

Magnetic studies of colossal magnetoresistance perovskites on macroscopic, mesoscopic and microscopic length scales

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Abstract. We have investigated magnetic correlations in various CMR manganites on macroscopic, mesoscopic and microscopic length scales by carrying out DC magnetization, neutron depolarization, and neutron diffraction measurements. We present here the effect of substituting Mn with Fe and La with Dy in the ferromagnetic $\text{La}_{0.7-x}\text{Ca}_x\text{MnO}_3$ ($x \sim 0.3-0.33$) compounds. Neutron diffraction has been used in order to characterize the long-range magnetic order and its gradual suppression by the substitution. Neutron depolarization study has been carried out in order to bridge the gap in our understanding regarding the nature of magnetic correlation obtained from the macroscopic and microscopic measurements. In particular, our study on $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ has established the fact that a true double exchange mediated spin-glass is insulating. In another study of La-site ionic size effect and its disorder in $(\text{La}_{1-x}\text{Dy}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, we have investigated the evolution of the length scale of magnetic ordering with a possible microscopic explanation and the results have been compared with that for the light rare earth substituted compounds.

Keywords. Colossal magnetoresistance perovskites; neutron depolarization; neutron diffraction.

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1. Introduction

Extensive research has been done on metallic, ferromagnetic manganites of the type $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, through doping the La^{3+} sites with trivalent rare-earths (Y, Pr, Dy, Tb, etc.) of different sizes and/or Mn site with both magnetic as well as non-magnetic ions of Ti, Al, Cr, Cu, Fe, Ge, Ga, In, etc. keeping the fixed Ca concentration (around 0.3) close to an optimum value in relation to the ferromagnetic interaction [1]. This is because they exhibit a range of extraordinary magnetic, electronic, and structural properties including colossal negative magnetoresistance (CMR), charge ordering, and the transport properties and also because of their potential technological applications [2,3]. In the doped state with mixed Mn^{3+} and Mn^{4+} valencies, the hopping of e_g electrons between two partially filled

d orbitals of neighboring Mn^{3+} and Mn^{4+} ions is facilitated by the orbital overlap $e_g(\text{Mn})-2p_\sigma(\text{O})-e_g(\text{Mn})$, and the strong on-site Hund's coupling between the t_{2g} core spins and the e_g electrons. This interaction, known as double exchange (DE) interaction, brings about simultaneous onset of ferromagnetic and metallic characters. The presence of ferromagnetic double exchange interaction and the $t_{2g}(\text{Mn})-2p_\pi(\text{O})-t_{2g}(\text{Mn})$ antiferromagnetic superexchange interactions along with the presence of disorder plays an important role in determining the magnetic and transport properties of these doped CMR manganites.

To date, much of the exploration to understand basic magnetic properties of these CMR perovskites has been done using mainly macroscopic probes such as AC susceptibility, DC magnetization etc. Though studies have been conducted using microscopic neutron diffraction technique, fewer studies have been reported where magnetic probes have been used on the same system covering different length scales such as macroscopic, mesoscopic and microscopic. This is particularly necessary for studying magnetic systems where frustration and disorder are present and lead to a variety of complicated magnetic ordering including spin-glass, cluster spin-glass, randomly canted ferromagnet etc. In such cases the nature of the magnetic correlation cannot be unequivocally determined by bulk magnetic measurements. Though neutron diffraction study gives the microscopic understanding of spin correlations in these compounds, a probe such as neutron depolarization is required to study the magnetic correlation on mesoscopic length scales which can bridge the gap in our understanding on the nature of magnetic correlation obtained from the macroscopic and microscopic measurements. We have carried out magnetic studies on a variety of Mn-based CMR perovskites using AC susceptibility, DC magnetization, neutron depolarization and neutron diffraction techniques covering macroscopic, mesoscopic and microscopic length scales [4–12]. I shall present some of our recent results from these studies.

2. Experimental

Polycrystalline samples with nominal compositions $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ and $(\text{La}_{1-x}\text{Dy}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ ($x = 0, 0.243$ and 0.347) were prepared by solid state reaction. DC magnetization measurements as a function of temperature and magnetic field were carried out using either a vibrating sample magnetometer (Oxford Instruments) or SQUID magnetometer (Quantum Design). The unpolarized neutron powder diffraction and neutron depolarization measurements were carried out at Dhruva reactor, Trombay [13–15].

3. Results and discussion

3.1 Mn-site substituted $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ -type perovskites

Several studies on the effects of Mn-site substitution by Fe, Al, Cr, Ge, In, Ti, Zn, Co, Ni, Cu or Ga in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ have been reported [1]. Generally, substitutions of Mn drastically lowers the Curie temperature and eventually produces spin-glass-like properties for higher level of substitution. Reasons underlying these

features may be the combined effects of substitution, viz. (i) a shifting of the average valence in the Mn–O–Mn network, (ii) changes in the band-structure and hence the conduction electron mediated DE interaction, (iii) magnetic dilution, and (iv) additional magnetic coupling. Substitution of Mn site may also cause lattice distortions due to changed ionic size. All these effects are generally intertwined, and can influence the magnetic behavior. Considering the complex influences generated by Mn-site doping we have studied the effects of substitution of Mn by Ga and Fe in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$. Because Mn^{3+} , Ga^{3+} and Fe^{3+} have almost identical ionic radii (~ 0.64 Å), no strong lattice effects would be introduced. The electron hopping from Mn^{3+} to Ga^{3+} and Fe^{3+} is also forbidden. Here we present the results of Fe-substituted $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ compound.

In a recent study of (i) the irreversibility between zero-field-cooled (ZFC) and field-cooled (FC) DC magnetization, (ii) the frequency and field dependence of the AC susceptibility anomaly, and (iii) the magnetoresistance, a spin-glass-type of behavior with $T_f = 42$ K was reported by Cai *et al* [16] for the $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ compound. An inconsistency of Cai *et al's* [16] result was the fact that they correlated the peak in resistivity around 42 K (where the metal-to-insulator transition and CMR effect have been found) with the spin-glass freezing temperature whereas, a true double-exchange-mediated spin-glass should be insulating as observed, e.g., in $(\text{La}_{2/3}\text{Tb}_{1/3})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ with $\rho = 10^{13}$ Ω cm [17] and $(\text{La}_{1-x}\text{Dy}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ with $x > 0.347$ [6,8,12].

In order to understand the true nature of magnetic ordering in $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$, we carried out DC magnetization, neutron diffraction, and neutron depolarization study. The temperature dependence of the inverse of the polarization ratio R of the transmitted neutron beam with an applied field of 25 Oe is depicted in figure 1. The procedure for obtaining polarization ratio R from the transmitted polarized neutron beam experiments is described elsewhere [13]. R^{-1} decreases continuously with decrease in temperature from 108 K and it attains a constant value below 20 K. The magnetic ordering temperature for this sample is thus estimated to be 108 K. From the observed depolarization an estimate of the average size of domains/clusters was made using the expression [13,18,19]

$$P_f = P_i \exp\left(-\alpha \left(\frac{d}{\delta}\right) \langle \Phi_\delta \rangle^2\right), \quad (1)$$

where P_i and P_f are the incident and transmitted neutron beam polarization, α is a dimensionless parameter $\approx 1/3$, d ($=6$ mm) is the effective thickness of the sample, δ is the average domain size, and $\Phi_\delta = (4.63 \times 10^{-10} \text{ G}^{-1} \text{ \AA}^{-2}) \lambda \delta B$ the precession angle. The internal mean induction $B(G) = 4\pi M_S \rho$ within a domain at low temperature was estimated from the bulk magnetization measurements. Here $M_S (= 15 \pm 5 \text{ e.m.u. g}^{-1})$, i.e., $0.56 \mu_B$ per Mn/Fe site) is the spontaneous magnetization in e.m.u. g^{-1} and ρ is the density of the material. The estimate of the average domain size, thus, gives $\sim 2 \mu\text{m}$. Here a homogeneous magnetic state is assumed. However, a phase segregation in the present system cannot be ruled out.

Though domains with net magnetic moments exist, our neutron diffraction study at 15 K does not show the presence of any magnetic Bragg intensity (figure 2). It is, therefore, suggested that the spins are highly canted in this compound. The canting of Mn/Fe site moments is assumed to be random (local) from site to site so that

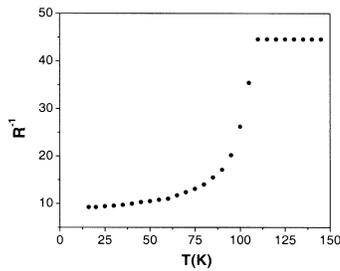


Figure 1. Inverse of polarization ratio (R^{-1}) vs. temperature measured at 25 Oe applied field.

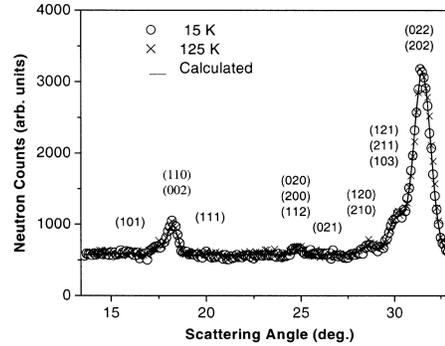


Figure 2. Rietveld refined neutron diffraction patterns for $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ at 125 and 15 K.

the ordered component of moments which gives a long range ferromagnetic ordering over the domain is quite less in magnitude ($<0.6 \mu_B$ per Mn/Fe site). Here the random substitutions of Mn^{3+} with Fe^{3+} can lead to a randomness of the signs of the local exchange coupling (DE ferromagnetic or the antiferromagnetic superexchange interaction prevails between Fe^{3+} and its neighboring Mn^{3+} , Mn^{4+} or Fe^{3+} (if there is any) along with co-existing $t_{2g}(\text{Mn})-2p_{\pi}(\text{O})-t_{2g}(\text{Mn})$ antiferromagnetic interactions) and may be responsible for the random (local) canted spin structure. Our study has shown that a previous interpretation of the magnetic ground state of the compound by Cai *et al* [16] was wrong and has established the fact that a true DE mediated spin-glass should be insulating [4]. The observed irreversibility between the ZFC and FC magnetization curves [16], as well as the characteristic dependency of AC susceptibility on frequency and amplitude of the AC field [16] seem to indicate the kinetic freezing of these domains of randomly canted spins, which strongly depends upon the cooling process.

3.2 La-site substituted $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ -type perovskites

Considering the complex influences generated by direct substitution of Mn sites, if one is interested in studying the ionic size effect on the magnetic properties of these $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ perovskites, it is desirable to focus on replacing La^{3+} by a non-magnetic ion (with 3+ ionic state) with different radius without changing the effective Mn valency and/or introducing any magnetic exchange interaction. Though extensive research has been done in this direction, there is a clear lack of understanding on (i) the evolution of the length scale of magnetic ordering in the ferromagnetic manganites with a decrease in the average size of the ions at the rare earth site and (ii) whether or not the magnetic phase diagram obtained for light rare earth ions at the La site holds for the heavy rare earth ions. In the present study, therefore, by replacing La^{3+} with heavy rare-earth ions of Dy^{3+} in $(\text{La}_{1-x}\text{Dy}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ perovskites with $x = 0$ (geometrical tolerance factor, $t = 0.916$), 0.243 ($t = 0.908$) and 0.347 ($t = 0.905$), we have investigated the evolution

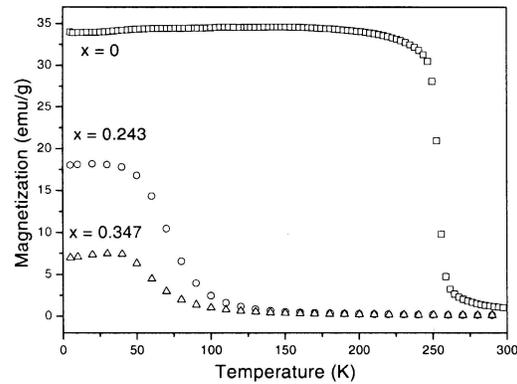


Figure 3. Temperature dependence of DC magnetization for $(\text{La}_{1-x}\text{Dy}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ with $x = 0, 0.243$ and 0.347 .

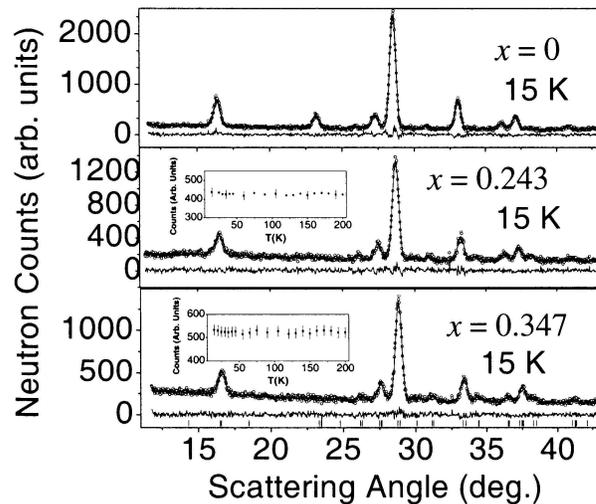


Figure 4. Neutron diffraction patterns at 15 K. Circles: Observed data. Solid lines: Rietveld refined patterns. Solid line at bottom: Difference patterns. Insets: Temperature dependence of intensities of the (110) and (002) Bragg peaks ($2\theta \approx 16.6^\circ$).

of the length scale of magnetic ordering with a possible microscopic explanation and compared with the results reported for the light rare earth compounds.

Figure 3 displays the temperature dependence of the field-cooled DC magnetization at 500 Oe. Magnetic transition temperatures are found to be 252, 70, and 60 K for $x = 0, 0.243$, and 0.347 samples, respectively, indicating that the substitution of Dy for La leads to a strong decrease in the magnetic ordering temperature. Figure 4 shows the observed and Rietveld refined neutron powder diffraction patterns at 15 K. Rietveld analysis shows an orthorhombic perovskite structure (space group Pbnm) with a ferromagnetic ordering for the $x = 0$ sample and with a net Mn-site

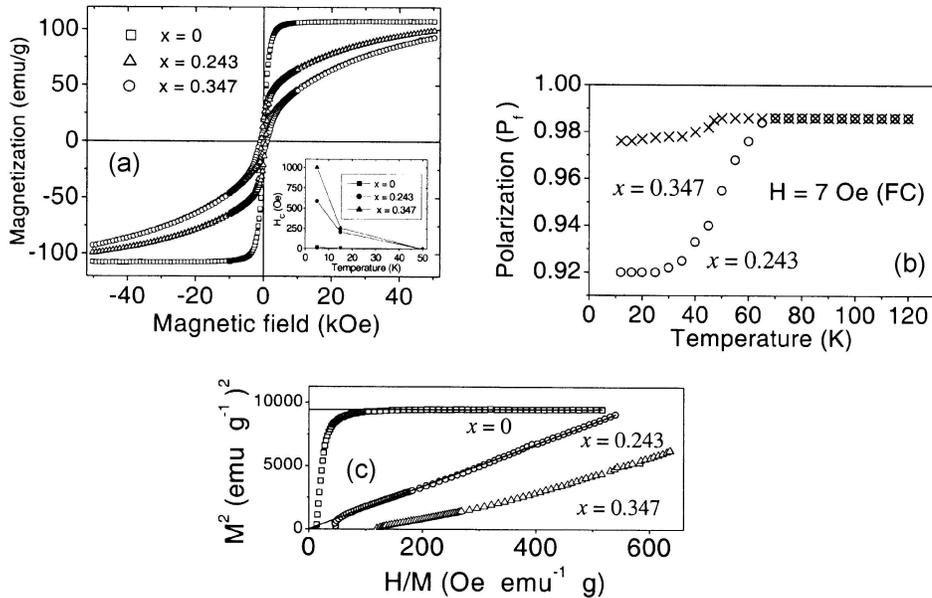


Figure 5. (a) M vs. T for $x = 0, 0.243$ and 0.347 samples at 5 K over all four quadrants (inset shows H_c vs. T), (b) temperature dependence of transmitted neutron beam polarization and (c) Arrott plots derived from figure 5a.

ordered moment of $3.42 \pm 0.06 \mu_B$ along the crystallographic c -direction as reported in literature. However, for both the $x = 0.243$ and 0.347 samples, patterns could be fitted with only nuclear intensities confirming the absence of any observable magnetic ordering. This suggests that the spins are randomly (local) canted with very low longitudinal ordered moments and/or spin-glass-like ordering.

Figure 5a shows the non-saturation of magnetization for the $x = 0.243$ and 0.347 samples implying a canted spin state with increasing canting angle with the increase of Dy substitution. The hysteresis loops show a sharp increase of coercivity at lower temperatures (below ~ 15 K) for the Dy-substituted samples (figure 5a, inset). As shown in figure 5b, for $x = 0.243$, the transmitted neutron beam polarization P_f shows a continuous decrease from ~ 65 K, before attaining a constant value below ~ 28 K confirming the presence of domains with net moments below 65 K. From the observed depolarization, the average size of domains was estimated using eq. (1). Here the spontaneous magnetization (M_S) = 4.5 e.m.u./g ($\sim 0.17 \mu_B$ per formula unit, well below the detection limit $\sim 0.5 \mu_B$ per Mn site in diffraction experiments), obtained from the ‘Arrott’ plot (figure 5c), has been used to estimate the domain size ($\sim 5 \mu\text{m}$ at 15 K). For $x = 0.347$, P_f slightly decreases below ~ 47 K (figure 5b), however, with no spontaneous magnetization (figure 5c).

With increasing Dy concentration, the tolerance factor t (= 0.916, 0.908, and 0.905 for $x = 0, 0.243$, and 0.347 , respectively) decreases. This shows an increase in the buckling of MnO_6 octahedra, causing a further decrease in the Mn–O–Mn bond angles below 180° [$162(1)^\circ$, $159.9(6)^\circ$ for $x = 0$, $156.5(9)^\circ$, $157.9(4)^\circ$ for $x = 0.243$, and $155.8(9)^\circ$, $157.5(8)^\circ$ for $x = 0.347$, obtained from Rietveld analysis

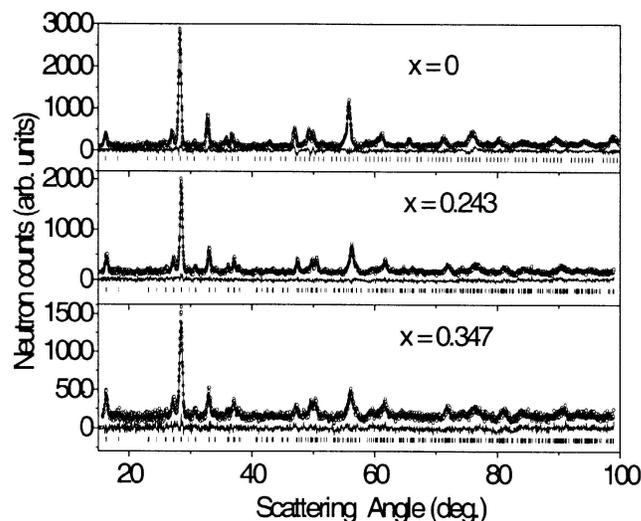


Figure 6. Rietveld analysis of RT neutron diffraction patterns.

of RT neutron diffraction patterns, shown in figure 6] and gives weaker transfer integral for the hopping of e_g electrons. Consequently, DE ferromagnetic interactions and coexisting $t_{2g}(\text{Mn})-2p_{\pi}(\text{O})-t_{2g}(\text{Mn})$ antiferromagnetic superexchange interactions compete more strongly depending on the structural distortion, giving rise to magnetically disordered states with canted ferromagnetic state for the $x = 0.243$ compound and a cluster-spin-glass state for the $x = 0.347$ compound. A random distribution of the Mn–O–Mn bond angles is also responsible for driving the system towards the cluster-spin-glass state.

Since the neutron diffraction study confirms that the ionic moment of Dy^{3+} does not show magnetic ordering down to 9 K [6], our experimental results essentially reflect how the average ionic size $\langle r_{\text{R}} \rangle$ and its variance σ of the La sublattice influences the magnetic order on different length scales. Terai *et al* [20] concluded that in $(\text{La}_{1-x}\text{Dy}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ for $x > 0.286$ ($t < 0.907$), only a spin-glass insulator phase appears at low temperatures. This spin-glass insulator phase was interpreted to be different from a ferromagnetic insulator that appears in the compounds containing light rare earth metal ions of Pr^{3+} and/or Y^{3+} , but similar to that reported by Teresa *et al* [17] for the heavy rare earth substituted compound $(\text{La-Tb})_{2/3}\text{Ca}_{1/3}\text{MnO}_3$. However, our study shows that even for Dy concentration as high as 0.347 ($t = 0.905$) a cluster glass state persists indicating similar behavior between the light and heavy rare earth substitutions in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$.

4. Summary and conclusion

We have investigated magnetic correlation in various CMR manganites using neutron depolarization technique and these results have been combined with the results of DC magnetization and neutron diffraction measurements. Neutron

diffraction has been employed in order to characterize the long-range magnetic order and its gradual suppression by the substitution. Neutron depolarization study has established the existence of magnetic domains/clusters. We have resolved the controversy regarding the magnetic nature of a double exchange (DE) mediated metallic $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{0.9}\text{Fe}_{0.1}\text{O}_3$ perovskite. The present study has shown the existence of ferromagnetic domains of $\sim 2 \mu\text{m}$, indicating that a previous interpretation of the magnetic ground state of the compound by Cai *et al* [16] was wrong and has established the fact that a true DE mediated spin-glass should be insulating. In another study, we have studied the effect of ionic size on magnetic properties through the substitution of La^{3+} ions (ionic radius: 1.216 Å) by Dy^{3+} ions (ionic radius: 1.083 Å) for the $(\text{La}_{1-x}\text{Dy}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ system. We have given a clearer understanding about the evolution of the length scale of magnetic ordering in $(\text{La}_{1-x}\text{Dy}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ compounds with a decrease in the average size of the ions at the rare earth site. The study shows a strong evidence for the presence of ferromagnetic correlation with large domains ($\sim 5 \mu\text{m}$) for $x = 0.243$ and a cluster spin-glass state for $x = 0.347$ in their low temperature insulating states contrary to what was concluded by Terai *et al* [20]. Our study also brings out the similarities of magnetic properties between light and heavy rare earth substituted $(\text{La}_{1-x}\text{R}_x)_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ CMR compounds. Since the Dy^{3+} moment does not order, our results essentially reflect how the average ionic size and its distribution of the La site influence the magnetic order.

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