Magnetic Properties

In this chapter the temperature- and magnetic field-dependent magnetization, magnetic susceptibility (χ) of the electron-doped manganites are discussed. Nature of the magnetic phase transition in addition to the order of the phase transition is discussed here. Thermoelectric power measurements on few compounds are also explained in this chapter.

6.1. Ca$_{0.85}$Pr$_{0.15}$MnO$_3$ (CPMO)

6.1.1. Magnetization

The magnetization of the sample was measured during cooling the sample in ZFC and FC protocols shown in Fig 6.1. It shows that the ZFC magnetization increases with decreasing temperature, exhibiting a peak and decreases very fast thereafter suggesting the sample undergo a magnetic phase transition from PM to AFM state. The Néel temperature ($T_N = 122$ K) has been determined as the temperature corresponding to the maximum of the dM/dT versus T curve. This transition is markedly sharp, as revealed by the narrow width of the dM/dT peak. Moreover, clear irreversibility between the FC and
ZFC magnetization curves below $T_{\text{int}} = 112$ K is also quite significant. The difference in the FC–ZFC magnetization below $T_{\text{int}}$ reflects competition between AFM coupled $t_2g$ and the incipient FM coupled $e_g$ states causing magnetic frustration. The existence of such a magnetically frustrated state has been explained on the basis of phase separation in the case of the PrCaMnO$_3$ system [1]. It has been observed that the FC magnetization

![Graph showing magnetization vs temperature](image)

increases below $T_{\text{int}}$. Similar features were observed in Ca$_{0.83}$Pr$_{0.17}$MnO$_3$ at 50 K associated with an appearance of FM moments in AFM phase [2]. The augmentation of the magnetization may be attributed to the appearance of a weak FM moment due to double exchange interaction between Mn$^{3+}$–Mn$^{4+}$ ions [3]. Furthermore, the plot of the inverse susceptibility ($\chi$) as a function of temperature have been studied (Fig. 6.2). It is evident that the paramagnetic susceptibility of the polycrystalline sample deviates significantly from the Curie–Weiss (CW) law. The slope of the reciprocal susceptibility changes at a temperature $T_p = 132$ K. We have fitted the reciprocal susceptibility (see the inset of Fig. 6.2) according to the paramagnetic law: $\chi = C/(T-\theta_{\text{CW}})$  (C is the CW constant and $\theta_{\text{CW}}$ is the CW temperature). The magnetic moment of CPMO can be expressed with the magnetic moments of individual ions as...
Magnetic properties

\[ \mu_{\text{eff}} = \sqrt{\mu_{\text{eff}}^2 \left( R \text{Ce}^{3+} \right)^2 \times 0.15 + \mu_{\text{eff}}^2 \left( M \text{n}^{3+} \right)^2 \times 0.15 + \mu_{\text{eff}}^2 \left( M \text{n}^{4+} \right)^2 \times 0.85} \]  

(6.1)

The theoretical values of \( \mu_{\text{eff}} \) for \( \text{Re}^{3+} = \text{Pr}^{3+} \) (\( s = 1 \)), \( \text{Mn}^{3+} \) (\( s = 2 \)) and \( \text{Mn}^{4+} \) (\( s = 3/2 \)) are 3.58\( \mu_B \), 4.9\( \mu_B \) and 3.87\( \mu_B \) respectively. The effective moment is determined from the Curie Constant \( (C = N \mu^2 / 2k_B; N \) is Avogadro Constant, \( k_B \) is Boltzmann constant) to be \( \mu_{\text{eff}} = 3.65\mu_B \). Thus the effective magnetic moment obtained from the linear fit is lower than the expected theoretical value \( \mu_{\text{eff}} = 4.27\mu_B \) (using Eq. 6.1), since the Mn ions are the mixture of \( \text{Mn}^{4+} \) and \( \text{Mn}^{3+} \). In order to solve this discrepancy the Curie–Weiss law should be modified and taken into consideration the effects of the Van Vleck paramagnetic susceptibility \( (\chi_{vv}) \) due to rare earth \( \text{Pr}^{3+} \) ions. The modified Curie–Weiss thus can be written as

\[ \chi(T) = \chi_{vv} + \frac{C}{T - \theta_{\text{CW}}} \]  

(6.2)

Subtracting the contribution of the Van Vleck susceptibility \( (\chi_{vv}) \) from the data [4], a CW behavior has been obtained as shown in the Fig. 6.2. We have fitted the data to the modified Curie–Weiss law (Eq. 6.2) with \( \chi_{vv} = 5.5 \times 10^{-3} \text{ emu mol}^{-1} \) and positive \( \theta_{\text{CW}} = \)
107 K and CW constant $C = 2.24$ corresponds to the effective magnetic moment $\mu_{\text{eff}} = 4.23\mu_B$, which is almost equal to the expected value (4.27$\mu_B$) for the sample. This excellent agreement with the theoretical value confirms the presence of both the Mn$^{4+}$ and Mn$^{3+}$ ions in this system. The value of $\theta_{C M}$ has been found to be less than $T_N$, which suggests that the strength of the antiferromagnetic ordering is not very strong in this system.
compound. The positive value of the paramagnetic Curie temperature $\theta_{\text{CP}}$ invokes special interest. On electron-doping of Ca$^{2+}$ ions by Pr$^{3+}$, G-type antiferromagnetic structure of pure CaMnO$_3$ transforms through a mixed state to an antiferromagnetic phase of C-type [5, 6]. In the C-type magnetic structure, the one-dimensional chains of parallel ordered Mn moments are oriented antiparallel to their neighboring chains. The FM exchange interaction along the chains is thought to arise from a double–exchange mechanism, with an orbital ordering coexisting with antiferromagnetic superexchange acting between the chains [7]. Therefore, the long–range ordering disappears at temperatures above $T_N$, while a short–range ferromagnetic order still remains. This short–range interaction region may be treated as a FM cluster. In Pr$_{0.5}$Sr$_{0.5}$MnO$_3$ compound, Flores et al. showed the presence of the ferromagnetic clusters in the PM phase [8]. To confirm the disappearance of the long range FM ordering, we have recorded isothermal magnetization curves above $T_N$ (see Fig. 6.3a). Normally in FM compounds the intercept of high–$H$ extrapolation of the plots on the positive $M$ axis provides non–zero magnetization associated with long range FM ordering [9]. None of these curves in Fig. 6.3a produces such a positive intercept above $T_N$, indicating the absence of typical long range FM ordering in the present sample. To study the order of magnetic phase transition, we have plotted $M^2$ vs. $H/M$ (Arrott plot) as shown in Fig. 6.3. According to the Banerjee criterion [10] a magnetic transition is expected to be of the first–order when the slope of Arrott plot is negative, whereas it will be of the second–order when the slope is positive. In the present case, the plots (Fig. 6.3a) reveal positive slope above 126 K indicating second order phase transition whereas negative slope below 126 K is seen in Fig. 6.3b signifies first order phase transition. The order of the phase transition has also been confirmed by Landau coefficient estimated by the fit of the magnetization data with equation of state, $H = A(T)M + B(T)M^3 + C(T)M^5$ [here $A(T)$ is an arbitrary constant, coefficient $B(T)$ would change sign according to the magnetic transition: $B(T) < 0$ for first order, $B(T) > 0$ for second order [11] and $C(T)$ can be either negative or positive] (see inset of Fig. 6.3b). The value of $B(T) = -117(4)$ Oe (gm/emu)$^3$ for $T = 114K$ and $113 \times 10^{-3}$ for $T = 144K$ was found to be negative below $T_N$ and positive above $T_N$. Hence, it is clear from the Arrott plots and the equation
of state that this compound shows second order magnetic transition above $T_N$ and first order transition below $T_N$. Such a phase transition has been observed in antiferromagnetic TbPdAl compound [12] and also antiferromagnetic RMnO$_3$ single crystals ($R =$ Dy, Tb, Ho, Yb) [13].

6.2. Ca$_{0.85}$Eu$_{0.15}$MnO$_3$

6.2.1. Magnetization

Figure 6.4 shows the temperature dependence of the magnetization $M(T)$ of the sample. Both the ZFC and FC data undergo a magnetic transition from paramagnetic to ferromagnetic state at $T_C = 122$ K defined as the inflection point of temperature
dependence of the magnetization curve, which can be found from the peak position of the $dM/dT$ curve. The FC and ZFC magnetization bifurcates very close to $T_C$. Further, the ZFC magnetization shows a gradual drop at 44.23 K, which can be attributed to partially canted spins in the ferromagnetic state of the sample. Fig. 6.5 shows $M$ vs $H$ curves for CEMO recorded at temperatures 5 K and 300 K. In the temperature range $T < T_C$, magnetization increases nonlinearly with increasing the magnetic field, however the
saturation magnetization is not attained. Meanwhile, in the region $T > T_c$ the $M$ vs $H$ curves become linear. Such behavior has been observed in the ferromagnetic and

![Graph 1](image1.png)

Figure 6.5: Field dependence of the magnetization of Ca$_{0.85}$Eu$_{0.15}$MnO$_3$ at $T = 5$ K and 300 K.

![Graph 2](image2.png)

Figure 6.6: Isotherms of $M^2$ vs $H/M$ (Arrott plot) at different temperatures close to $T_c$.

paramagnetic regimes of perovskite manganites [19-21]. A hysteresis loop observed at 5 K that indicates ferromagnetism at low temperature whereas the increases linearly increasing magnetization with the field indicates paramagnetism near room temperature as
shown in Fig. 6.5. To get a deep insight into the magnetic phase transition and the influence of the interplay among various degrees of freedom at $T_c$ in CEMO, we have done a critical analysis of magnetic properties in terms of Arrott plot; $M^2$ versus $H/M$ shown in Fig. 6.6. The positive slope on the $M^2$ vs $H/M$ plot, indicates second-order magnetic transition in the present sample [21]. Mathematically, the second order transition can be described by the critical exponents $\beta$, $\gamma$ and $\delta$. The exponents are obtained through asymptotic relations [21]

$$M_s(T,0)=M_0(-\varepsilon)^\beta$$

$$\chi_0^{-1}(T)=(h_0/M_0)^{\gamma/\delta}$$

$$M = DH^{1/\delta}$$

where $M_0$, $h_0$, and $D$ are the critical amplitudes, and $\varepsilon = (T - T_c)/T_c$ is the reduced temperature. It was observed that the values of the critical exponent embraces the mean–field theory ($\beta = 0.5$, $\delta = 1.0$), 3D isotropic nearest–neighbor Heisenberg model ($\beta = 0.365$, $\delta = 1.33$), and 3D Ising model ($\beta = 0.325$, $\delta = 1.24$). However, to obtain exactly these parameters, we used the modified Arrott plot [22] by plotting $M_s$ vs $T$ and $\chi_0^{-1}(T)$.

Figure 6.7: Temperature dependence of the spontaneous magnetization $M_s$ and the inverse initial susceptibility $\chi_0$. The solid lines are the best fit to Eqs. (6.3) and (6.4) respectively.
vs $T$ as shown in Fig. 6.7 (left and right panel). We have obtained $\beta = 0.388\pm0.023$ and $\gamma = 0.981\pm0.007$, by best fitting $M_s(T)$ to Eq. (6.3) and $\chi_0^{-1}(T)$ to Eq. (6.4) respectively.
Concurrently, two $T_C$ values obtained from Eq (6.3) and (6.4) are $126.53\pm0.71$ K and $120.29\pm0.54$ K respectively. Their average value is thus $T_C = 123.41$ K. In addition, the magnetization data was also analyzed in terms of the Kouvel–Fisher (K–F) method and the values of the critical exponent compared with that values obtained from Arrott plot. According to Kouvel et al, the equation of state can be written as [23]

$$M_S(T)[dM_S/dT]^{-1} = (T-T_C)/\beta$$  \hspace{1cm} (6.6)

$$x_o^{-1}(T)[d^2x_o/dT^2]^{-1} = (T-T_C)/\gamma$$  \hspace{1cm} (6.7)

According to these equations, the plots of $M_S(T)[dM_S/dT]^{-1}$ and $x_o^{-1}(T)[d^2x_o/dT^2]^{-1}$ as a function of $T$ should yield a straight line with slope $1/\beta$ and $1/\gamma$ respectively and the intercepts on $T$ axes equals to $T_C$. The results are shown in the Fig 6 8a. We have found the critical exponent $\beta = 0.389\pm0.003$ and $\gamma = 0.991\pm0.004$ The isotherm magnetization data near $T_C$ have been plotted according to Eq. (6.5) in log–log scale as shown in the Fig. 6 8b. From the best fit with Eq (6.5) at high magnetic field, we have obtained $\delta = 3.33\pm0.005$. The critical exponents from the scaling analysis are related to the Widom scaling relation $\delta_w = 1+\gamma/\beta$ [24]. It is determined that $\delta_w$ to be about 3.54. Thus, the critical exponents obtained from K–F method obey the Widom scaling relation. The value of critical exponent for our CEMO is reliable and comparable with other manganites [25–28]. Gehrnง et al [29] found that a Mn–ion triplets containing one hole, i.e., a Mn$^{3+}$–Mn$^{4+}$–Mn$^{3+}$ cluster has a significant binding energy of about half the binding energy of the bulk. These large spin moments enhance the dipole–dipole interaction in the case of Heisenberg model. The obtained value of $\beta$ in our sample is higher than that expected in the Heisenberg model. This might be due to the above mentioned dipole–dipole interactions, which reveals an existence of short–range ferromagnetic order in CEMO. The magnetic equation of state in the critical region can be written as

$$M_S(H, \varepsilon) = |\varepsilon|^{-\beta} \int f_\varepsilon(\frac{H}{|\varepsilon|})^{\delta/\beta}$$  \hspace{1cm} (6.8)

where $f_\varepsilon$ for $T > T_C$ and $f$ for $T < T_C$, respectively, are regular functions. Eq (6.8) implies that $M |\varepsilon|^{-\beta}$ as a function of $|H| |\varepsilon|^{-\delta/\beta}$ produces two universal curves. one for temperatures below $T_C$ and the other for temperatures above $T_C$. In order to check
whether our data in the critical region obey the magnetic equation of state as described by Eq. (6.8), $M \propto |H|^{-\beta/\nu}$ as a function of $H$ evaluated at $T = T_c$. Interestingly, all the points fall on two curves, one for $T < T_c$ and the other for $T > T_c$. This suggests that the value of the critical exponents and $T_c$ are reasonably accurate and in agreement with the scaling hypothesis.

### 6.3. Ca$_{0.85}$Dy$_{0.15}$MnO$_3$ (CDMO)

#### 6.3.1 Magnetization

We have investigated the temperature dependence of magnetization in ZFC and FC conditions at a field of 50 Oe of the compound as shown in Fig. 6.9. The temperature dependent magnetization shows FM to PM transition at $T_c = 112$ K, which can be found from the minima of the $dM/dT$ curve (see inset of Fig. 6.9). A strong irreversibility in the magnetization has been observed at 117 K (defined as the irreversibility temperature $T_m$).

![Figure 6.9: Temperature dependence magnetization of CDMO at the magnetic field $H = 50$ Oe in the ZFC and FC regimes. Inset shows the variation of $dM/dT$ vs $T$.](image)

as indicated by the large bifurcation in the FC and ZFC curves. This bifurcation below $T_c$ can be attributed to the inhomogeneous mixture of a FM and cluster glass–like phase originate from lack of long-range ferromagnetic ordering. Surprisingly, the ZFC magnetization gradually decreases around 65 K. It is worth noting that the parent
compound CaMnO$_3$ is a paramagnetic insulator at high temperature and becomes a $G$-type antiferromagnetic insulator at $T_N = 125$ K with a weak canting of about $0.3^\circ$ [32]. On substitution of smaller ionic radius leads to decrease $A$-site ionic radius $<r_A>$ consequently the magnetic ordering changes to $A$-type antiferromagnetic (AFM) and then to CE-type AFM. With further decrease in $<r_A>$, the system goes to cluster glass-like state. Thus the drops in ZFC magnetizations may be due to the presence of cluster glass-like. Similar cluster glass-like behavior has been observed in electron doped manganites such as Ca$_{1-x}$Sm$_x$MnO$_3$ [33]. The properties of low-temperature FM phase in the CDMO sample has been also characterized by magnetization measurement at 5K (see Fig. 6.10). This curve clearly shows expected patterns of hysteresis with a qualitatively FM nature (see upper inset of Fig. 6.10). The magnetization does not saturate within the applied field range. The non-saturating $M-H$ nature is possibly suggests the presence of cluster glass-like phase at low temperature. From the Arrott plot, a positive intercept has been found with a spontaneous magnetization ($M_s$) of about 30 emu/g indicating the second order phase transition (see lower inset of Fig. 6.10). The plot of the inverse susceptibility (see Fig. 6.11) has been found to be linear in the high-temperature paramagnetic region showing Curie–Weiss type behavior. We have fitted $1/\chi$ according to the law, $\chi = C/(T-\theta_{CW})$ ($C$ is the CW constant and $\theta_{CW}$ is the CW temperature). The value of $\theta_{CW}$ has been found to be equal to 28 K (Fig. 6.11). The positive value of Curie–Weiss temperature further confirms the presence of FM exchange interaction in this manganite.

The theoretical magnetic moment of CDMO can be calculated as $\mu_{eff} = 5.76\mu_B$ from Eq (6.1) using the theoretical values of $\mu_{eff} = 10.6\mu_B$ for Dy$^{3+}$, 3.87$\mu_B$ for Mn$^{4+}$ having electronic configuration ($t_{2g}^1e_g^0$) and 4.9$\mu_B$ for Jahn–Teller active high spin Mn$^{3+}$ ($t_{2g}^2e_g^1$), we have obtained. The effective moment is determined from the Curie Constant ($C = N\mu^2/3k_B$) to be $\mu_{eff} = 15.59\mu_B$. This large value of $\mu_{eff}$ indicates that the magnetism in the PM state of the compound includes a contribution of short range of FM clusters [34]. The existence of short range clusters in that manganite suggests the presence of the magnetic inhomogeneities in the high-$T$ PM state which generates the possibilities of the
existence of Griffiths phase in this compound. From the Currie–Weiss fitting in the PM state we have observed that $\chi$ interestingly deviates from Curie–Weiss behavior in the

Figure 6.10: Field dependence of the magnetization at $T = 5\text{K}$ (main panel). Upper inset shows the enlarged view of the hysteresis loop and lower inset represents the Arrott plot.

form of a sharp downturn as the temperature is lowered. This downturn in $1/\chi$ can be regarded as Griffiths phase [35]. The onset of the downturn is denoted as Griffiths temperature $T_G$ (i.e. the temperature where $1/\chi$ deviates from the Curie–Weiss behavior) which has been found to be 187K. The observed value of $T_G$ is higher than that for the Sm$^{3+}$ based manganites ($T_G = 140 \text{K}$) [36]. This is attributed to the smaller ionic radius of Dy$^{3+}$ as compared to that for Sm$^{3+}$ ions. Substitution of Ca$^{2+}$ by smaller ionic radius weakened the lattice effects and delocalized the charge carriers. Thus the FM double exchange interaction is enhanced, consequently enhances the value of $T_G$. The origin of the expected GP in this compound may be explained considering the accommodation strain at grain boundaries. It is important to consider the effect of the strain here as it is observed in low electron–doped manganites particularly for $x \leq 0.15$. The crystal structures of electron–doped manganites change from an orthorhombic PM state at high temperature to phase separated system (mixing of orthorhombic and monoclinic state) below the magnetic phase transition temperature ($T_C$). The compound becomes disordered
due to the monoclinic phase and hence a strain is produced along the grain boundaries of the orthorhombic phase. Since $T_m$ have been found to be greater than $T_C$, so we may considered that a weak strain extend to the temperature above $T_C$, i.e. the strain facilitate to survive the FM cluster in PM matrix. It is important to mention here that the GP is not coupled with the MR behavior in the present electron doped system. These two independent properties have also been observed in other electron doped manganites.

We have studied further about the Griffiths singularity by power–law behavior viz.

$$\chi^{-1} \propto (T - T_C^R)^{\lambda}$$

(6.9)

The exponent $\lambda$ ($0 \leq \lambda \leq 1$) signifies deviation from the CW behavior [37] and $T_C^R$ is the critical temperature of the random FM where susceptibility diverges. The plot of $1/\chi$ as a function of reduced temperature ($T = T_C^R$) in log–log scale is shown in Fig. 6.12. The plot displays two distinct linear regimes ($300\text{K} \geq T > T_G$ and $T_C > T > 5\text{K}$). There exists a noticeable singularity between the Griffiths and high temperature PM phases ($T_G > T >$...
From the linear fit in GP regime, the values of $T_C^R$ and $\lambda$ are found to be 80K and 0.87 respectively. The value of $\lambda$ has been observed larger than those values obtained for different manganites [38]. This larger value can be attributed to the fact that large lattice disorder in our compound as expected in polycrystalline manganites [39].

Further it should be noted that in this system, the orthorhombic and monoclinic phases coexist and the magnetically frustrated phase separation is accompanied by the lattice mismatch, which is closely related to the appearance of the Griffiths phase. In the weakly disordered system, the accommodation strain is considered to be responsible for the intrinsic inhomogeneity or phase separation. It has been observed that in the electron–doped manganites $\text{Ca}_{0.48}\text{La}_{0.15-x}\text{Y}_x\text{MnO}_3$ [40], the monoclinic C–type AFM phase transition temperature gradually decreases with increasing $x$. The shear strain comes into play due to the lattice mismatch between the monoclinic and orthorhombic phases. Consequently orthorhombic phase is distorted with temperature. The effect of the shear strain on the Jahn–Teller(JT) splitting of $\text{MnO}_6$ octahedra in the residual orthorhombic phase is reduced with increasing $x$ which favors the development of the Griffiths phase [40]. Similarly in $\text{Ca}_{0.48}\text{Sm}_{0.15}\text{MnO}_3$, orthorhombic and monoclinic phases,

![Graph](image-url)

Figure 6.12: The log(1/$\chi$) vs log($T/T_C^R -1$) plot. Solid line indicates a linear fitting
corresponding to the G–AFM with FM and C–AFM components are found in present
Thus the residual orthorhombic phase at the lower temperatures becomes distorted,
yielding an additional JT effect. Therefore, the GP appears in the temperature range 115 K
to 137 K [41] So there may be a close relationship between the phase separation and the
Griffith phase in our present sample.

6.2. References
14020 (1996)
(1985)
[8] R C Flores, N S Bingham, M H Phan, M A Toraja, C Leighton, V Franco, A Conde, T
Magn Magn Mater* 323, 2949 (2011)
(2011).
(1996)
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