Inverse and enhanced magnetocaloric properties of $HoCrO_3$

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Abstract:

We report on the magnetic and magnetocaloric properties of 50% Fe^{3+} doped polycrystalline $HoCrO_3$ compounds in the vicinity of magnetic transitions. Due to complex magnetic interactions, we do see multiple transitions in χ *vs.* T graph pertinent to $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds related with Ho^{3+} ordering, Cr^{3+} ordering and spin – reorientation (SR). Due to re-orientation of spins, metamagnetic transitions are evident in low field regime of M *vs.* H. Quantified values of $-\Delta S_M$ around Ho^{3+} ordering infer that indeed Fe^{3+} substitution helped in enhancing magnetocaloric effect of $HoCrO_3$ compound. Such an enhanced $-\Delta S_M$ values are ascribed to increase in canting of Fe/Cr spins. Present results would be helpful in developing magnetic refrigerant materials for space applications particularly below 30 K.

Keywords: Magnetocaloric effect, magnetization crossover, metamagnetic transition, spin – re-orientation

Introduction:

In recent years, refrigeration based on magnetic materials particularly using magnetocaloric effect (MCE) phenomenon has gained much attention in view of its application in future magnetic refrigeration technology due to its higher energy efficiency and environmental safety over the conventional gas compression refrigeration[1-3]. MCE is a magneto-thermal phenomenon, in which the temperature of a magnetic material changes when it is exposed to a magnetic field adiabatically[4]. A magnetic materials with a large change of magnetic entropy $\Delta S_M(T,H)$ or adiabatic temperature (ΔT) and a sufficiently large value of refrigeration capacity (RC) are promising candidates for magnetic refrigeration[5]. A plethora of compounds have been investigated to study the MCE in alloys like $Ni_{52.6}Mn_{23.1}Ga_{24.3}$[6], $Gd_5(Si_2Ge_2)$[7], $MnFeP_{0.45}As_{0.55}$[8] as well as in oxide materials such as $Tb_{0.67}R_{0.33}MnO_3$ (R = Dy, Y and Ho)[9] and $La_{1-x}Ca_xMnO_3$[10].

As for as oxide materials are concerned, distorted perovskite family of canted antiferromagnets, orthoferrites ($RFeO_3$)[11] and orthochromites ($RCrO_3$)[12] have attained much interest due to their unique physical properties and complex spin structure between the rare-earth (R) and the transition metal (TM) ions. $RFeO_3$ and $RCrO_3$ compounds have been explored for their MCE properties and suitability for magnetic refrigeration applications[13-15]. For example, a large MCE value of ΔS ~ 8.4 J/kg-K and RC ~ 217 J/kg at 15 K and 4 T has been observed in $DyCrO_3$ due to ordering of Dy^{3+} at 2.3 K[14]. Yin *et.al,* reported large MCE value of ΔS ~ 10.5 J/kg-K at 4 T around Dy^{3+} ordering (14 K) in $DyFe_{0.5}Cr_{0.5}O_3$ compound[15]. Yet in another compound, $HoCrO_3$, large value of MCE has been reported and the values are ΔS ~7.2 J/kg-K and RC ~ 408 J/kg at 20 K and at 7 T[16]. Although several reports have shown MCE on various magnetic materials like $Dy_{1-x}Sc_xNi_2$[17], $R_{1-x}La_xNi_2$ (R = Tb, Dy, Ho)[18], Dy_2Cu_2Cd[19], TmAgAl[20], TmZn[21], Er_2Cu_2In[22], Eu_4PdMg[23], etc… as this field is highly demanding numerous new materials needs to be explored for various applications. Particularly, much attention is required to search for new materials with giant MCE below 30 K for utilization in space applications[1, 24].

In this context, $HoCrO_3$ is a compound which shows large value of ΔS (~7.2 J/kg-K) below 30 K. It is evident from the above discussion that substitution of Fe^{3+} in $DyCrO_3$ for Cr^{3+} has enhanced -ΔS values around Dy^{3+} ordering[15]. Hence, we believe that Fe^{3+} would play a crucial role in enhancing MCE in our present $HoCr_{0.5}Fe_{0.5}O_3$ compound around Ho^{3+} ordering. In addition, it also has been believed from neutron diffraction data that up on adding 50% of Fe to Cr, spin reorientation (SR) transition would be evident[25] due to an interaction between Ho^{3+} and Fe^{3+} moments. Such a SR transition would be associated with a change in magnetization direction from $G_xA_yF_z$ (Γ_4) to $F_xC_yG_z$ (Γ_2), where G_x, A_y, and F_z stand for spin component along x, y, and z axis in terms of Bertaut's notation, respectively[26], which can lead to large change in $-\Delta S_M$. Calculation of entropy change around SR transition is also aim of our present paper. Apart from the SR and Ho^{3+} ordering, indeed there exists a transition due to Cr^{3+}, which may also give large change in MCE. Hence, in the present work, we explored MCE properties of $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds around Ho^{3+}, Cr^{3+} and SR transition temperatures. In addition, we also studied the nature of magnetic transition in aforesaid compounds through Arrott plots. Sailent features of present manuscript are (a) up on adding 50% of Fe^{3+} to Cr^{3+}, enhanced value of MCE is evident in $HoCr_{0.5}Fe_{0.5}O_3$ compound (b) magnetization crossover is evident in $HoCrO_3$ compound and metamagnetic transition prevails around Ho^{3+} ordering in both $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds (c) Spin reorientation (SR) transition is apparent in $HoCr_{0.5}Fe_{0.5}O_3$ compound around 150 K.

Experimental Details:

Polycrystalline $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds were prepared by conventional solid state reaction method using High purity oxide powders of Ho_2O_3, Fe_2O_3, and Cr_2O_3 (purity > 99.9%) (Sigma-Aldrich chemicals India) as starting raw materials. The temperature (T) dependent magnetization (M) (M *vs.* T) and magnetic field (H) dependent magnetization (M *vs.* H) measurements were performed using a Quantum Design magnetic property measurement system (MPMS) in the temperature range of 5 – 300 K. Magnetization isotherms (M *vs.* H) were measured at different temperature ranges and up to a maximum magnetic field of 6 T. Before we perform each measurement of M *vs.* H, the sample was warmed upto a temperature greater than ordering temperature of transition metal to remove the magnetic history.

Results and Discussion:

The phase purity of $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds were confirmed[27] at room temperature using powder x - ray diffraction (XRD) (PANalytical X-ray diffractometer) with Cu - K_α radiation ($\lambda = 1.5406$ Å) and with a step size of 0.017^o in the wide range of the Bragg angles 2θ (20^0 - 80^0) as shown in Fig. 1. From the Fig.1, it is observed that the indexed reflections are allowed for a compound with $GdFeO_3$ type distorted perovskite structure with a space group of *Pbnm*. We do not see any impurity phase within the detectable limits of the XRD. The structural parameters obtained from the Rietveld refinement has been published elsewhere[27]. The increase in the lattice parameter is evident from the refinement with increasing Cr^{3+} content, which is consistent with the fact that ionic radius of Cr^{3+} (0.615 Å) is smaller than that of Fe^{3+} (0.645 Å).

Fig. 2(a) shows the temperature (T) *vs.* susceptibility (χ) graph in zero field cooled (ZFC) conditions. It is evident from the figure that the Cr^{3+} moments ordered antiferromagnetically (AFM) at 142 K. Such AFM is believed have canting nature with AFM axis at 142 K (T_N). On the other hand, transition due to Ho^{3+} moments is evident at 8 K (T_N^{Ho})[28]. Fig. 2(b) shows χ *vs.* T graph for $HoCr_{0.5}Fe_{0.5}O_3$ compound. In 50% Fe substituted compound, in addition to AFM and Ho^{3+} (13 K) ordering, we also could able to realize a transition due to SR[25]. The origin of such SR is due to change in magnetization from $G_xA_yF_z$ (Γ_4) to $F_xC_yG_z$ (Γ_2), where G_x, A_y, and F_z stand for spin component along x, y, and z axis in terms of Bertaut's notation, respectively. Such a SR transition is evident around 150 K (T_{SR}) and we also ascribe such SR in $HoCr_{0.5}Fe_{0.5}O_3$ compounds to complex exchange interaction between the Fe^{3+} and the Ho^{3+} ions[29]. Indeed, there is a shift for Ho^{3+} ordering from 8 – 13 K and T_N from 142 – 273 K up on adding 50% Fe to Cr. The obtained T_N and T_{SR} values are in good agreement with the literature[25, 28].

As there are multiple transitions in both the compounds, we do expect a large change in entropy around these transitions. Hence, in order to quantify change in entropy we performed the M *vs.* H measurements in the vicinity of the magnetic transitions for both the $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$compounds. Fig. 3(a)-(d) shows first quadrant magnetization isotherms of $HoCrO_3$ (at 2 – 10 K and 136 – 146 K with an interval of 2 K) and $HoCr_{0.5}Fe_{0.5}O_3$ (at 5 - 20K with an interval of 3 K and 120 – 200 K with an interval of 10 K) compounds with a maximum magnetic field of 6 T. A field induced metamagnetic transition is evident in the low magnetic field region for all M *vs.* H graphs pertinent to $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds as shown in Fig. 3(a) and 3(b). Now we define the critical field (H_C) as field below which the material shows AFM behaviour and exhibits ferromagnetic (FM) behaviour above this field. Such a field induced transition in low field region can be ascribed to the onset of a first order metamagnetic transition (from original AFM state to FM state).

Evidenced metamagnetic transition may be due to the magnetization reversal of those ions whose magnetic moments are directed opposite to the applied magnetic field and the similar behaviour has been observed in the single crystals of $DyCrO_3$ as the rotation of Dy^{3+} and Cr^{3+} moments[30]. From Fig.3 (a), it is evident that there is a magnetization crossover (which is shown as an inset of Fig. 3(a)) around the AFM→ FM transition, which can be ascribed as a result of the competition between the Zeeman energy due to the applied external field and the strong magneto-crystalline anisotropy energy around the metamagnetic transition[31].

H_C values are obtained from the first derivative of M *vs.* H curve in low field region as shown in inset of Fig. 3 (b). The variation of H_C with temperature for $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ is shown in Fig 4(a) and 4(b). In both the compounds initially H_C increases up to a transition pertinent to Ho^{3+} ions and above which it diminishes. The increase in H_C up to Ho^{3+} ordering temperature can be explained as follows. For a perfect antiferromagnetic (AFM) system, below transition, in principle the H_C should increase due to the strong AFM nature. However, we do see a decreasing trend in our sample due to the presence of both ferromagnetic (FM) and AFM phases. Neutron diffraction study on $HoFeO_3$ compound[32] has been revealed that the Ho^{3+} moments order in a distorted antiferromagnetic (AFM) configuration and each Ho^{3+} moment consists a magnetic moment with a magnitude of 7.5 μ_B in (001) plane and makes an angle with respect to [010] direction so as to produce a net ferromagnetic moment of 3.4 μ_B per $HoFeO_3$ molecule parallel to [100] at 1.25 K. Hence, the observed behavior of H_C can be attributed to the temperature dependent competition between AFM and FM phases. Fig. 4 (c) depicts the variation of magnetization (M) with the applied magnetic field (H) recorded at 5 K for both $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds. Indeed, there is an enhanced magnetization in $HoCr_{0.5}Fe_{0.5}O_3$ compound compared with $HoCrO_3$ due to larger magnetic moment of Fe^{3+} ions compared to that of Cr^{3+} ions. The increase in FM component in

$HoCr_{0.5}Fe_{0.5}O_3$ compound might be a reason why we do see lower value of H_C in comparison with $HoCrO_3$.

Fig. 3 (c) depicts the M *vs.* H graphs around AFM transition in $HoCrO_3$ compound. It is evident that in low field region, indeed there exists a curvature due to a weak ferromagnetic component. However, such transition is very weak. Above 142 K, we do not see any curvature for M *vs.* H graphs at low field region as a result of paramagnetic phase. We also tried to map the variation of magnetization with magnetic field around SR transition in $HoCr_{0.5}Fe_{0.5}O_3$ compound. Fig. 3 (d) indicates M *vs.* H loops measured for $HoCr_{0.5}Fe_{0.5}O_3$ compound during spin reorientation (SR) transition.

As there are multiple transitions in both the compounds, we do expect a large change in entropy around these transitions. Hence, we calculated magnetic entropy change ($-\Delta S_M$) from isothermal magnetization curves using well known Maxwell's equation as follows

$$\Delta S_M(T,H) = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T}\right)_H dH ----(1),$$

where $H_{\max}$ is the maximum value of external applied field. From the above equation, it can be noticed that the value of $-\Delta S_M$ depends on both values of magnetization (M) and $\left(\frac{\partial M}{\partial T}\right)_H$.

The larger values of $-\Delta S_M$ can be obtained when the values of M and $\left(\frac{\partial M}{\partial T}\right)_H$ are large in the magnitude[33]. Quantified values of $-\Delta S_M$ and its temperature variation is shown in Fig. 5 (a) – (d). Here, Fig. 5(a) and 5(b) depicts the $-\Delta S_M$ *vs.* T around Ho^{3+} ordering for $HoCrO_3$ ($-\Delta S_M \sim 6.99$ J/kg.K at 9 K) and $HoCr_{0.5}Fe_{0.5}O_3$ ($-\Delta S_M \sim 8.18$ J/kg.K at 12.5 K) compounds respectively. Large values of $-\Delta S_M$ in both the compounds can be ascribed to evidenced metamagnetic transition and the Ho^{3+} ordering. Reason for the enhancement in the value of $-\Delta S_M$ in $HoCr_{0.5}Fe_{0.5}O_3$ compound compared to that of the $HoCrO_3$ compound can be explained as follows. Essentially, $HoCrO_3$ is distorted type perovskite material and crystallizes in orthorhombic structure with a space group of Pbnm[34]. For an ideal perovskite Cr-O1-Cr bond angle must be 180°. However, due to the distortion as a result of tilting of CrO_6 octahedra in $HoCrO_3$, there would be a change in Cr-O1-Cr bond angle (146.2°)[27], which is distinctly different from an ideal perovskite. This distortion decreases the orbital overlap and leads to non collinear antiferromagnetic structure of Cr^{3+} ions with a weak ferromagnetic component. Obtained bond angle value from Rietveld refinement pertinent to Fe(Cr)-O1-Fe(Cr) is smaller for $HoCr_{0.5}Fe_{0.5}O_3$ (145.3°) in comparison with the $HoCrO_3$ (146.2°) compound. This indicates an increase in canting of spins and hence an enhancement in the $-\Delta S_M$ value for $HoCr_{0.5}Fe_{0.5}O_3$ compound in comparison with $HoCrO_3$. The increase in canting angle of Fe/Cr sublattice with AFM axis for $HoCr_{0.5}Fe_{0.5}O_3$ has been evident from the neutron diffraction data on $HoFe_{1-x}Cr_xO_3$ solid solutions[25]. The values of MCE obtained for $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds in the vicinity of Ho^{3+} ordering temperature are large when compared to $DyMnO_3$[35] ($-\Delta S_M \sim 6.8$ J/kg.K at 7T and 10 K) , $SmFe_{0.5}Mn_{0.5}O_3$[36] (5.6 J/kg.K at 18 K and with 7 T) and $HoCr_{0.7}Fe_{0.3}O_3$[37] (6.83 J/kg.K at 20 K and with 7 T). The MCE values are found to be smaller compared to that of $DyCrO_3$[14] and $DyFe_{0.5}Cr_{0.5}O_3$[15], which could be due to larger magnetic hysteresis exists in the present $HoCr_{0.5}Fe_{0.5}O_3$[27] compound, which leads to more energy loss in the thermal process and small values of MCE. However, the $-\Delta S_M$ obtained in the present study are smaller compared to giant MCE material such as TmZn[21], $ErMn_2Si_2$[38], Tm_2Cu_2In[22], HoPdIn[39] and $RE_2Cu_2O_5$ (RE = Dy and Ho)[40] in the low temperature region.

From the Fig. 5(a), it is evident that $-\Delta S_M$ values shows both positive and negative values as though there exists re-entrant magnetocaloric effect. Such an unusual nature of re-entrant inverse MCE in $HoCrO_3$ compound has been not observed earlier[16]. The reason for such an intriguing phenomenon may be due to the subtle changes in relative orientations of Ho^{3+} and

Cr^{3+} moments occurs with a variation of temperature and/or magnetic field[41]. Earlier inverse magnetocaloric effect has been observed around SR transition in single crystals of $HoFeO_3$[42]. We conceive from our observation that magnetization crossover and complex interaction between FM and AFM phases might be a reason for re-entrant MCE behaviour for the present compound. From Fig. 5 (c) and 5(d), observed $-\Delta S_M$ value of 1.05 J/kg.K (around 141 K for $HoCrO_3$) and 0.61 J/kg.K (around 125 K for $HoCr_{0.5}Fe_{0.5}O_3$) at 6 T can be ascribed to the Cr^{3+} ordering and the spin-reorientation transition respectively.

It is believed that the magnitude of the magnetic entropy change at a particular magnetic phase transition and its dependence on temperature and magnetic field strongly depend upon the nature of the corresponding phase transition[43], so that it is essential to determine the nature of magnetic phase transitions in the compounds. To do this, the first quadrant magnetization isotherms were plotted in the form of Arrott plots[44] which can be deduced from Ginzburg-Landau theory in the close vicinity of the magnetic transition. The thermodynamic potential with Ginzburg-Landau type expansion which includes the magnetostatic field energy (*MH*) near the magnetic transition is as follows:

$$G(T,M) = G_0 + \alpha M^2 + \beta M^4 + ... - MH \qquad \text{... (2)}$$

where α, β are the Landau coefficients dependent on temperature. In the equilibrium condition, $\frac{\partial G}{\partial M} = 0$, the equation (2) reduces to $H/M = \beta M^2 + \alpha$. According to Banerjee's criterion[45], a negative slope of H/M *vs.* M^2 at some point indicates the first order magnetic transition. On the other hand a positive slope of H/M *vs.* M^2 indicates the second order magnetic transition. Fig. 6(a)-(d) shows the Arrott plots corresponding to magnetization isotherms shown in Fig. 3(a)-(d) respectively. The negative slope of H/M *vs.* M^2 for the Fig. 6(a) - (c) corresponding to $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds indicates the first order magnetic phase transition, while the positive slope of $^{\mathrm{H}}/_{\mathrm{M}}$ *vs.* M^2 for the Fig. 6(d) corresponding to $HoCr_{0.5}Fe_{0.5}O_3$ indicates the second order magnetic phase transition which is in agreement with the literature[46].

Conclusions:

Due to complex magnetic interactions, we do see multiple transitions in χ *vs.* T graph of $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds. M *vs.* H graph infer that the magnetization crossover is evident around Ho^{3+} ordering in $HoCrO_3$. On the other hand, metamagnetic transitions are prevailed in the low field regime of M *vs.* H graph around Ho^{3+} ordering. Indeed, there is an enhancement in the saturation magnetization up on adding Fe^{3+} to Cr^{3+} due to large magnetic moment of Fe. Re-entrant magnetocaloric effect is evident in $HoCrO_3$, which may be due to magnetization crossover and complex interactions. We trust that the large values of MCE obtained for $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds makes them promising candidates for magnetic refrigeration applications below 30 K.

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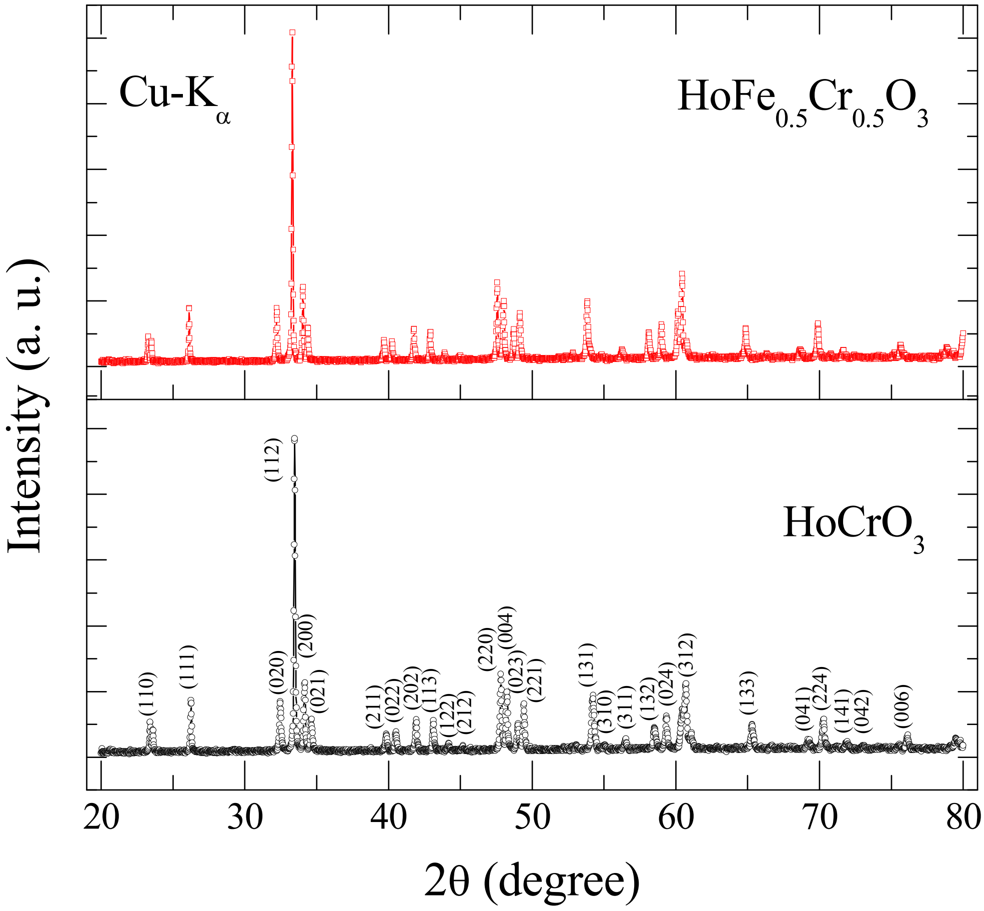

Fig.1: Powder x-ray diffraction patterns pertinent to $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ recorded at room temperature.

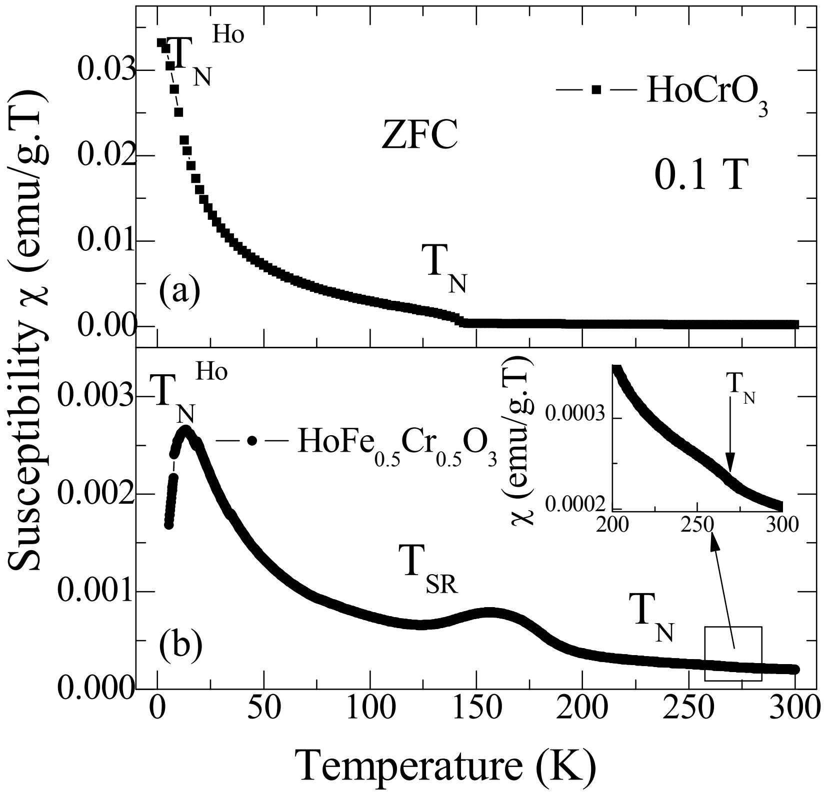

Fig. 2: Temperature (T) dependence of susceptibility (χ) pertinent to $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds measured at 0.1 T under zero field cooled condition (ZFC).

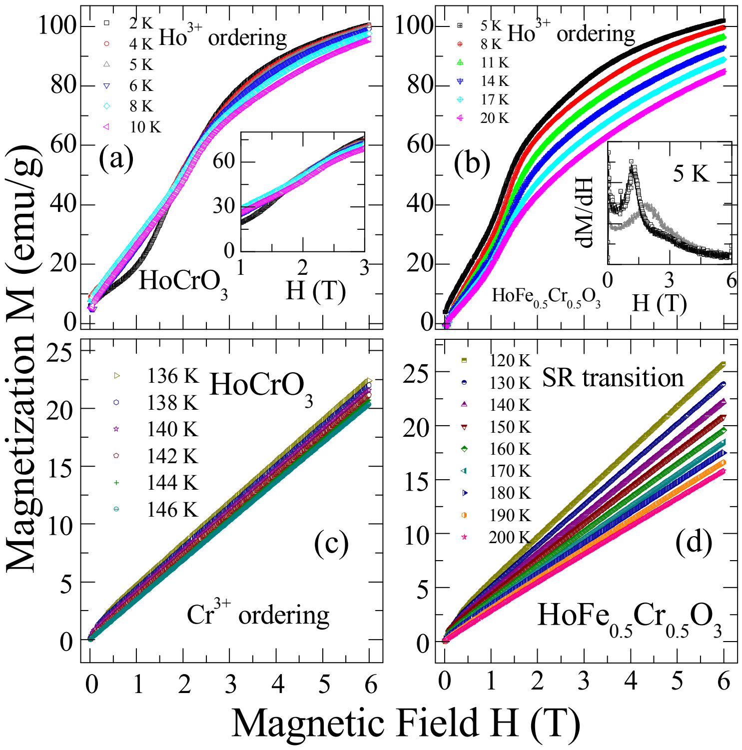

Fig. 3: (a – d) First quadrant magnetization isotherms near the transition temperature with an applied field up to 6 T for $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds. Magnetization crossover is shown as an inset of Fig.2 (a). Inset of Fig. 2(b) shows dM/dH *vs.* H for both the compounds corresponding to M *vs.* H measured at 5 K.

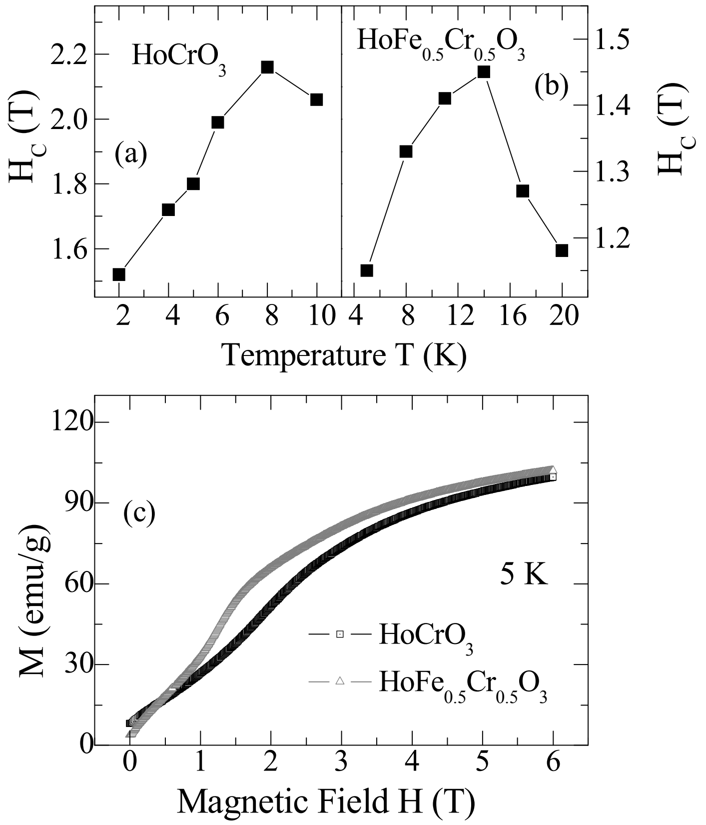

Fig. 4: (a) & (b) Temperature dependent variation of critical field (H_C) for HoCrO$_3$ and HoCr$_{0.5}$Fe$_{0.5}$O$_3$ compounds respectively (c) M *vs.* H graph measured at 5 K for both the compounds.

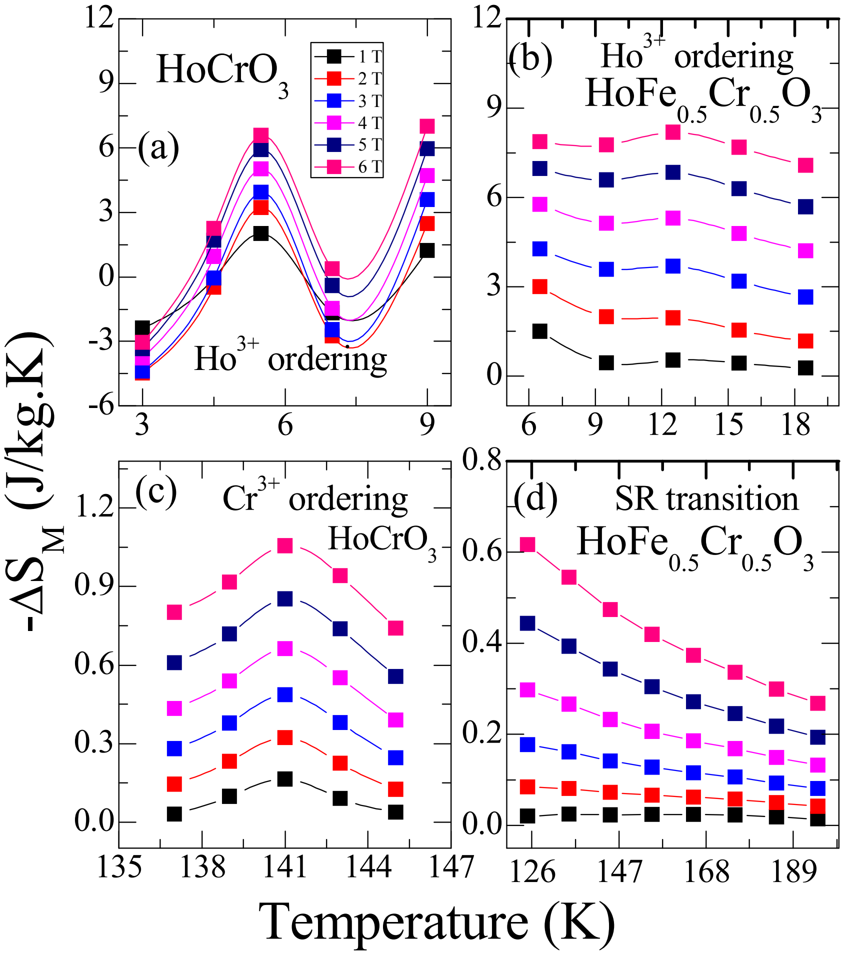

Fig. 5. (a – d) Temperature dependence of the magnetic entropy $-\Delta S_M$ obtained from magnetization M *vs.* H data for $HoCrO_3$ and $HoCr_{0.5}Fe_{0.5}O_3$ compounds.

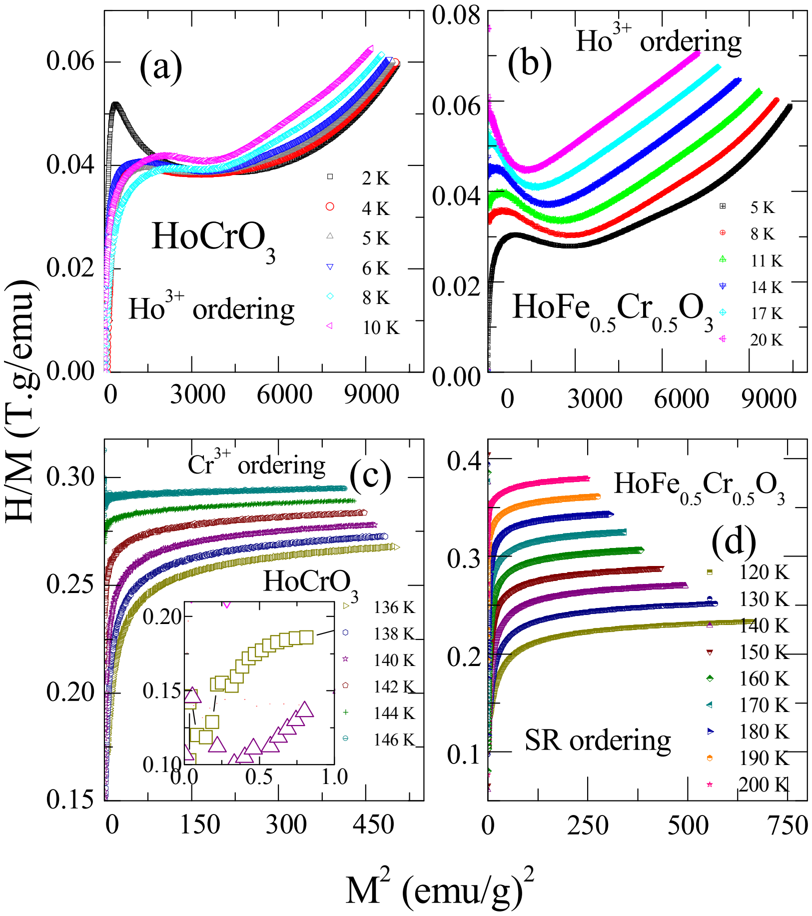

Fig. 6: Arrott plots corresponding to magnetization isotherms for HoCrO$_3$ and HoCr$_{0.5}$Fe$_{0.5}$O$_3$ compounds.