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**Magnetization Reversal in Fe Doped SmCrO<sub>3</sub>**Venugopal Rao Bakshi<sup>a</sup>, Vittal Prasad Bandi<sup>b</sup>, Narsinga Rao Gade<sup>c</sup>, Chou F C<sup>c</sup> and  
Suresh Babu Devarasetty<sup>\*a</sup>\*<sup>a</sup>Department of Physics, Osmania University, Hyderabad, India, [bakshivenu\\_9@yahoo.com](mailto:bakshivenu_9@yahoo.com).<sup>b</sup>Department of Physics, Nizam College (Osmania University), [vittal\\_bandi@yahoo.co.in](mailto:vittal_bandi@yahoo.co.in)<sup>c</sup>Centre for Condensed Matter Physics, National Taiwan University, Taipei, Taiwan, R.O.C, [nsrao@phys.ntu.edu.tw](mailto:nsrao@phys.ntu.edu.tw)**Abstract**

The compound SmCr<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> perovskites were prepared by citric acid route. The samples were characterized by XRD and SEM. The temperature and field dependent magnetization measurements were carried out in the temperature range of 5K to 400 K at 0.01T field and -5T to 5 T field at 2K. SmCrO<sub>3</sub> compound has shown two magnetic transition temperatures (T<sub>N1</sub> and T<sub>N2</sub>) at 197 K and 38 K. The observed behavior at 197 K is the characteristic of anti-ferromagnetic ordering of Cr<sup>3+</sup> moments with weak ferromagnetism. The drop in magnetization below 38 K is due to the spin reorientation of Sm<sup>3+</sup> in anti ferromagnetic arrangement and Cr<sup>3+</sup> spins. The doping of Fe in SmCrO<sub>3</sub> compound has shown a decrease in T<sub>N1</sub> and also the two magnetization reversals at 177K and 57K. The magnetic behavior at low temperatures is (T < T<sub>N1</sub>) explained in the context of competition among moments of rare earth (Sm) and transition metal ion (Cr/Fe). The existence of the two magnetization reversals offers the characteristic switching of magnetization without changing the direction of the applied magnetic field.

*Keywords:* Magnetization; Perovskite; Switching; Anti-Parallel; Canted; Spin reorientation;

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## 1. Introduction

The Rare earth orthochromites and orthoferrites with the general formula  $ABO_3$  (A is a non-magnetic alkali, alkaline earth or rare earth ion and B is a transition metal cation) have a perovskite structure with orthorhombic distortion and an Anti-ferromagnetic ground state. These materials are attracting research interest because of their potential applications as multifunctional materials [Sardar et al(2011)]. These materials possess variations of physical properties under the action of external magnetic field. The synthesis, structural, magnetic and electrical properties of perovskite orthochromites containing rare earth elements have been well documented in the physics and chemistry literature over the last few decades [Bertaut et al(1966), Geller et al(1971), Satoh et al(1997), Shamir N et al(1981), Tripathi et al (1980), Siemons et al(2007) and Tsushima et al(1970)]. The recent theoretical predictions of magneto electric coupling between the rare earth and  $Cr^{3+}$  ions along with the experimental observations of magnetic properties in some of the rare earth orthochromites has renewed interest in these materials [Sahu J et al (2007), Serrao et al (2005) and Zvezdin et al (2008)]. Some studies have shown that magnetization reversal would be useful for applications like Volatile memories [P.Mandal et al (2010) and J Mao et al (2011)] and spin resolving devices for charged particles [H.Adachi et al (1999)]. The flip of magnetization is different from that of ordinary magnetic systems, in which the magnetization is switched by changing the direction of H. In the perovskite materials, the magnetic properties are generally determined by the B-site cations and thus alloying different kinds of cations in the site may induce a variety of interesting phenomena has been observed by many researchers [P D Battle et al (1995)].

In this paper we report the doping effect of Fe on the temperature dependent and field dependent magnetic properties of  $SmCrO_3$  system prepared by citric acid route.

## 2. Experimental

Polycrystalline powders of  $SmCr_{1-x}Fe_xO_3$  ( $x=0.0, 0.2$ ) (The samples with  $x=0.0$  and  $x=0.2$  are denoted as S00 and S02 respectively throughout the paper) were prepared by the citric acid route as reported in our previous paper [B.Vittal Prasad et al (2011)]. The powders were annealed at 650 °C for 2 h. Circular pellets were pressed at 4000  $kg\,cm^{-2}$  in uniaxial disc. These pellets were sintered at 1200 °C for 4h. Sintered pellets were characterized by X-ray diffraction (XRD) using SHIMADZU XRD – 7000 using monochromatic  $Cu\ K\alpha$  radiation. Microstructure and the grain size distribution of the sintered pellets were studied using a Scanning Electron Microscope (SEM) HITCHIS-3400 N. The field dependent and temperature dependent magnetic measurements are performed using MPMS make Quantum Design Inc (USA) with the precision of 0.5K for temperature and 0.33 Oe for magnetic field. The FC and ZFC were measured at a field of 0.01T and in the temperature range of 5K to 400K. The isothermal magnetization curves were measured in the field range of + 5T to -5T at 2K.

## 3. Results And Discussions

All the samples were characterized by room temperature XRD. Fig 1 shows the XRD patterns of the S00 and S02. The observed spectra are of a single phase. All the peaks were indexed to orthorhombic system associated with space group Pbnm. The lattice parameters were determined using UFIT Powder diffraction data analysis software [M.Evain (1992)]. The cell parameters for these samples are given in the Table 1. The lattice parameters for x=0.0 are well in agreement with that reported in literature [1]. The lattice parameters were found to be increased with doping of Fe. Such an increase is associated with the incorporation of bigger Fe<sup>3+</sup> ion (0.645 Å) into the site of smaller Cr<sup>3+</sup> ion (0.615 Å). The fact of single phase and gradual increase in lattice parameters imply the incorporation of Fe<sup>3+</sup> ion into Cr<sup>3+</sup> ion in SmCrO<sub>3</sub> perovskite.

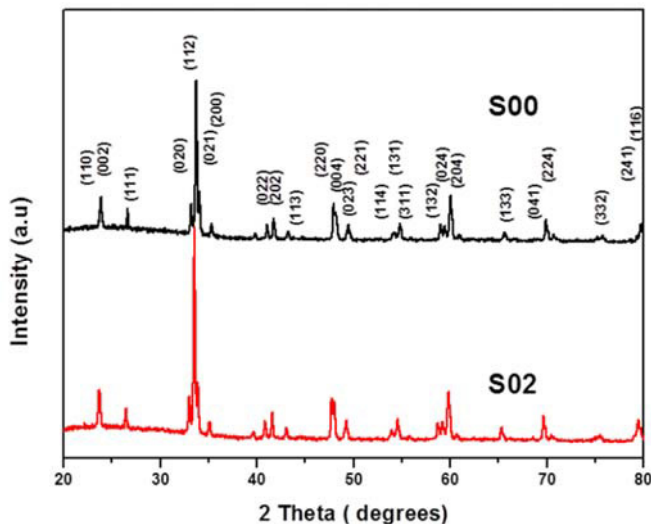


Fig 1: XRD pattern of S00 and S02

Table 1: The lattice parameters of S00 and S02

Sample	a(Å)	b(Å)	c(Å)	V(Å) <sup>3</sup>
S00	5.373(2)	5.505(1)	7.655(3)	226.481(2)
S02	5.384(1)	5.525(1)	7.669(1)	228.176(2)

The Fig 2 shows the temperature dependent magnetization measurements of  $\text{SmCrO}_3$  in both ZFC and FC modes at 0.01T. The transition temperatures are estimated by plotting the differential magnetization  $dM_{\text{FC}}/dT$  vs  $T$  as shown in inset of Fig 2. It can be seen that there exists two magnetic transitions  $T_{\text{N1}}$  and  $T_{\text{N2}}$  at 197 K and 38 K respectively, which are well in agreement with the literature [1]. The  $T_{\text{N1}}$  (197K) is a typical sharp transition temperature from paramagnetism at high temperature to weak ferromagnetism at low temperatures. According to earlier studies [K.Yoshii et al (2000)]  $T < T_{\text{N1}}$ , the rare earth chromites are possibly canted anti ferromagnetic with weak ferromagnetism.

It is known from literature [2] that  $\text{LnCrO}_3$  system at room temperature crystallizes in orthorhombic structure with space group Pbnm with four molecules per unit cell and exhibit canted antiferromagnetism (CAFm) order of localized  $\text{Cr}^{3+}$  moments with Neel temperature ( $T_{\text{N1}}$ ) in temperature range 112-282K [Cooke et al (1974), Guo P Y et al (2011), Nomura et al (1978), Khattak P C et al (1977), Arakawa T et al (1981), Bertaut et al (1966) and Taguchi H et al (1995)] and dielectric transition ( $T_{\text{E}}$ ) in the 472-516K range [C R Serrao et al (2005), J R Sahu et al (2007) and K.Ramesha et al(2007)]. At transition temperature  $T_{\text{N2}}$ , the Ln spins begin to reorder anti ferromagnetically.

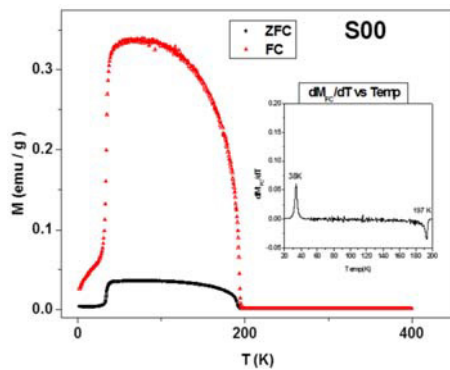


Fig 2: Temperature dependent magnetisation curve of  $\text{SmCrO}_3$  at 0.01T ( The inset shows the  $dM_{\text{FC}}/dT$  vs  $dT$ )

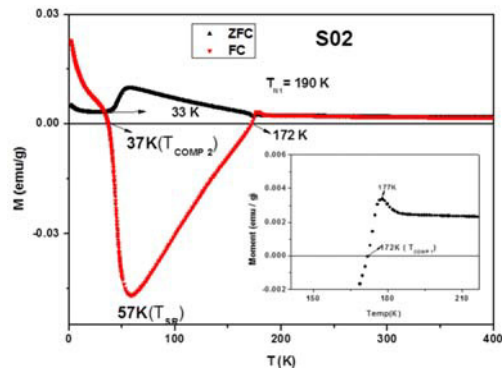


Fig 3: Temperature dependent magnetisation curve of S02 at 0.01T

In  $\text{CrO}_6$  octahedron, in perovskite cell, at low temperatures the super exchange (SE) interaction between the large spins on the nearest  $\text{Cr}^{3+}$  ions sandwiching  $\text{O}^{2-}$  ions is generated, resulting in antiparallel spin configuration. Due to orthorhombic distortion of  $\text{SmCrO}_3$  structure, Cr-O-Cr bond angle slightly deviates from  $180^\circ$ , resulting in residual electron spin, originating from imperfect super exchange interaction and showing  $\text{SmCrO}_3$  is a canted anti ferromagnetic below  $T_{\text{N1}}$  (197 K). The weak ferromagnetic component is due to the AFM exchange interaction between  $\text{Cr}^{3+}$  spins [Nirat ray et al (2008) and Morishita et al (1981)]. For this compound the FC magnetization exhibited positive values and lies above the ZFC magnetisation [K.Yoshii et al (2000)]. These are the behaviour of

the magnetic materials usually observed. The FC magnetization of  $x= 0.2$  (S02) sample exhibited negative polarity as observed in Fig 3. This can be understood in terms of random orientation of magnetic domains.

The fig 3 shows the temperature dependent magnetization (both FC and ZFC modes) of S02 at 0.01T. The transition temperature  $T_{N1}$  is observed at 190K, canted anti ferromagnetic transition. The decrease in  $T_{N1}$  value with 20% Fe doping can be understood in connection with change of  $Cr^{3+}$ -O-  $Cr^{3+}$  /  $Fe^{3+}$  angle governing the anti-ferromagnetic interaction. The FC magnetization shows a broad peak at 177K (shown in inset of Fig 3). A continuous decrease leads to a compensation temperature ( $T_{comp1}$ ) of 172K, below which the polarity of magnetization becomes negative. The magnetization becomes minimum at 57K and abruptly increases at this temperature, this temperature is attributed to a spin reorientation ( $T_{SR}$ ) [Kenji Yoshii (2012)]. The ZFC curve also shows the spin reorientation at 57K, where a peak is observed in ZFC curve. The polarity of the FC magnetization turns positive again at 37K, denoted as  $T_{comp2}$ . The interaction between  $Sm^{3+}$  and  $Cr^{3+}$  /  $Fe^{3+}$  becomes increasingly important below  $T_{SR}$  (57K) thereby the magnetisation increases continuously and leads to zero values at 37K. The characteristic feature of S02 sample is the polarity of the magnetization flipped between positive and negative by changing the temperature only. This is different from the phenomenon in ordinary magnetic materials, in which the magnetization

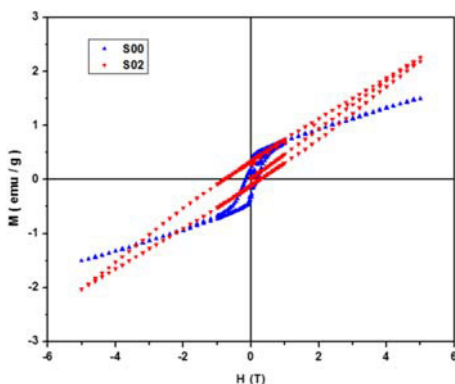


Fig 4: Field dependent magnetisation curves of S00 and S02 at 2K

Table 2: The  $M_{max}$ ,  $M_r$  and  $H_c$  values for S00 and S02

Sample	$M_{max}$ (emu / g)	$M_r$ (emu / g)	$H_c$ (T)
S00	1.46	0.39	0.21
S02	2.18	0.34	0.81

is flipped by changing the direction of the applied field. This fact gives hints for switching magnetization. Below  $T_{\text{comp2}}$ , a clear crossover between ZFC and FC curves was observed at 33K ( $T_{\text{cross}}$ ). The cross over effect is related to the impact of the paramagnetic  $\text{Sm}^{3+}$  ions, whose magnitude becomes more prominent at lower temperatures. The canted anti ferromagnetism of the ( $\text{Cr}^{3+} + \text{Fe}^{3+}$ ) network and the behavior of the  $\text{Sm}^{3+}$  sublattice contributes independently to the total magnetization. However, during FC cycle the ferromagnetically interacting transition metal ( $\text{Cr}^{3+} / \text{Fe}^{3+}$ ) sublattices will impose a local field over  $\text{Sm}^{3+}$  moments. The resultant magnetization hence is the superposition of magnetic moments at both the sublattices (transition metal / rare earth). The inversion of the magnetic moment can be considered as a consequence of the anti ferromagnetic exchange interaction between the  $\text{Sm}^{3+}$  site and the  $\text{Cr}^{3+} / \text{Fe}^{3+}$  sites.

Fig 4 gives the isothermal MH loops for S00 and S02 samples at 2K, indicating the presence of ferromagnetism in both the samples. None of the samples reached the saturation upto 5T field. The  $M_{\text{max}}$ ,  $M_{\text{r}}$  and  $H_{\text{c}}$  were estimated from the MH curves for the samples and are presented in Table 2.

As discussed earlier,  $\text{SmCrO}_3$  is canted AFM due to Cr-O-Cr exchange interaction below  $T_{\text{N1}}$ . As  $\text{Fe}^{3+}$  ions are incorporated into B-site, three exchange interactions may be present due to the random distribution of the B-site cations as Fe-O-Fe, Fe-O-Cr and Cr-O-Cr. It is well known that Cr-O-Cr and Fe-O-Fe are AFM interactions, whereas Fe-O-Cr superexchange interaction shows FM interaction [D.Treves (1965)], which enhances the magnetization with incorporation of Fe.

## Conclusions

The temperature dependent magnetisation of  $\text{SmCrO}_3$  shows two transitions at  $T_{\text{N1}}=197\text{K}$  and  $T_{\text{N2}}=38\text{K}$ . The  $T_{\text{N1}}$  is the transition from paramagnetic at high temperature to canted anti ferromagnetism at low temperatures. At  $T_{\text{N2}}$ , rare earth spins begin to re order in anti ferromagnetic arrangement. The doping of 20% of Fe in  $\text{SmCrO}_3$  decreased the  $T_{\text{N1}}$  to 190K. In  $\text{SmCrO}_3$ , the FC and ZFC magnetization behave like usual magnetic materials, whereas doping of 20% of Fe in  $\text{SmCrO}_3$  shows two magnetization reversals. The existence of the two magnetization reversals offers the characteristic switching of magnetization without changing the direction of the applied magnetic field.

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