Unconventional electronic and magnetic properties of 3d-4f double perovskite material

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Double perovskite based magnets wherein frustration and competition between emergent degrees of freedom are at play can lead to novel electronic and magnetic phenomena. Herein, we report the structural and magnetic properties of an ordered double perovskite material Ho2CoMnO6. In the double perovskite with general class A2BB′O6, the octahedral B and B′-site has a distinct crystallographic site. The Rietveld refinement of XRD data reveal that Ho2CoMnO6 crystallizes in the monoclinic P21/n space group. The X-ray photoelectron spectroscopy confirms the charge state of cations present in this material. The temperature dependence of magnetization and specific heat stabilization of magnetic ordering and charge states is further analyzed through electronic structure calculations. The latter also infers the compound to be a narrow band gap insulator with the gap arising between the lower and upper Hubbard Co-d subbands. Our results demonstrate that anti-site disorder and complex 3d-4f exchange interactions in the spin-lattice account for the unconventional electronic and magnetic properties in this promising double perovskite material.

INTRODUCTION

Spin correlations and interplay between competing degrees of freedom can lead to exotic physical phenomena in novel magnetic materials [1–6]. The transition metal and rare-earth based magnetic materials are promising candidates to harbor exciting electronic and magnetic properties that could serve as a test bed for establishing theoretical conjectures. In addition, it offers a viable ground to realize the rich potentials of novel magnets with the aim to tailor the surprising properties of these materials to address the pressing technological challenges in material science in energy harnessing, spintronics, quantum computing, and high density data storage devices [7–20]. In this regard, the rare-earth double perovskite (DP) oxides [21], A2BB′O6 (A = Rare earth ions or alkaline ions; B/B′ = transition metal ions) [22, 23] with rock salt type ordered structure offer an attracting venue in view of their multi-functional properties owing to the co-existence of magneto-electric coupling, magneto-dielectric effects, tunable pyroelectric, ferroelectric properties, multiferroicity, spin polarized conductivity, and superconductivity [24–26]. Also, DP offers a highly flexible structure wherein external perturbations such as chemical pressure, electric and magnetic fields can tune the underlying magnetism and spin dynamics. Furthermore, DPs wherein spin correlation, frustration and spin-orbit coupling are at play, offer a rich platform to realize exotic quantum states such as spin liquid, unconventional magnetic ordering, spin-orbit driven phenomena, and topological states with emergent excitations [27–33]. DPs are excellent candidates for potential applications such as, magnetic memory, sensors and solar cell to name a few. For an example, the multiferroic material HoMnO3 with a ferroelectric transition and large polarization of 56 mC/m2 shows large mag-
netocaloric effects [34, 35]. Therefore, the double perovskite R$_2$CoMnO$_6$ (R = rare earth) offer an ideal venue for hosting interesting electronic and magnetic properties, which depend on the size of R ions [36] for example, the spin-phonon coupling decreases upon replacing La with smaller rare-earth ions. Recent theoretical prediction of multiferroicity in Y$_2$NiMnO$_6$ [37] also indicates the significance of the type of rare-earth ion in realizing myriads of complex magnetic ordering phenomena in these double perovskites. The DP materials generally crystallize into two structures either ordered or disordered based upon the B/B’-site ordering. The ordered structure prefers to be in monoclinic space group with P21/n symmetry and the disordered one crystallizes in orthorhombic space group with Pnma symmetry. The ordered DPs A$_2$B’B’O$_6$, generally host ferromagnetic (FM) interaction due to superexchange interactions. But the co-existence of B$^{3+}$/B’$^{3+}$ ions as a disorder, introduces competing antiferromagnetic (AFM) interactions in the spin-lattice [38, 39]. The magnetic properties of double perovskites are well interpreted following the cationic ordering and Goodenough-Kanamori (GK) rule [40, 41], which suggests ferromagnetic ground state in these systems. Whereas the deviations from the GK rule due to cationic disorder leads to the departure from the ferromagnetism also. The DPs with heavier rare-earth elements show unconventional properties such as magnetization reversal and inverse exchange bias in Er$_2$CoMnO$_6$ [42], negative magneto-capacitance in Yb$_2$CoMnO$_6$ [43], anisotropy magnetic properties and giant magnetocaloric effect in Tb$_2$CoMnO$_6$ [35], Y$_2$CoMnO$_6$ shows multiferroic behavior owing to the presence of competing interactions [44] while the steps in magnetic hysteresis loop is ascribed to anti-site disorder in this double perovskite [45, 46]. In a similar vein, La$_2$CoMnO$_6$ hosts FM ordering and cluster glass phenomena driven by anti-site disorder [47]. The unconventional ground states of such DPs are consequence of the B-site cationic ordering and their nonvalence states. Most of the Co/Ni/Mn-based ordered DPs exhibit ferromagnetic (FM) insulating ground state, which is best modeled by the superexchange interactions among B$^{2+}$/B’$^{4+}$ ions via adjacent oxygen ions. The complex interplay between 3d-4f interactions in double perovskites of type R$_2$CoMnO$_6$ can lead to rich and diverse physical phenomena such as spin-glass, multiferroicity, Griffiths phase, magnetoresistance, exchange bias and magnetocaloric effect. In these materials, perturbations such as the choice of cations play a crucial role in modifying the underlying electronic and magnetic properties [33]. Double perovskite magnetic materials without disorder are ideal to test theoretical conjectures, however, the experimental realization of such a structure poses a great challenge owing to anti-site disorder and defects. This invoke to look for new double perovskites with suitable combination of rare-earth and transition metal ions wherein the disorder could be controlled precisely, offer a viable ground to realize exotic electronic and magnetic phenomena. In this context, the recently synthesized promising double perovskite Ho$_2$CoMnO$_6$ offers a new ground to explore complex magnetic ordering and electronic properties. In view of the smaller atomic radius of Ho$^{3+}$, it is predicted to impact the FM ordering greatly compared to other DPs. In Ho$_2$CoMnO$_6$, competition between Co$^{2+}$-O-Mn$^{4+}$ FM superexchange interaction and Co$^{2+}$-O-Co$^{2+}$ or Mn$^{4+}$-O-Mn$^{4+}$ AFM interaction, which are further modulated by the active Ho$^{3+}$ spins, could lead to unconventional ground state properties. A complete picture concerning the exact charge state, electronic structure, exchange interactions, disorder and spin-phonon coupling is essential to understand the underlying mechanism that drive non-trivial magnetism in this novel class of double perovskite material.

In this work, we have investigated the structural, magnetic and electronic properties of the polycrystalline samples of a partially site-ordered double perovskite Ho$_2$CoMnO$_6$ (henceforth HCMO). The ordered DPs of type A$_2$B’B’O$_6$ have two sub-lattices consisting of BO$_6$ and B’O$_6$ octahedra, which form a rock-salt type ordering. The disorders in the form of anti-site disorder (ASD), i.e. site exchange between B/B’ ions, are unavoidable that might induce competing exchange interactions in these materials. HCMO crystallizes in a monoclinic structure with the space group symmetry P21/n, which is typically found in most of the cation-ordered double perovskite systems. Our X-ray Photoelectron Spectroscopy (XPS) results reveal the exact charge state of cations in HCMO. It shows a long-range ferromagnetic ordering around 79 K owing to the Co$^{3+}$-O$^2-$ -Mn$^{4+}$ superexchange interactions. The dc susceptibility, ac magnetization and specific heat results are consistent with such a phase transition. We also observed the existence of Griffiths-like phase above the ferromagnetic transition temperature ($T_c \approx 79$ K), which is reflected by a prominent down-turn behavior in the temperature dependent inverse susceptibility curves well-above $T_c$. Moreover, the system re-entered in a glassy state (known as the re-entrant spin-glass state) below $\approx 37$ K, which is manifested as the frequency dependent broad peak in the ac susceptibility data. The observations of the Griffiths-like phase and re-entrant glassy state could be attributed to the presence of the inherent anti-site disorder and competing interactions in HCMO. Interestingly, HCMO shows large magnetocaloric effect (the corresponding isothermal magnetic entropy change is found to be $\Delta S_m \approx 13.5$ J/kg-K at 15 K) much below the ferromagnetic transition temperature. Raman spectroscopy results point toward the presence of spin-phonon coupling in this novel double perovskite material. The density functional theory calculations are performed on HCMO to find the plausible ground state magnetic ordering and charge states. A detailed electronic structure analysis establishes the experimentally observed charge states. The
ground state magnetic ordering is found to be AFM2 where the Ho spins form G-type antiferromagnetic arrangement while Co and Mn spin sublattices forms ferromagnetic ordering. No particular ordering between Ho and Co/Mn spins is observed.

**EXPERIMENTAL DETAILS**

The polycrystalline sample of Ho$_2$CoMnO$_6$ was synthesized by conventional solid-state reaction route using highly pure initial ingredients. At first, the stoichiometric amount of Ho$_2$O$_3$ (99.999%, REacton), CoO (99.9995%, Alfa-Aesar) and MnO$_2$ (99.9%, Alfa-Aesar) was mixed well. Then this mixture was pressed into a pellet and placed in an alumina crucible and heated at 800°C for 24 hours, 900°C for 48 hours, 1000°C for 48 hours, and finally 1250°C for 60 hours respectively in a box furnace with several intermediate re-grinding and pelletization.

Powder X-ray diffraction (XRD) measurements were performed at room temperature with Cu-K$_\alpha$ radiation ($\lambda = 1.54182$ Å) on a Rigaku SmartLab diffractometer and was analyzed by Rietveld method [48] using FULLPROF software [49]. Magnetization measurements were carried out in the temperature range $5.0 \leq T \leq 370$ K and in the field range $0 \leq H \leq 70$ kOe using a Quantum Design, SQUID VSM. For the low-field magnetization measurements, the reset magnet mode option of the SQUID VSM was used to remove any stray or remanent field. Specific heat measurements were performed in the temperature range $1.9 \leq T \leq 200$ K in zero field using the heat capacity option of a Quantum Design, PPMS. X-ray photoelectron spectroscopy (XPS) experiments were performed by using a scanning X-ray microprobe system equipped with a monochromatic aluminum K$_\alpha$ X-ray source (1486.6 eV) and a multi-channeltron hemispherical electron energy analyzer of PHI 5000 VERSAPROBE II, Physical Electronics system. The survey scan, as well as core-level spectra, were measured at an emission angle of 45° with a pass energy of 50 eV and 11.750 eV, respectively. The binding energy calibration was done by using C 1s located at 284.6 eV. All the photoelectron measurements were performed inside the analysis chamber with an average base vacuum of $7.0 \times 10^{-10}$ mbar. A charge neutralizer was used in order to compensate for the surface charging of the samples. The total energy resolution, estimated from the width of the Fermi edge taken from a cleaned polycrystalline gold sample, was about 400 meV for monochromatic aluminum K$_\alpha$ line with a pass energy 11.750 eV for core level. Ar-ion sputtering has been performed at 3keV energy for 30 minutes with a raster area of 4 mm × 4 mm. The electronic structure was investigated using XPS Valence Band spectra. Raman spectra were recorded using a Jobin Yvon Horiba LABRAM-HR 800, micro-Raman spectrometer equipped with a 473 nm excitation diode laser, 1800 lines mm$^{-1}$ grating, an edge filter for Rayleigh line rejection and a charge coupled device (CCD) detector giving a spectral resolution of $\sim 1$ cm$^{-1}$ in back-scattering mode. The laser was focused to a spot size of $\sim 1$ µm onto the flat surface of the sample using a 50× objective lens. The low temperature Raman measurements were performed employing Janis make liquid He flow type cryostat with a temperature stability of $\pm 0.5$ K.

![Figure 1](image)

**RESULTS AND DISCUSSION**

**A. XRD and Crystal structure**

We have analysed the crystal structure of HCMO using Rietveld refinement method with the monoclinic space group $P2_1/n$ (space group no.: 14) and obtained the goodness of fit parameter $\chi^2 = 1.24$. The refined lattice parameters obtained from the analysis, $a = 5.2326$ Å, $b = 5.5869$ Å and $c = 7.4737$Å and $\beta = 90.12^\circ$ are in agreement with the previous reports [50, 51].
Rietveld refinement results are presented in Fig. 1(c) and the resulting atomic coordinates and goodness of Rietveld refinement are summarized in Table I. Although the crystal structure is derived from the $A_2BB'O_6$, in the present case the symmetry is lower and the Co$^{2+}$ and Mn$^{4+}$ cations are distributed with a 1:1 ratio and have distinct B-site in this ordered double perovskite material. Fig. 1(a) shows the double perovskite crystal structure of Ho$_2$CoMnO$_6$ with MnO$_6$ and CoO$_6$ octahedra within a unit cell. Fig. 1(b) shows that the Co$^{2+}$ and Mn$^{4+}$ ions along $a$-axis are constituting a uniform spin-chain among themselves with a minimum bond distance 5.233Å. Whereas, the Mn-Co bond along $c$-axis is forming a uniform spin-chain with a bond distance of 3.737Å and most likely the dominant interaction pathway in HCMO. To confirm this scenario, we also calculated the electronic structure using Density Functional Theory (DFT).

Table I: The crystallographic data of Ho$_2$CoMnO$_6$ obtained from Rietveld refinement. The goodness of the Rietveld refinement as defined by the following parameters are $R_p$: 2.30%; $R_{wp}$: 2.99%; $R_{exp}$: 2.69%; $\chi^2$: 1.24

| Atom | Wyckoff position | x    | y    | z    | Occupancy |
|------|------------------|------|------|------|-----------|
| Ho   | 4e               | 0.0203 | 0.0715 | 0.2508 | 1.000     |
| Co   | 2d               | 0.0000 | 0.5000 | 0.0000 | 1.000     |
| Mn   | 2c               | 0.5000 | 0.0000 | 0.0000 | 1.000     |
| O1   | 4e               | 0.3180 | 0.3120 | 0.0550 | 1.000     |
| O2   | 4e               | 0.3000 | 0.2880 | 0.4500 | 1.000     |
| O3   | 4e               | 0.6022 | 0.9614 | 0.2380 | 1.000     |

B. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a powerful technique to probe the valence states and ligand coordination of the constituting elements in any material. In the XPS study of a material having open-shell ions, a core electron vacancy along with the open-shell gets coupled to produce the multiple structure. In addition to the main photoelectron peak features, the associated satellite peaks, chemical shifts and their relative intensities are also useful to estimate the oxidation states and ligand coordinations [52, 53]. A prior knowledge of the electronic structure of a material is essential to explain many of its physical properties. Hence, to understand the electronic structure of the present material HCMO, we have studied its XPS spectra. All the peak positions have been assigned from the National Institute of Standard Technology (NIST) database [54]. The deconvolution analysis of the core level XPS peaks of the relevant ions have been carried out using the combination of Lorentzian and Gaussian distribution functions.

The survey scan XPS spectra recorded at 300 K have been shown in Fig. 2(a), which confirms the presence of the elements Ho, Co, Mn, O and C in the system. No other extrinsic elements have been detected, thus confirming the sample purity. The observation of the C 1s peak is common and it is attributed to the extrinsic molecules absorbed from the air at the surface.

The core level Co 2p XPS spectrum can provide many important information viz., spin state, nominal valence state etc. [52, 53, 55, 56]. Its shake-up satellite peaks are produced by poorly screened states whereas the main peaks are originated from the well-screened states. The satellite peaks in particular are very sensitive to the valence states of the cobalt ions. Fig. 2(b) demonstrates the core level Co 2p XPS spectrum. It comprises of two main spin-orbit coupling peaks i.e. Co 2p$_{3/2}$ and Co 2p$_{1/2}$ positioned at the 779.43 eV and 795.1 eV respectively. The two broad peaks situated above the main peaks are assigned as the charge transfer satellite peaks. Eventually, such prominent satellite peaks above the main peaks are typically observed in Co 2p XPS spectra of the systems containing divalent Co$^{2+}$ ions while such satellite peaks are merely absent or very weak for systems having trivalent Co$^{3+}$ ions [52, 53, 55]. Hence, the observation of the satellite peaks in the present Co 2p XPS spectrum indicates the presence of Co$^{2+}$ ions in HCMO. It is worth to mention here that the asymmetry and broadening of the observed peaks are indicative of the presence of mixed valence states of the Co ions [53, 55, 56]. The peak positions and line-shape of the observed Co 2p XPS spectrum
is similar to the earlier reports showing mixed valence Co ions [53]. Again, the doublet separation between the spin-orbit coupling peaks is typically found to be 15.9 eV for CoO and 15.3 eV for Co$_2$O$_3$. For the present system, the Co 2p doublet separation is observed to be 15.6 eV which suggests for the existence of both Co$^{2+}$/Co$^{3+}$ ions. The Co 2p XPS spectrum has been deconvoluted to estimate the concentrations of the different Co ions (Co$^{2+}$/Co$^{3+}$) as shown in the Fig. 2(b). Although Co$^{2+}$ ions are found to be predominantly present in the system but the presence of Co$^{3+}$ ions is also unavoidable. This in turn gives rise to competing exchange interactions in HCMO.

The core level Mn 2p XPS spectrum of the present system is depicted in Fig. 2(c). This spectrum is broadly divided into two spin-orbit coupling peaks i.e. Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$, which are situated at 641.7 eV and 653.4 eV respectively. The values of the Mn 2p$_{3/2}$ peak positions in compounds Mn$_2$O$_3$ and MnO are reported to be 641.3 eV and 642.2 eV, respectively [54]. Hence, the observed value of Mn 2p$_{3/2}$ peak position in HCMO suggests the existence of mixed valence states of Mn ions (Mn$^{3+}$/Mn$^{4+}$). For the present system, the spin-orbit splitting energy ($\Delta E$) in Mn 2p XPS spectrum is found to be $\approx 11.7$ eV. On the other hand, $\Delta E$ for MnO$_2$ and Mn$_2$O$_3$ are reported to be 11.8 eV and 11.6 eV, respectively. Thus, the observed intermediate value of $\Delta E \approx 11.7$ eV can be presumably attributed to the mixed oxidation states of Mn ions (Mn$^{3+}$/Mn$^{4+}$) [53]. The deconvolution analysis of the Mn 2p XPS peaks and the concentrations of the relevant Mn$^{3+}$/Mn$^{4+}$ ions have been depicted in Fig. 2(c). The O 1s core level XPS spectrum is illustrated in the inset of Fig. 2(d), which comprises of two peaks. The most intense peak at 529.1 eV can be ascribed to the O$^{2-}$ ions while the smaller broad peak at 531.3 eV is known to be associated with the less electron rich oxygen species (viz., O$_2^-$, O$_3^-$ or O$^-$) owing to the adsorption of oxygen at the surface [52, 53].

The valence band (VB) XPS spectrum is illustrated in Fig. 2(d). It is clear from Fig. 2(d) that no electronic states are available near the Fermi level ($E_F$). This is a clear indication of the insulating nature of HCMO. The observed VB spectrum is made up of four peaks marked as A, B, C and D. The first spectral feature A lying immediately below Fermi energy (0-1 eV) can be attributed to the extended hybridized states of Co 3d ($e_g$) and Mn 3d ($e_g$) [52, 53]. The next two features marked as B and C can be primarily attributed to the hybridization of states of Mn 3d($t_{2g}$), Co 3d($e_g$) and Ho 4f along with O 2p states [52, 53]. The last peak in VB spectrum denoted as D is seemingly related to the hybridization of the extended Mn 3d($e_g$), Co 3d($e_g$) with O 2p states while some other minor contributions owing to the O 2p-Co/Mn 4sp and O 2p-Ho 5sd oxygen bonding states [52, 53].

C. Magnetization and specific heat

Figure 3: (a) The temperature dependence of inverse magnetic susceptibility in 100 Oe field while its inset shows a closer view of the temperature dependence of magnetization recorded in ZFC-FC modes in 100 Oe, which shows a bifurcation at $T = 79$ K. (b) The down-turn behavior of $1/\chi$ in different fields indicates the onset of Griffiths phase below $T_G = 90$ K. Inset displays log-log plot of the power law analysis of magnetic susceptibility in 100 Oe. (c) Temperature dependence of specific heat of HCMO in zero field. A clear peak around 73 K is due to the long range ordering.

In HCMO, one expects competing exchange interactions due to the presence three different magnetic ions with different energy scale of interactions in the spin-lattice with inevitable disorder. The presence of competing interactions may drive the system towards an unconventional magnetic state. In order to probe the ground
state magnetic properties of this material, we measured the dc magnetization $M(T)$ as a function of temperature on a hard pellet of HCMO in zero field cooled (ZFC) and field cooled (FC) mode in several magnetic fields ($H$) using a Quantum Design, SVSM. The magnetic susceptibility data show a paramagnetic behavior at high temperature and an anomaly around ~ 79 K suggesting the presence of a magnetic phase transition. The susceptibility data were fitted with the Curie-Weiss (CW) law given by Eq. \( \chi^{-1} = \left( \chi_0 + \frac{C_{RE}}{T-\theta_{RE}} + \frac{C_{TM}}{T-\theta_{TM}} \right)^{-1} \), where \( \chi_0 \), \( C_{RE}/\theta_{RE} \) and \( \theta_{TM} \) are temperature independent susceptibility (arising from the diamagnetic core and paramagnetic Van-Vleck contributions), Curie constant and the Curie-Weiss temperatures for rare-earth and paramagnetic Van-Vleck contributions, respectively. In HCMO, the magnetic properties are governed by both rare-earth \( \text{Ho}^{3+} \) and transition metal ions, respectively. In HCMO, the magnetic properties are governed by both rare-earth \( \text{Ho}^{3+} \) ions and transition metal ions (Co\( ^{2+} \) and Mn\( ^{4+} \)). The main features of our observations from the magnetization measurement are described below. There is a long range FM ordering around 79 K due to the superexchange interaction between Co\( ^{2+} \) and Mn\( ^{4+} \) magnetic moments. From the CW fit, we obtained \( \theta_{RE} = -4.2\, K \), \( C_{RE} = 30.307\, K\, cm^3/mol \) and \( C_{TM} = 3.695\, K\, cm^3/mol \). The negative value of \( \theta_{TM} \) possible indicating the presence of a weak antiferromagnetic interaction between Ho\( ^{3+} \) moments and the sub-lattice consisting of transition metal ions Co\( ^{2+}/\text{Mn}^{4+} \) or associated with the crystal electric field excitations of \( ^5I_8 \) multiplet of the Ho\( ^{3+} \) ion. Ho\( ^{3+} \) moments may undergo a phase transition at lower temperature below 2 K. While the positive value of \( \theta_{TM} \) indicates a ferromagnetic interaction between Co\( ^{2+} \) and Mn\( ^{4+} \) in the host spin-lattice. The presence of AFM and FM interactions suggest a frustrated spin-lattice in this material. The obtained effective magnetic moment \( \sqrt{3C\mu_B} \) for transition metal cations is 5.44 \( \mu_B \). This value of \( \mu_{\text{eff}} \) is close to that of the theoretically expected one \( \mu_{\text{theo}} = \sqrt{\mu_{\text{eff}}(\text{Co}^{2+}) + \mu_{\text{eff}}(\text{Mn}^{4+})} \) for the Co\( ^{2+} \) (3d\( ^7 \), \( S = 3/2 \)) and Mn\( ^{4+} \) (3d\( ^3 \), \( S = 3/2 \)) sublattice system \( \mu_{\text{eff}}(\text{Co}^{2+})/\mu_B = 5.47 \). The observed power law behavior \( \chi(T)^{-1} \propto (T - T_C^R)^{(1-\lambda)} \), where \( T_C^R \) is the random critical temperature and \( \lambda \) is the magnetic susceptibility exponent, which lies in the range \( 0 < \lambda < 1 \). Following the procedure reported in literature \([59, 67, 68]\), we first estimated the value of \( T_C^R = 30 \, K \) in the paramagnetic region above \( T_C \). The blue solid lines, in the inset of Fig. 3 (b), represent the fit to the experimental data following that power law. Using this value of \( T_C^R \), fitting was performed in the GP regime to obtain a value \( \lambda_{\text{GP}} = 0.93 \). In the high temperature regime, we obtained \( \lambda_{\text{TM}} = 0.06 \), signifying that the system has entered a completely paramagnetic phase. The ZFC-FC bifurcation below \( T_c = 79 \, K \) in an applied field of 100 Oe as shown in the inset of Fig. 3(a), indicates the presence of a glass-spin \([69]\) state in HCMO. The FC magnetization increases upon lowering the temperature below 79 K and tends to saturate at low temperature indicating the polarization of \( 4f \) (Ho\( ^{3+} \)) moments in an applied magnetic field. In order to gain further insights into the magnetic ordering and the low-energy excitations in HCMO, we measured the specific heat of HCMO at constant pressure \( C_p(T) \) in the \( T- \) range \( 1.9 \leq T \leq 200 \) K in zero field. The sharp anomaly around 73 K in the \( C_p(T) \) vs \( T \) data supports the presence of a long-range FM ordering observed in the dc magnetization data. The enhancement of specific heat below 5 K (see Fig. 3(c)) suggests the onset of a phase transition at much lower temperature owing to Ho\( ^{3+} \) moments that is ascribed to the presence of a weak exchange interaction between 4f moments.

### D. AC Susceptibility

The splitting of ZFC and FC curves below ~ 79 K suggests that a spin-freezing mechanism is at play which could be associated with anti-site disorder and frustration in HCMO. AC susceptibility is a very sensitive probe to track spin freezing mechanism and shed insights into the characteristics of magnetization dynamics in the ordered state of the frustrated magnets. Generally, the spin dynamics slow down below the freezing temperature \( T_f \) owing to the cluster formation of spin domains. In order to confirm the dc susceptibility results and understand glassy behavior of this frustrated magnet, we performed AC susceptibility measurements at several frequencies. Fig. 4(a) shows the imaginary part of the AC susceptibility \( \chi''(T) \) which shows a sharp peak at the FM ordering temperature \( T_c = 79 \, K \) and a broad maximum around \( T_f = 30 \, K \). The maximum at \( T_f = 30 \, K \) shifts towards higher temperature upon increasing the frequency indicating a glassy spin dynamics leading to a slow relaxation of magnetization. To investigate the variation of \( T_f \) with frequency, we have scaled it following the scaling law relevant for critical dynamics \([70, 71]\) given by
Here, $T_c$ is the freezing temperature where $f$ stands for the corresponding frequency for which $\chi''(T)$ attains a maximum, $T_0$ is the equivalent spin-glass freezing temperature when $f\rightarrow 0$ Hz and $H_{DC}\rightarrow 0$ Oe, and $\tau_0$ is related to the characteristic spin flipping time ($f_0 = \frac{1}{\tau_0}$); $\nu$ is the dynamical critical exponent. Fig. 4(b) shows the critical dynamic scaling fit. The best fitting yields $\tau_0 = 10^{-8}$ s, $T_0 = (29.3 \pm 0.2)$ K, and $\nu = (5.29 \pm 0.04)$, which is in reasonable agreement with that expected for a cluster spin-glass state ($4 < \nu < 12$). For a canonical spin-glass system, $\tau_0$ lies between $10^{-12}$ s and $10^{-13}$ s, which is smaller than the observed value of $10^{-8}$ s by few orders. The longer relaxation time $\tau_0$ indicates that the spin-freezing characteristics are of cluster-glass type rather than atomic.

To explore further the characteristics of inter-cluster interactions, well-known Vogel-Fulcher (VF) model (see Eq.2) was employed in fitting the relaxation time $\tau$ vs. $T$ curve. Fig. 4(c) shows the corresponding VF model fit.

$$\tau = \tau_0 \exp \left( \frac{E_A}{k_B(T - T_0)} \right)$$

where $T_0$ represents inter-cluster interaction strength and $E_A$ is the activation energy required to overcome the barrier of the metastability of the spin-glass (SG) state. The best fitting yielded for $\tau_0 = 10^{-7}$ s, $T_0 = (26.8 \pm 0.1)$ K, and $E_A/k_B = (53.1 \pm 0.4)$ K. The large value of $\tau_0$ is expected from interacting magnetic spin clusters. All the above features point towards the stabilization of a re-entrant spin-glass (RSG) ground state below $T_1 = 30$ K.

We also measured the isotherm magnetization at several temperatures and Fig. 5(a) shows the corresponding plot. As depicted in Fig. 5(a), the magnetization increases upon increasing the external magnetic field and does not saturate up to 7 T. Using the magnetic isotherm data around $T_c$, we have plotted the modified Arrott plot [72, 73] considering mean field model (where the critical exponents are $\beta = 0.5$ and $\gamma = 1$), which corroborates the presence of ferromagnetic order in this material. Fig. 5(b) represents the corresponding Arrott plot with a set of parallel lines near $T_c = 79$ K in high field. The nonlinear behavior of Arrott curves suggests the presence of inhomogeneous magnetism possibly related to the fact that the unavoidable disorder strongly affects the underlying spin dynamics of HCMO [74].

External perturbations such as magnetic field play a crucial role in modifying the ground state properties and internal energy of double perovskite based magnetic materials under study [75]. The temperature variation in magnetic materials leading to change in entropy due to an adiabatic change of external magnetic field is known as magnetocaloric effect relevant for magnetic refrigeration [76, 77]. Geometric frustration can play an important role in the enhancement of the change in magnetic entropy in the presence of a magnetic field, which in turn

![Figure 4](image-url)
can lead to large magnetocaloric effect in double perovskites [78]. In order to extract the temperature dependence of the change in magnetic entropy in HCMO, we have measured magnetization isotherms at several temperatures. For the characterization of the magnetocaloric response of a material, three main parameters can be studied: the isothermal magnetic entropy change, $\Delta S_m$; the adiabatic temperature change, $\Delta T_{ad}$; and the refrigerant capacity. Generally, $\Delta S_m$ can be calculated indirectly from the experimental magnetization curves using Maxwell’s relation.

$$\Delta S_m = \mu_0 \int_0^H \left( \frac{\delta M}{\delta T} \right)_H \delta H$$  \hspace{1cm} (3)

The resulting temperature dependence of the magnetic entropy change $\Delta S_m$ in different applied magnetic fields are shown in Fig. 5(c). In ferromagnetic systems, the magnetic field align the moments along the field direction by overcoming the thermal fluctuations, leading to a decrease of the magnetic entropy change, $\Delta S_m < 0$. Whereas, the external magnetic field plays a vital role in rotating the spins against their preferential directions yielding an increase of magnetic entropy, $\Delta S_m > 0$ in antiferromagnetic materials [79, 80]. As depicted in Fig. 5(c), a peak in $-\Delta S_m$ around $T_C$ corroborates a phase transition from a paramagnetic state to a ferromagnetically ordered state. The value of $\Delta S_m$ increases upon lowering the temperature and attains a maximum value $\sim 13.5$ J/kg-K at low temperature in a magnetic field of 7 T. The enhancement of $-\Delta S_m$ at low temperature indicates the onset of a magnetic ordering most likely due to an weak exchange interaction between $\text{Ho}^{3+}$ moments. As presented in Fig. 5(c), HCMO shows large magnetocaloric effect (the corresponding isothermal magnetic entropy change is found to be $\sim 13.5$ J/kg-K at around 15 K) much below the ferromagnetic transition temperature [51]. The obtained large value of magnetic entropy change owing to adiabatic magnetization is quite unusual in double perovskites, which suggests that HCMO is a promising candidate for magnetic refrigeration technology. Furthermore, the variation of the maximum value of entropy change i.e. ($\Delta S_m|_{\text{max}}$) with the magnetic field obeys a power law ($\propto H^n$) reflecting a second order phase transition, where $n$ is a temperature dependent parameter [81]. The power law fit as shown in the inset of Fig. 5(c) yields a magnetic-ordering parameter $n = 0.881$, which is close to that of the value obtained in another double perovskite Dy$_2$CoMnO$_6$ [82]. The value of the exponent $n$ which is related to the the critical exponents ($\beta$ and $\gamma$) near the $T_C$ and it is defined as $n = 1 + \frac{\beta}{(\gamma+\beta)}$ [83]. The obtained value of the parameter $n$ indicates that the magnetic order in HCMO might be best described by modified Arrott plots viz. - 3D-Heisenberg model, the 3D-Ising model, or tri-critical model than the mean-field framework, which invokes further studies.

Figure 5: (a) Magnetization isotherms at several temperatures. (b) The modified Arrott plot of isotherm magnetization following mean field approximation. (c) The magnetic entropy change $\Delta S_m$ as a function of temperature showing a peak at FM ordering temperature with $T_c = 79$ K. Inset shows the maximum value of magnetic entropy change $|\Delta S_m|_{\text{max}}$ vs. $H$ with a power law fit represented by a solid red line.

E. Raman Spectra

The complex interplay between emergent degrees of freedom may harbor interesting magnetic properties in double perovskites. Raman spectroscopy is an ideal probe to track exotic collective excitations in correlated quantum magnets and material that harbor competing magnetic ordering phenomena. This technique has been successful in revealing interesting insights into the structural phase transition, phonon characteristics and spin–phonon cou-
ppling of many perovskite based oxide materials [84–86]. In order to understand the coupling between spin and phonon in HCMO, we measured Raman spectra down to 10 K. The Raman spectra are presented in Fig. 6(a) which shows the most prominent Raman band at 635 cm\(^{-1}\) and another less intense band at 515 cm\(^{-1}\). As the less intense Raman band at 515 cm\(^{-1}\) is not shifting that much with respect to temperature, we focused our data at 635 cm\(^{-1}\) band. We have fitted each Raman spectra by a Lorentzian peak profile (shown for a few selected temperatures) to determine the exact peak position and the full width at half maxima as well. Fig. 6 (b) shows the plot of the temperature dependence of Raman shift. The Raman shift increases upon decreasing the temperature and this shift suddenly drops below 90 K, which indicates the dominant role of ferromagnetic ordering on phonon frequencies in this material. Such temperature dependence of Raman shift could be associated with (i) anharmonicity, as proposed by Balkanski [87] in the absence of structural phase transitions, and (ii) spin–phonon coupling. The anharmonicity of phonon modes can be represented by the following relation

\[ \omega_{\text{anh}}(T) = \omega_0 - C\frac{1}{2}(e^{\frac{\hbar \omega}{k_B T}} - 1) \]  

(4)

\[ \Delta \omega(T) = \omega_{\text{anh}}(T) - \omega_0 \propto \frac{M^2(T)}{M_{\text{max}}^2} \]  

(5)

where, \( \omega_0 \) and \( C \) are adjustable parameters. At high temperature, the Raman shift of the most intense Raman band at 635 cm\(^{-1}\) follows the anharmonic behavior as shown in Fig. 6(b). A noticeable deviation of the Raman shift in the close vicinity of Griffiths temperature \( T_G = 90 \) K suggests the softening of phonon modes associated with spin-phonon interactions possibly due to stretching of \((\text{Co/Mn})\text{O}_6\) octahedra in HCMO [86, 88]. Such behavior across \( T_G \) is known to occur due to the spin-phonon coupling ascribed to the role of lattice vibrations in tuning the exchange integral in a magnetic material. The onset of softening of phonon modes around the Griffiths temperature indicates the existence of short range ordering way up to \( T_G \). It is worth to mentioning that such magnetic-order-induced renormalization of phonon frequencies [84, 85] has been observed in several double perovskites such as \( \text{La}_2\text{CoMnO}_6 \) [86] \( \text{Ba}_2\text{NiMnO}_6 \) [89]. Understanding the role of competing magnetic order and spin correlations in tuning the phonon frequencies in double perovskite is an interesting setting in the context of novel material design. As per the phenomenological model employed in Refs. [84, 85], the phonon renormalization is proportional to the spin-spin correlation of the localized nearest neighbor spins. In the mean field approximation, the spin-spin correlation between \( \text{Co}^{2+} \) and \( \text{Mn}^{4+} \) spins is proportional to \( M^2(T)/M_{\text{max}}^2 \) in the present double perovskite, where \( M(T) \) represents the average magnetization per magnetic ion at a temperature \( T \). Below \( T_G = 90 \) K, \( \Delta \omega(T) \) closely follows relation 5 which is shown within the inset of Fig. 6(b). Our Raman results rule out the presence of a structural phase transition in HCMO in the temperature range of investigation. The existence of spin-phonon coupling suggests an innate connection between magnetism and lattice in this 3d-4f double perovskite.

F. Electronic and Magnetic structure of HCMO from Density Functional Theory (DFT) calculations

In order to gain further insights into the experimentally observed charge state and magnetic configurations,
Table II: The relative energy differences ($E_{\text{rel}}$) in meV/f.u. with respect to the most stable magnetic configuration and corresponding local spin magnetic moments at Ho, Co and Mn in $\mu_B$. The unbracketed and bracketed terms in $E_{\text{rel}}$ represent the relative energies without and with considering $U_{\text{eff}}$ on Mn.

| Config | GGA | $U = 0$ | $U_{\text{eff}} = 2\text{eV}$ | $U_{\text{eff}} = 4\text{eV}$ | $U_{\text{eff}} = 6\text{eV}$ |
|--------|-----|---------|------------------|------------------|------------------|
|        |     | Ho  | Co  | Mn  | Ho  | Co  | Mn  | Ho  | Co  | Mn  | Ho  | Co  | Mn  | Ho  | Co  | Mn  |
| FM     | 3.81| 2.30| 2.90| 18.15(8)| 3.92| 2.45| 2.90| 16.27(6.25)| 4   | 2.57| 2.88| 13.7(4.37)| 4.15| 2.78| 2.81|
| AFM1   | 72.73| 3.80| 2.20| 2.94| 39.84(25.55)| 3.90| 2.50| 2.80| 35.42(15.27)| 3.98| 2.70| 2.7| 33.19(7.52)| 4.05| 2.85| 2.83|
| AFM2   | 72.87| 3.82| 2.22| 2.92| 0 | 3.92| 2.45| 2.92| 0 | 4 | 2.58| 2.880 | 2.82|
| AFM3   | 83.56| 3.8 | 2.35| 2.94| 14.43(10.58)| 3.92| 2.43| 2.91| 21.08(13.55)| 4 | 2.6 | 2.88 | 26.28(15.81)| 4.13| 2.78| 2.82|
| AFM4   | 72.73| 3.80| 2.20| 2.94| 39.84(25.55)| 3.90| 2.50| 2.80| 35.42(15.27)| 3.98| 2.70| 2.7| 33.19(7.52)| 4.05| 2.85| 2.83|

Figure 7: Panel (a) The five considered magnetic arrangements, namely, ferromagnetic (FM), antiferromagnetic AFM1, AFM2, AFM3 and AFM4, respectively. The AFM1, AFM2 and AFM4 configurations are designed in such a way that Ho atoms form A-type, G-type and C-type antiferromagnetic arrangements whereas in the AFM3 configuration the Co and Mn atoms form G-type arrangements while keeping ferromagnetic interaction between Ho atoms. Panel (b) The spin and atom resolved DOS of most stable magnetic configuration AFM2 as a function of $U_{\text{eff}}$. The $U_{\text{eff}}$ is varied uniformly on Ho and Co ($U_{\text{eff}} = 2$, 4 and 6 eV) atoms while keeping zero for Mn. The inset depicts the DOS for the GGA case. Panel (c) The variation in DOS by keeping $U_{\text{eff}}$ fixed on Mn while varying on Ho and Co.
density functional theory (DFT) calculations were carried out to find the ground state electronic and magnetic properties of HCMO. The calculations were carried out on five magnetic configurations namely, FM, AFM1, AFM2, AFM3 and AFM4 (see Fig. 7). For this purpose, we considered experimentally obtained crystal structure and used the projector augmented wave (PAW) [90] method as implemented in the Vienna ab-initio simulation package (VASP) [91]. The generalized gradient approximation (GGA) was chosen for the exchange-correlation functional. The effect of strong correlation approximation (GGA) was chosen for the exchange-correlation functional. The Brilluion zone integration were carried out using 8 × 8 × 4 and 12 × 12 × 6 k-meshes to achieve the self-consistency and to obtain the densities of states (DOS), respectively. The PAW basis functions include 2s and 2p orbitals for O; 4f, 5d and 6s orbitals for Ho; and 3d and 4s orbitals for Co and Mn.

To examine the magnetic structure, we have designed various magnetic configurations which are depicted through Panel-(a) of Fig. 7. In these configurations various antiferromagnetic arrangements have been considered on Ho such as A-type (AFM1), G-type (AFM2) and C-type (AFM4) while keeping ferromagnetic interaction between Co and Mn whereas in one of the configurations (AFM3), the Ho-Ho interaction is maintained to be ferromagnetic while keeping G-type antiferromagnetic arrangement for Co and Mn. In Table-II, we list the relative energies of the five magnetic configurations as a function of $U_{\text{eff}}$ for two cases. For the first case the onsite correlation strength is varied uniformly on Co and Ho ($U_{\text{Mn}} = 0$) whereas for the second case a moderate value is fixed on Mn ($U_{\text{eff}} = 2$ eV) while varying $U_{\text{eff}}$ uniformly on Ho and Co. A primary electronic structure analysis of spin polarized GGA DOS ($U_{\text{eff}} = 0$) (see inset in Fig. 7) suggests that the exchange splitting for Mn is nearly the same as the crystal field splitting ($\Delta_{\text{ex}} \approx \Delta_{\text{cr}}$) [93]. As a result, there are no partially occupied states at the Fermi level and a gap exists even without considering the onsite correlation effect. On the other side, for Co, $\Delta_{\text{ex}} > \Delta_{\text{cr}}$ and the Fermi level is partially occupied with the down-spin channel of $2g$ manifold which gives rise to metallicity in the system. Therefore, finite correlation strength is required on Co to open up a gap whereas $U_{\text{eff}}$ on Mn is hardly required. Furthermore, the robustness of the magnetic structure is also analyzed for a moderate value of $U_{\text{eff}} = 2$ eV on Mn.

As inferred from Table-II, under independent electron approximation (GGA) a FM ground state is preferred which is contrary to the experimentally reported Curie Weiss behavior where the negative value of $\theta_{\text{WE}}$ infers an antiferromagnetic ground state. Often such discrepancy in magnetically active transition metal oxides arises due to lack of appropriate measure of strong correlation effect. In this regard as discussed earlier we have carried out GGA + U calculations that reveal AFM2 configuration, where Ho stabilize G-type ordering while Co and Mn possess ferromagnetic ordering, forms the ground state. In addition we find that any kind of antiferromagnetic ordering among Co and Mn results in higher energy configuration. For example, the configuration AFM3, where nearest neighbor Co and Mn are antiferromagnetically oriented, is at least two orders higher in energy as compared to the ground state. This further validates the positive value of $\theta_{\text{TM}}$ suggesting FM interaction as obtained experimentally.

The local magnetic moments listed in Table-II along with the orbital projected DOS, shown in Fig. 7, describes the electronic and magnetic structure of HCMO. As can be clearly seen, for Mn, irrespective of $U_{\text{eff}}$, in the majority spin channel the $t_{2g}$ states are occupied and the $e_g$ states are empty whereas in the minority spin-down channel the $d$ states are completely unoccupied inferring a 4+ charge state with the $3\mu_B$ spin moment arising from $(t_{2g})^6(e_g)^0$ electronic configuration. For Co and Ho, the $d$ and $f$ states are completely occupied in the majority spin channels while in the minority spin channel they are partially occupied highlighting the $2+\text{ and } 3+$ charge states with $t_{2g}(t_{2g})^6(e_g)^2$ and $f(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow\down arrow. The stabilization of the Co$^{2+}$ and Mn$^{4+}$ electronic configurations in the octahedral environment matches with the hypothesis proposed by Parida et al. [93] and demonstrate the case where the exchange field is comparable or greater than the crystal field split.

CONCLUSIONS

We synthesized high-quality polycrystalline samples of the double perovskite Ho$_2$CoMnO$_6$, which crystallizes in monoclinic $P2_1/n$ space group. X-ray photoelectron spectroscopy unveil the exact charge state of cations in this material. The hysteresis loop at 5 K isotherm in the M-H curve confirms a FM state owing to superexchange interaction between 3d moments Co$^{2+}$-O-Mn$^{4+}$. The specific heat confirms the presence of ferromagnetic long-range ordering. The ZFC-FC bifurcation at $T_c = 79$ K in low field $H = 100$ Oe, indicates the presence of spin-freezing in this double perovskite material, which is also supported by the frequency dependent ac susceptibility data. Also, the Vogel-Fulcher and critical slowing model fits point towards the stabilization of a re-entrant spin-glass ground state below $T_1 = 30$ K as the spin flipping has a longer relaxation time compared to...
conventional spin-glass. The presence of competing interactions and anti-site disorder lead to such a spin-glass state in HCMO. In addition, magnetization results point towards the existence of a disordered Griffiths-like phase and short-range order above $T_c$ in this material. The temperature dependent Raman spectra supports the bulk magnetization results. Our Raman spectroscopy results suggest the significant contribution of spin-phonon coupling in the magnetically ordered state that arises from the phonon mediated modulation of the exchange integral in this material. The presence of spin-spin correlations is manifested by the deviation of the spectral line-shift from its anharmonic nature in the proximity of $T_G = 90$ K. The relatively large value of magnetocaloric entropy change, $\Delta S_m \approx 13.5$ (J/kg-K) much below the FM ordering temperature suggests that HCMO is a promising candidate for magnetic refrigerant applications. The electronic structure calculations corroborate the experimentally observed charge states and provide insights into the magnetic ordering in this double perovskite. The ground state magnetic ordering is found to be the one where the Ho spins form G-type antiferromagnetic arrangement while Co and Mn spin sublattices constitute ferromagnetic ordering. Furthermore, our calculations reveal that the present double perovskite is a narrow band gap insulator which is consistent with XPS results. Due to strong correlation effect in the spin minority channel, the Co-$t_{2g}$ manifold splits into lower and upper Hubbard subbands to create a narrow gap. The spin majority channel has a natural band gap due to the crystal field split of the Mn-$d$ states. Further studies are desired to understand the complex interplay between emergent degrees of freedom leading to interesting physical phenomena in this 3$d$-4$f$ based double perovskite that may shed deep insights relevant in the context of novel material with competing magnetic order.

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