM ordering of Ru spins at around 28 K is not affected. This is in general agreement with earlier reports on Sr$_2$RuREO$_6$ system [1-3,8].
Low field $\frac{M}{T}$ behaviors of Sr$_2$RuGdO$_6$ and Sr$_2$RuREO$_6$ systems in applied fields of 10 and 40 Oe respectively are shown in Fig. 3. It is generally believed that various minor magnetic transitions/anomalies gets wiped out in higher applied fields. The $ZFC \frac{M}{T}$ plot (Fig 3) of Sr$_2$RuGdO$_6$ in applied field of 10 Oe is very similar to that as observed for the same sample under magnetic field of 1000 Oe (Fig 2). In particular all the magnetic transitions are seen in terms of an $AFM$ like transition at 32 K, $FM$ component below 25 K to 10 K, and super-paramagnetic like behavior down to 4K. Further an $AFM$ transition presumably due to $T_N$ (Gd) is seen below around 3 K. Above 32 K the system is purely paramagnetic.

The $M/T$ behavior of Sr$_2$RuREO$_6$ system in an applied field of 40 Oe and in $ZFC$ situation is depicted in inset of Fig.3. Clear $AFM$ like transition, originating from Ru spins is seen below 28 K. This compound remains $AFM$ down to 5 K, and no other magnetic anomalies are visible. Interestingly the magnetic susceptibility above 28 K does not appear to be purely paramagnetic. Detailed fitting of the magnetic susceptibility for Sr$_2$RuREO$_6$ system is reported in ref. [3]. In general Eu is in trivalent non-magnetic state and possess large amount of temperature independent contribution to the paramagnetic susceptibility of Ru in Sr$_2$RuREO$_6$ system [3]. In our recent paper (ref. 8) we measured the Mossbauer spectra of Sr$_2$RuREO$_6$ system at 90 and 4.2 K. The well-defined single magnetic spectrum at 4.2 K indicated the exchange field induced on the Eu ions by the Ru sheets. The estimated induces magnetic moment on the Eu ions is: $0.35\mu_B$. The fact that the negative effective quadrupole interaction at 4.2 K is just half of the quadrupole interaction at 90 K indicates clearly that the induced magnetic hyperfine field is along the c –axis (Type I AFM) as stated by Cao et. al [9] on Sr$_2$RuYO$_6$. Combining the results in ref. 3, 4, 8, 9 and the present outcome, one can say that these compounds possess complex magnetic structure in case of magnetic rare earths and Y. In particular the $AFM$ ordering of Ru spins turn into canted $FM$ and super paramagnetic behavior.
in case of Y [9] and magnetic rare earths [3,4,8]. There is an urgency to revisit the neutron scattering experimentations on the Sr$_2$RuY/REO$_6$ compounds. Though the magnetic structure is mainly due to the $AFM$ ordering of Ru spins below say 30 K, the detailed magnetization and Mossbauer spectroscopy under various applied fields do indicate towards canting of $AFM$ moments and appearance of $FM$/Spin-glass structure [9].

To further elucidate the magnetism of Sr$_2$RuREO$_6$ system, we show the $M(H)$ plots of both RE = Gd and Eu compounds at close temperature intervals up to applied fields of 5 Tesla in Figs 4-6. Fig. 4 shows the $M/H$ plot for Sr$_2$RuGdO$_6$ at 5 K with $H = \pm 5$ Tesla. Though no loop opening is seen, a spin flop like situation occurs at around $H = \pm 1$ Tesla, which is marked as $T^{SF}$. A similar behavior is shown very recently in ref. 4. The $M/H$ plot for Sr$_2$RuEuO$_6$ at 5 K with $H = \pm 5$ Tesla is shown in inset of Fig.4, which is linear with field. This shows that Sr$_2$RuEuO$_6$ is $AFM$ at 5 K and no indication of any spin flop like situation is seen. Clearly the magnetic structure of Ru spins in non-magnetic RE containing Sr$_2$RuEuO$_6$ is different than that of magnetic RE based Sr$_2$RuGdO$_6$. The $M/H$ plots of both RE = Gd and Eu based Sr$_2$RuREO$_6$ system at 15 K are shown in Fig. 5. The situation at 15 K is very similar to that as at 5 K, in terms of $T^{SF}$ for Gd (main panel, Fig. 5), and $AFM$ like structure for Eu compound (inset II, Fig.4), the important difference is the opening of $M/H$ loop for Sr$_2$RuGdO$_6$ (upper inset I, Fig.4). It seems that Sr$_2$RuEuO$_6$ is $AFM$, the Sr$_2$RuGdO$_6$ has a $FM$ component. To further elucidate the $FM$ component of Sr$_2$RuGdO$_6$ system, we show in Fig. 6 the low field $M/H$ plots of this system. Clear $M/H$ loop opening at 20 K for Sr$_2$RuGdO$_6$ system indicates towards the $FM$ component in this system. On the other hand the $M/H$ plot for Sr$_2$RuEuO$_6$ at 20 K is completely linear (inset Fig.6). Interestingly at 30 and 40 K the $M/H$ data for Sr$_2$RuGdO$_6$ and Sr$_2$RuEuO$_6$ systems is linear, without any $FM$ like hysteresis/opening, plots not shown. Summarily one can say that, though non-magnetic rare earth containing Sr$_2$RuEuO$_6$ system
remains $AFM$ below 30 K, in $\text{Sr}_2\text{RuGdO}_6$ system the $AFM$ ordered Ru spins at 30 K develops a $FM$ component with in the $AFM$ arrangement. The $AFM$ ordering of Ru spins in $\text{Sr}_2\text{RuREO}_6$ systems below 30 K is known to be due to Ru-O-O-Ru coupling [1-3,4]. In case of $\text{Sr}_2\text{RuGdO}_6$ system the $AFM$ ordering of Ru spins seems to develop a $FM$ component through possible Ru-O-RE interactions below 20 K due to magnetic RE (Gd).

In conclusion, we can safely conclude that the high magnetic moment of $8\mu_B$ for Gd$^{3+}$ influences the $AFM$ ordering of Ru in case of Gd/Ru-211O$_6$, which is obviously absent in case of non-magnetic RE containing Eu/Ru-211O$_6$. There is a possibility that Ru-O-RE interactions take place along with Ru-O-O-Ru coupling and hence in case of magnetic RE (Gd), the $AFM$ ordering of Ru is influenced, but not in case of non-magnetic Eu.

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FIGURE CAPTIONS

Fig. 1 X-Ray diffraction patterns of Sr$_2$RuREO$_6$ with RE = Gd and Eu

Fig. 2 Magnetization ($M$) versus temperature ($T$) plot for Sr$_2$RuGdO$_6$ sample in field-cooled ($FC$) situation under an applied field of 1000 Oe, inset exhibits the same for Sr$_2$RuREO$_6$ system

Fig. 3 Magnetization ($M$) versus temperature ($T$) plot for Sr$_2$RuGdO$_6$ sample in zero-field-cooled ($ZFC$) situation under an applied field of 10 Oe, inset exhibits the same for Sr$_2$RuREO$_6$ system at applied field of 40 Oe.

Fig. 4 $M/H$ plot for Sr$_2$RuGdO$_6$ in applied fields of $\pm$ 5 Tesla at 5 K, inset exhibits the same for Sr$_2$RuREO$_6$ system

Fig. 5 $M/H$ plot for Sr$_2$RuGdO$_6$ in applied fields of $\pm$ 5 Tesla at 15 K, inset I exhibits the same for low field of $\pm$ 3000 Oe. Inset II is the high field ($\pm$ 5 Tesla) $M/H$ plot for Sr$_2$RuREO$_6$ system at 15 K

Fig. 6 $M/H$ plot for Sr$_2$RuGdO$_6$ in applied fields of $\pm$ 5000 Oe at 20 K, inset shows $M/H$ plot for Sr$_2$RuREO$_6$ system at 20 K in applied fields of $\pm$ 5 Tesla
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FIG. 1.

\begin{center}
\includegraphics[width=0.8\textwidth]{fig1.png}
\end{center}

$\text{EuSr}_2\text{RuO}_6$

$\text{GdSr}_2\text{RuO}_6$

$I$ (arb. units)

$2(\theta)$ Angles
FIG. 2.

![Graph showing magnetic properties of EuSr$_2$RuO$_6$.](image)

- **Super-Para**
- **FM**
- **$T_N$**

- **EuSr$_2$RuO$_6$**
  - **H = 1000 Oe**
  - **Field-Cooled**

**Graph Details:**
- **$M$ (emu/g)**
- **$T$ (K)**
- **$T_N$**
- **$H$ = 1000 Oe**
- **Field-Cooled**
FIG. 3.
FIG. 4.

![Graph showing magnetization (M) vs. magnetic field (H) for GdSr$_2$RuO$_6$ at T = 5 K.](image)

FIG. 5.

![Graph showing magnetization (M) vs. magnetic field (H) for GdSr$_2$RuO$_6$ at T = 15 K.](image)
FIG. 6.

$\text{GdSr}_2\text{RuO}_6$

$T = 20 \text{ K}$

$M$ (emu/g) vs. $H$ (Oe)

Inset: $\text{EuSr}_2\text{RuO}_4$

$T = 20 \text{ K}$

$M$ (emu/g) vs. $H$ (Koer)