Influence of Nd on the magnetic properties of $Nd_{1-x}Ca_xMnO_3$: an ESR study

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Abstract

The role played by the Nd ions in the magnetic properties of \(Nd_{0.5}Ca_{0.5}MnO_3\) and \(Nd_{0.7}Ca_{0.3}MnO_3\) is studied using static magnetization, neutron diffraction and high frequency (9.4 – 475\(GHz\)) Electron Spin Resonance. We show that the Nd ions are weakly coupled to the Mn ions via ferromagnetic exchange and are responsible for the peculiar ferromagnetic resonance observed in the FM phase of both compounds (ground state below 120K for \(x=0.3\), high field state for \(x=0.5\)). We then use ESR to look for magnetic phase separation in the low field, CO phase of \(Nd_{0.5}Ca_{0.5}MnO_3\). We show that there is no trace of the FM phase imbedded in the CO phase, contrary to what is observed in \(La_{0.5}Ca_{0.5}MnO_3\) or \(Pr_{0.5}Sr_{0.5}MnO_3\).
The perovskite manganites, $R_{1-x}A_xMnO_3$, where $R$ is a trivalent rare earth element (La, Pr, Nd, Sm etc.) and $A$ is a divalent alkaline earth element (Ca, Sr), are strongly correlated electron systems distinguished by their large variety of magnetic and electronic states. Three types of order are observed: charge order (CO) of the $Mn^{3+}$ and $Mn^{4+}$ charges; orbital order (OO) of the manganese 3d orbitals and antiferromagnetic (AF) or ferromagnetic (FM) order of the magnetic moments. The various types of order are related, e.g. the onset of orbital order induces an antiferromagnetic order with the same symmetry. On the other hand, the ferromagnetic double exchange interaction between $Mn^{3+}$ and $Mn^{4+}$ ions leads to a metallic ferromagnetic state with charge delocalization and no orbital order. The type of order and the ordering temperature may be tuned by the choice and concentrations of the doping elements $R^{3+}$ and $A^{2+}$; these affect the bonding length, angle and disorder of the Mn-O-Mn overlapping orbitals and the relative concentration of $Mn^{3+}$ and $Mn^{4+}$ ions. A sufficiently large magnetic field may suppress the OO or the CO and stabilize a FM state. In the Ca compounds, the charge ordered state is quite stable: there is no delocalized state with a FM order at any temperature in zero magnetic field. In the typical examples, $Nd_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$, there is a transition to a CO state at $250K$ and an antiferromagnetic state at $160K$. A high magnetic field destroys the CO state and stabilizes the FM delocalized state.

The strength of spatial and dynamical fluctuations of the order in paramagnetic (PM), CO or AF manganites balanced close to the delocalization - localization transition is one of the much debated questions. Allodi et al. observed, using NMR, a separation between ferromagnetic and antiferromagnetic phases in $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Sr_{0.5}MnO_3$. The coexistence of the charge ordered and ferromagnetic metallic phases has been observed by electron microscopy in other $R_{1-x}Ca_xMnO_3$ compounds also.

In this Rapid Communication, we study the $Nd_{1-x}Ca_xMnO_3$ manganites belonging to the Ca family. We present magnetization and electron spin resonance (ESR) data together with neutron diffraction determination of the Mn and Nd moments for the $x = 0.3$ ($Nd_{0.7}Ca_{0.3}MnO_3$) and $x = 0.5$ ($Nd_{0.5}Ca_{0.5}MnO_3$) compounds. We show that the magnetic...
moment of the trivalent Nd ion has little influence on the magnetic phase diagram of the system as it is only weakly coupled by a ferromagnetic exchange to the Mn ions. The magnetic resonance spectra are, however, sensitive to the Nd moment that is increased by the coupling to the Mn sublattice. Once the role of Nd on the spectrum is understood, we use ESR to look for magnetic phase separation. We show that, there are no static FM domains in the low field CO state of the $Nd_{0.5}Ca_{0.5}MnO_3$ compound.

Preparation of the powder samples is described elsewhere [3], [6]. The neutron diffraction data presented here were performed at ILL and are part of a detailed study to determine the crystallographic structure, charge order and magnetic transitions in zero field. The magnetic phase diagrams of our samples constructed from static magnetization data in fields up to $23T$ are in agreement with those of Tokunaga et al [7]. The X band ($9.4GHz$) and Q band ($35GHz$) ESR spectra were recorded with conventional Brucker spectrometers on few mg loosely packed powder samples with $7\mu m$ typical grain size. A home made spectrometer [8] was used at higher frequencies ($95 - 475GHz$) with a superconducting magnet up to $12T$ and a resistive magnet for higher fields. The sample was pressed into $9mm$ diameter, $0.9mm$ thick pellets with a density of $82\%$ for the high field ESR measurements. The magnetic field was oriented along the axis of the cylindrical pellet. In this geometry, the demagnetizing fields shift the resonance to higher fields by $\delta H_{dem} \simeq \mu_0 M$ and the shift data were corrected accordingly using the static magnetization, $M$, measured on the same sample.

The ground states in zero magnetic field are FM and AF for the $x = 0.3$ and $x = 0.5$ compounds respectively. In the $x = 0.3$ compound, the paramagnetic CO state orders below $T_{CO} = 240K$ into a FM state at $T_C = 120K$. In the $x = 0.5$ compound, the transition to the paramagnetic CO state at $T_{CO} = 250K$ is well above the AF ordering temperature, $T_N = 160K$ in zero magnetic field. A magnetic field of about $15T$ is required to stabilize the FM state below $275K$. In this high field, the CO state is entirely suppressed.

Fig.1 shows the static magnetic susceptibility, $\chi_{DC}$, determined from the magnetization measured in a field of $0.33T$. The susceptibility measured by the ESR intensity follows $\chi_{DC}$ in the PM state of both the 0.3 and 0.5 compounds. The maximum observed in $\chi_{DC}$ for
$x = 0.5$ at the CO transition is confirmed. For $x = 0.3$, $\chi_{DC}$ increases continuously as the temperature decreases from the paramagnetic state to 75K, i.e. well into the FM state. The ordered magnetic moments of the Mn and Nd ions measured by neutron diffraction in zero field are shown on Fig.2. The Mn moments order below 120K while the Nd contribution is visible only below 50K. The Nd moment is still increasing between 10K and 2K. A similar neutron diffraction study in the AF state of the $x = 0.5$ compound showed no magnetic order of the Nd subsystem. We relate the upturn in $\chi_{DC}$ below 25K in the antiferromagnetic state of $x = 0.5$ compound (Fig.1b) to the increase of the paramagnetic Nd moment within the antiferromagnetically ordered Mn system. Thus, both the static susceptibility and neutron data confirm that the coupling of Nd to the Mn ordered lattice is weak, and much weaker in the AF than in the FM state.

The ESR data discussed below show that the coupling between Nd and Mn is ferromagnetic and is well observable both in the FM and PM states. Above $T_C = 120K$, i.e. in the paramagnetic state of the $x = 0.3$ compound, a single symmetric ESR line is observed. The spectrum broadens below the FM ordering temperature; as the temperature is lowered a double peaked structure develops that shifts to lower fields (Fig3a). The shift is far larger and in opposite direction than the corrections due to demagnetization effects. We observe a similar ESR spectra at 475GHz in the high field FM state of the $x = 0.5$ compound (Fig3b). The single line centered around 17T in the PM state becomes double peaked in the FM state below $T_C = 275K$. At low temperatures, the demagnetization corrected shifts of both components are large and negative. We note that the unusual features of the resonance, the double peaked shape and large shift, are specific to manganites containing Nd. In $La_{0.67}Ca_{0.33}MnO_3$, a compound that is ferromagnetic below 280K, the ESR of an epitaxial film showed no unusual feature [9]. In this case the spectrum in the ferromagnetic phase could be described by demagnetization effects and a relatively small magnetic anisotropy. Long range structural or magnetic phase inhomogeneities may lead to spectra with several components as observed in $La_{1-x}Ca_xMnO_3$ [10] and $La_{1.35}Sr_{1.65}Mn_2O_7$ [11] but in this case the temperature dependence of the various components are unrelated.
The large shift with temperature of all components of the spectra in the FM state of \( Nd_{1-x}Ca_xMnO_3 \) for both \( x = 0.3 \) and 0.5 indicate that these are phase homogeneous compounds. We suggest that the spectra below \( T_C \) are the ferromagnetic resonance of the ferromagnetically ordered Mn moments weakly coupled by a ferromagnetic exchange to the paramagnetic Nd moments. As discussed above the neutron diffraction and magnetization data show that Nd moments are weakly coupled to the Mn ferromagnetic system. We assume that this coupling is so weak that Nd and Mn do not have a common resonance. This will happen if the spin lattice relaxation of Nd due to e.g. phonons is sufficiently rapid so that there is no bottleneck between the Mn and Nd subsystems. The spin relaxation and g factor anisotropy broadens the Nd ESR beyond observability. The shift of the Mn ferromagnetic resonance is then due to the exchange interaction between Nd and Mn: \( \delta H_{Mn} = \lambda M^{Nd} \). The observed anisotropy for \( \delta H_{Mn} \) results from the Nd g anisotropy.

In Fig.2 the average shift of the Mn ESR line is compared to the temperature dependence of the Nd moment measured in zero field. In the ESR experiment the polarization of Nd arises from the external field, the ferromagnetic interaction with the ordered Mn sublattice and the ferromagnetic interaction between Nd moments. Inter-neodymium interactions are small above 50 K. In the FM state the polarization of Nd by the external field is smaller than the polarization due to the Mn sublattice. Indeed, at 10K the shift (thus the Nd moment) increases little (8%) between 95GHz and 285GHz (roughly 2T and 9T central fields), at 60K this increase is much more important (140%). Thus at 10K the extrapolation to zero external field and the moment of 0.9\( \mu_B \) per Nd ion measured by neutron diffraction yields the scale for the larger (smaller) Mn shift of \( \lambda = 2.4T/\mu_BNd \) (1.3T/\( \mu_BNd \)). We extract the Nd susceptibility in the whole temperature range 10K – 300K (Fig.1a) using the average value of \( \lambda = 1.8T/\mu_BNd \). The same analysis can be applied to the high field FM phase of \( Nd_{0.5}Ca_{0.5}MnO_3 \). At 50K, the same Nd g anisotropy is found. Taking the same value for \( \lambda \) for both compounds ( \( x = 0.3 \) and \( x = 0.5 \)), we estimate the Nd susceptibility (Fig1.b). In both samples the Nd susceptibility increases faster than 1/T at low T while the Mn moments are nearly saturated. This shows that Nd orders ferromagnetically at much lower
temperature than Mn and confirms that the coupling of the Nd to the Mn ordered lattice is weak, and much weaker in the AF state than in the FM state.

We examine now the low field, paramagnetic CO phase of $Nd_{0.5}Ca_{0.5}MnO_3$. The above discussion shows clearly the kind of spectrum expected from phase separated FM domains within the PM state: if long range FM domains existed in this material then these would be detected as separate lines or at least as an increased tail at the low field side of the spectra since the Nd moments shift the Mn ESR strongly to lower fields. Fig.4 presents typical spectra taken in the CO phase of $Nd_{0.5}Ca_{0.5}MnO_3$ as well as the temperature dependence of the line position. The susceptibility measured by ESR follows the general trend of the static magnetic susceptibility (Fig.1b), the difference is due to the Nd contribution which is not present in the ESR susceptibility. It is clear that the ESR spectra, in the CO phase at low fields, are simpler than in the high field induced FM phase. The line remains symmetric and centered around $g = 1.99$ in the whole temperature range between 160$K$ and 300$K$. There is no shift of the resonance line contrary to what is observed in the FM phase. As shown in the inset of Fig. 4b, no extra peaks or asymmetry in the lineshape are observed. Besides, at 230$K$, the line width in the CO phase is smaller than the total spread of the ferromagnetic spectrum in the FM state. Therefore we conclude that there is no trace of FM domains embedded in the CO matrix. The scenario of phase separation does not hold, contrary to what is observed in $La_{0.5}Ca_{0.5}MnO_3$ or $Pr_{0.5}Sr_{0.5}MnO_3$ [4]. In those compounds, the ferromagnetic phase is more easily stabilized by an applied magnetic field; the energy difference between the CO and FM phases is reduced and the phase separation scenario may be valid: the FM phase may nucleate into the CO phase. In Nd compounds, as well as in Pr compounds, the energy difference is larger and the nucleation of the ferromagnetic phase occurs only at high fields, closer to the CO-F transition. The stability of the CO phase is quite robust against changes in the $Mn^{3+}/Mn^{4+}$ concentration: at $x = 0.4$, we observe a similar behavior as for $x = 0.5$. It is only at $x = 0.3$ that a ferromagnetic state prevails in zero magnetic field.

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I. FIGURE CAPTIONS

**Figure 1**: temperature dependence of the DC magnetic susceptibility ($\blacksquare$), ESR manganese susceptibility ($\Delta$) normalized at room temperature and Nd susceptibility ($\square$) calculated from ESR line shifts at $0.33T$ for $Nd_{1-x}Ca_xMnO_3$, $x = 0.3$ (Fig.1a) and $x = 0.5$ (Fig.1b). The magnetic and charge order transitions have been determined by neutron diffraction at zero field.

**Figure 2**: temperature dependence of the Mn ($\blacksquare$) and Nd ($\▲$) ordered ferromagnetic moment determined by neutron diffraction as well as the average ESR line shift ($\bigcirc$) at $95GHz$ for $Nd_{0.7}Ca_{0.3}MnO_3$.

**Figure 3**: ESR absorption line position (corrected from the sample demagnetization field) as a function of temperature in $Nd_{0.7}Ca_{0.3}MnO_3$ taken at $95GHz$ (a) and in $Nd_{0.5}Ca_{0.5}MnO_3$ FM phase taken at $475GHz$ (b). the dotted line corresponds to $g = 1.99$. Insert: ESR absorption spectrum at different temperatures.

**Figure 4**: ESR absorption line position (corrected from the sample demagnetization field) as a function of temperature in $Nd_{0.5}Ca_{0.5}MnO_3$ taken at $95GHz$. The dotted line corresponds to $g = 1.99$. Insert: ESR absorption spectrum at different temperatures.
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(a) $x = 0.3$
95 GHz

(b) $x = 0.5$
475 GHz
$x = 0.5$

95 GHz
Magnetic moment ($\mu_B$) vs. Temperature (K)

- **Mn**: $x = 0.3$
- **Nd**

- Temperature ($T$), Line shift ($T_C$)