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Griffiths like robust ferromagnetism in $Co_{3-x}Mn_xTeO_6$; ($x = 0.5, 1, 2$)

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ABSTRACT

We report near room temperature ferromagnetic (FM) as well as low temperature antiferromagnetic (AFM) correlations in $Co_{3-x}Mn_xTeO_6$ (CMTO); ($x = 0.5, 1, 2$) solid solutions, using thorough DC magnetization studies. For all x, CMTO shows not only short-range robust FM order ~185 K, but also long range enhanced AFM order ≤45 K. Griffiths-like FM interactions show up in magnetization data; it exists over an extended temperature range and remains unsuppressed in magnetic field as large as 1 T, indicating its robustness. Variations in both FM and AFM phases as a function of Mn concentration also support our observation of anomalous behavior in the average bond distances and charge states (JAP 116: 074904 (2014)). Further, an attempt towards the structural insight into the observed complex magnetic behavior by using network like structural analysis has been drawn. These observations make CMTO an interesting magnetic system from fundamental and application perspectives.

1. Introduction

Coexistence of magnetic interactions of opposite nature leading to complex magnetic behavior has been seen in numerous magnetic systems for example, in manganites and cobaltites owing to their enormous potential applications in different fields [1–4]. Griffiths phase (GP), first proposed by Griffith [5–8], presents the competition between the ferromagnetic (FM) and antiferromagnetic (AFM) interactions under random potential [5]. Disorder sets in such a way that different values of exchange coupling may be assigned randomly to different sites of the lattice. This causes existence of short-range FM clusters when $T_C < T < T_{GP}$ (here, T_C represents the FM Curie temperature, whereas, T_{GP} is the Griffiths phase temperature at which the FM clusters begin to nucleate). The intermediate regime is known as GP. A sharp downturn in the inverse magnetic susceptibility (as a function of temperature) is the Hallmark of GP [5–8]. This downturn in the thermal behavior of χ^{-1} is an important observation that distinguishes GP from smeared phase transition because, the latter gives rise to an upward curvature in χ^{-1} vs T above T_C, deviating from Curie – Weiss (CW) law [5–8]. The softening of the downturn in χ^{-1} with the progressive increase in field is another typical signature of GP. The basic characteristics of GP regime is that above T_C there exists finite but nano size clusters with FM correlated spins [3–5].

Role of Griffiths like ferromagnetism (well accepted phenomenon in CMR: Colossal Magneto Resistance [1–4]) in multiferroic (MF) systems cannot be overemphasized. We show that the presence of such a phase in multiferroics can add to a great advantage. MFs (exhibit either coupling between electronic and magnetic orders (type II) or a separate single order (type I)), offer great opportunities for applications in information storage, spin electronics, magneto-electronics and solar cells. A number of MFs possessing cationic and anionic non-stoichiometry are further essential in many other applications such as energy conversion, oxygen sensing, oxygen storage etc [9]. During last few decades, type II MF materials which are of practical interest are found only at very low temperatures except a few [10]. Besides understanding on the mechanism of coupling of these ferroic orders, designing and finding new MF materials are some of the frontier research activities [11,12]. Undoubtedly, controlling and coupling of various 'ferro or antiferro' magnetic orders at room temperature are of immense interest [10–14]. Enhancement of these couplings at much higher temperatures may possibly be achieved by various ways like internal chemical pressure (through doping) and other external perturbations [15,16]. Many of the doped compounds become intrinsically inhomogeneous due to random distribution of cation sizes, their different valence/spin states and strong competition between different ordering tendencies and present

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great advantage in the field [15,16]. Compounds on doping, not only show the enhanced magnetoelectric coupling at higher temperature but also coexistence of more than one magnetic interaction, e. g. coexistence of AFM and FM. [15–17].

Co_3TeO_6 (CTO), a low symmetry (monoclinic: C2/c) type II MF at low temperatures, shows complex magnetic structure with a sequence of AFM transitions [18]. Mn_3TeO_6 (MTO), on the other hand, crystallizes in higher symmetry (Rhombohedral: $R\bar{3}$) type I multiferroic, exhibits similar AFM transition at low temperature [19]. Its structural details can be found elsewhere [18,19]. MTO and CTO show AFM transitions (T_N, the Neel temperature) at around 23 K and 26 K, respectively [18,19]. In contrast, Mn doped CTO {($Co_{3-x}Mn_xTeO_6$ (CMTO); ($x = 0.5$, 1 and 2)} or Co doped MTO not only enhances the AFM transition temperature [20,21]. but also show possible high temperature FM correlations (for $x = 0.5$) [17]. Our recent structural and spectroscopic studies on this material suggest possible structural origin of this enhancement in AFM transition of CMTO [17], which was not understood earlier [20,21]. For $x \geq 0.5$, increase in lattice parameters and average transition metal – oxygen (TM – O) bond distances with increasing Mn concentration is corroborated with the magnetic behavior of enhanced AFM transition temperatures. Together with these, relative ratios of Co^{3+}/Co^{2+} and Mn^{3+}/Mn^{2+} (or TM^{3+}/TM^{2+}), which has been observed through XANES analysis at Co and Mn K-edges, found to be maximum at around $x \sim 0.5$. At this particular concentration, average <Co/Mn-O> bond lengths are found to be lowest. Approximately at the same concentration, maximum $T_N \sim 45$ K has been observed and could be correlated with the structural and spectroscopic results, which show anomalous behavior in average bond lengths and charge ratios at $x \sim 0.5$ [17]. In this report, on the other hand, we describe a probable mechanism behind the observance of high temperature FM correlations (along with enhanced AFM ordering) in these solid solutions, not reported so far.

2. Experimental details

Single phasic polycrystalline CMTO ($x = 0.5$, 1 and 2) solid solutions were synthesized using conventional solid state reaction route [17]. The reactants were used as commercial cobalt oxide Co_3O_4 (Alfa Easer 99.7%), Mn_3O_4 (Alfa Easer 99.99%) and tellurium dioxide TeO_2 (Alfa Easer 99.99%). The ground oxide mixtures were calcined at 700 °C for 10 h and then recalcined at 800 °C for ~25 h as a second step. For each step of calcinations and sintering (~850 °C for 2 h), the pellets were made by applying 2 tons of pressure. Thorough structural and spectroscopic characterizations were performed using Synchrotron X-ray at Indus-2 synchrotron source, India [17]. DC magnetization measurements were carried out using a SQUID magnetometer (MPMS5 by Quantum Design).

3. Results and discussion

3.1. Magnetic behavior of $Co_{3-x}Mn_xTeO_6$ (x = 5, 1 and 2)

Fig. 1(a) [17], (b) and (c) shows temperature dependent magnetization (M vs T) for CMTO ($x = 0.5$, 1.0, and 2.0) solid solutions performed at a constant magnetic field of 100 Oe. All these DC magnetization data have been recorded under both zero field cooled (ZFC) and field cooled (FC) conditions, as shown in Fig. 1. We have also used constant magnetic fields of 10 kOe and 50 kOe during the magnetization measurements which will be discussed further. It is interesting to note that the observed magnetic behavior for all the composition is similar (Fig. 1) but much richer than those reported earlier [20,21]. Looking from room temperature side, in Fig. 1, samples exhibit interestingly paramagnetic (PM) to FM like transition at a characteristic temperature T_C (Curie temperature) ~185 K, which is same (within ±2 K) for all the samples, and is the main focus of the present report. This feature in the magnetization curves is followed by the AFM transitions at $T_N \sim 45$ K, 40 K and 30 K (as shown by double headed arrow in both ZFC and FC curves), for 0.5, 1.0 and 2.0 Mn content, respectively. However, in literature [20,21], the only reported transitions for these solid solutions were AFM like and at temperatures ≤ 40 K. These values (reported earlier ~40 K and observed presently ~ 45 K) are much higher compared to the Neel temperatures observed in either of the compounds CTO (26 K) and MTO (23 K) separately [18,20,21]. We have corroborated this enhancement with our earlier structural and spectroscopic results, which are explained via variations in average bond lengths and average charge ratios as a function of Mn concentration [17]. Further, to the best of our knowledge, there is no FM correlation and hence no corresponding transition is reported so far in these compounds [20,21]. We, on the other hand, observe a FM like transition at T ~ 185 K along with a bifurcation in ZFC and FC curves for all the samples (see Fig. 1(a)–(c)). In literature [22,23], the bifurcation in FC–ZFC magnetization data has been attributed to the presence of a spin-glass, cluster-glass, super-PM behaviour etc. We attribute this feature to a PM to FM like transition. As discussed earlier in several other reports [22,23], the temperature derivative dM/dT of the FC magnetic data resembles FM like transition, and is shown in the inset of Fig. 1(a)–(c). The existence of such type of FM correlations (below T_N) in the AFM ground state, reported earlier for various other compounds [6–8], have been understood as the presence of FM interaction in the AFM phase, and is demonstrated below. The signature of FM correlation is confirmed through the

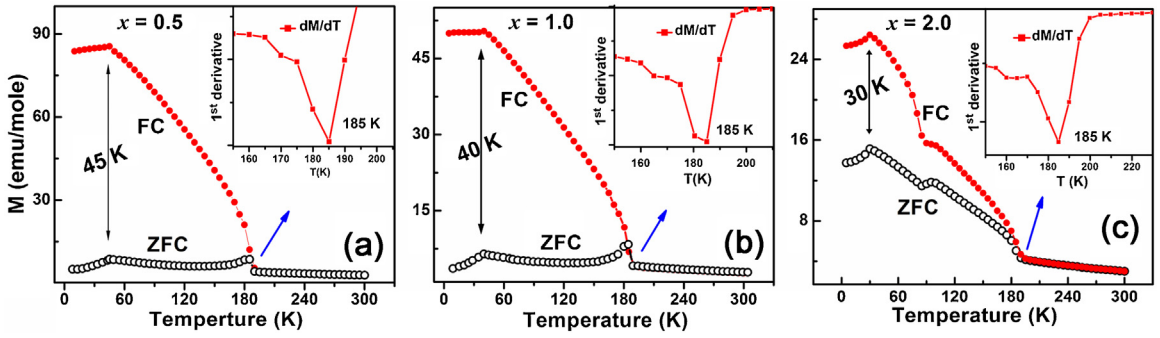

Fig. 1. (a)–(c) Low magnetic field DC magnetization in ZFC/FC protocol (taken at 100 Oe) for $x = 0.5$, 1.0 and 2.0 indicates AFM transitions at 45 K, 40 K and 30 K, respectively followed by ferromagnetic like transition at around 185 K. Insets show dM/dT to assign exact high temperature transition.