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LETTER TO THE EDITOR

Collapse of the charge ordering gap of $Nd_{0.5}Sr_{0.5}MnO_3$ in an applied magnetic field

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Abstract. We report results of tunneling studies on the charge ordering compound $Nd_{0.5}Sr_{0.5}MnO_3$ in a magnetic field up to 6 T and for temperature down to 25 K.We show that a gap ($2\Delta_{CO} \approx 0.5$ eV opens up in the density of state (DOS) at the Fermilevel (E_F) on charge ordering ($T_{CO} = 150$ K) which collapses in an applied magnetic field when the charge ordered state melts. There is a clear correspondence between the behaviour of the resistivity and the gap formation and its collapse in an applied magnetic field. We conclude that a gap in the DOS at E_F is necessary for the stability of the charge ordered state.

In recent years colossal magnetoresistance (CMR) in hole-doped rare-earth manganites has been the subject of intense research efforts [1–4]. These oxides belong to the ABO_3 class of perovskite oxides and contain a mixed valency of Mn, which occupies the B site. The A site is occupied by rare-earth ions like Nd, La, Pr etc or by divalent ions like Pb, Ca, Sr etc. These oxides have the general formula $R_{1-x}M_xMnO_3$, where R is La, Nd etc and M is Ca, Sr, Pb etc. One of the most interesting properties of these materials is the insulator to metal transition which occurs when these materials are cooled below their ferromagnetic Curie temperature (T_c). This phenomenon is shown by materials for $0.2 < x < 0.5$ and also the stability of the ferromagnetic metallic state depends on the size of the A-site cation. When smaller ions are substituted in the A-site, the ferromagnetic T_c is lowered and makes the ferromagnetic state unstable at low T [5, 6]. For certain values of x (particularly when $x \approx 0.5$) the unstable ferromagnetic state can make a transition to an insulating state when cooled much below T_c [7]. This phenomenon is called charge ordering (CO) where there is a real space ordering of Mn^{3+} and Mn^{4+} ions in alternate sublattices. This transition is also associated with large lattice distortions [7–9]. For the particular compound studied, i.e. $Nd_{0.5}Sr_{0.5}MnO_3$, the charge ordering at temperature T_{CO} is accompanied by a spin ordering to an antiferromagnetic state. The type of charge ordering and spin ordering depends on the radius of the R and M cations.

It has been shown in an earlier report that a charge ordering gap opens up in the density of states (DOS) near the Fermi level (E_F) of these materials, when the sample is cooled below T_{CO} [10]. The formation of the gap was detected through tunneling studies using a scanning tunneling microscope (STM). We call this gap the CO gap, Δ_{CO}. In $Nd_{0.5}Sr_{0.5}MnO_3$ the limiting value of $\Delta_{CO}(T \rightarrow 0)$ was measured to be about 0.25 eV and $\Delta_{CO} \rightarrow 0$ as $T \rightarrow T_{CO}$ [10]. Photo electron spectroscopy also detected a gap in the DOS at E_F of similar magnitude for the compound $Pr_{0.5}Sr_{0.5}MnO_3$ [11]. The value of the gap is rather

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large compared to the temperature at which the CO takes place. In fact $2\Delta_{CO}/k_BT_{CO} \approx 40$. Interestingly, the value of Δ_{CO} is comparable to the scale of nearest neighbour Coulomb interaction and a recent theory predicts formation of such a gap on CO transition [12]. A significantly smaller gap was measured in the compound $La_{0.5}Ca_{0.5}MnO_3$ using the infrared absorption method and the observed gap was about five times the transition temperature [13].

The charge-ordered state in materials like $Nd_{0.5}Sr_{0.5}MnO_3$ is unstable in a magnetic field. The applied field can 'melt' the CO state leading to the re-emergence of the ferromagnetic metallic state. The field needed to melt the CO state depends on the temperature. Details can be found in [7, 14].

In this letter we address an important question: what happens to Δ_{CO} when the charge ordered state is melted by the application of a magnetic field? We introduce instability in the CO state by application of a magnetic field and follow the behaviour of Δ_{CO}. The results presented here are the first tunneling studies carried out in the CO state in the presence of a magnetic field. We have carried out the experiment using a variable temperature STM on the widely studied CO compound $Nd_{0.5}Sr_{0.5}MnO_3$. We make the following three main observations: (a) application of the magnetic field reduces Δ_{CO} and for a high enough magnetic field this CO gap collapses ($\Delta_{CO} \rightarrow 0$), (b) the magnetic field at which the CO gap collapses depends on the T/T_{CO} ratio and closely follows the H–T phase diagram obtained from the resistivity data. (c) For $T/T_{CO} \ll 1$ there is a distinct signature of a two phase state, when the magnetic field is varied and the CO state melts.

The sample used in this work was prepared by the solid state method and is polycrystalline in nature. The sample was characterized by x-ray and titration. A detailed description of the sample preparation and characterization is given in [4]. The resistivity (ρ) as a function of temperature is shown in figure 1. The ρ against H curves for two temperatures are shown in figure 2. We find that the $T_c = 240$ K and $T_{CO} = 150$ K which are close to the values $T_c = 255$ K and $T_{CO} = 158$ K found for the single crystalline samples of the same material [7]. The ρ of the single crystal for $T > T_{CO}$ is $\sim 10^{-3}$ Ω cm which is similar to our sample. However, the jump in ρ for the single crystal when T goes below T_{CO}, is about four orders of magnitude [7]. Also, the transition in ρ at $T \approx T_{CO}$ is much sharper for the single crystal. The somewhat smeared nature of the transition for the polycrystalline sample (mostly arising due to disorder) will not affect the determination of the gap Δ_{CO} for $T \ll T_{CO}$ but it can affect the value of Δ_{CO} close to T_{CO}.

The tunneling spectroscopy (TS) investigation was carried out with a home made variable temperature high vacuum STM, using a platinum-rhodium tip. Details of the experimental procedure are given elsewhere [10, 15]. In this experiment, at each temperature $I_t \approx 1.5$ nA was first established at a bias ≈ 1.4 V. Since the observed Δ_{CO} is less than 1 eV, this ensured that the tip did not crash against the sample in order to maintain a constant current when a gap opens up below T_{CO}. The tunneling spectra for $T = 109$ K and for different field values are shown in figure 3. The gap which opens up at E_F (which corresponds to the zero bias) for $T < T_{CO} = 150$ K can be clearly seen for the spectra taken at low magnetic fields and is marked in the figure as $2\Delta_{CO}$.

The ρ against T curve in a field of 6 T is shown in the inset of figure 1 along with the zero field data. The observed results depend on whether the data have been taken for field cooled (FC) or zero field cooled (ZFC) samples. The sequence of the change in T and H is mentioned in the figure caption. The applied magnetic field on the ZFC sample shifts the T_{CO} to lower temperatures (curve 2). Curve 3 shows the data on the FC sample where the CO does not set in down to 4 K in a field of 6 T. In figure 2 we show the ρ against H data at two temperatures $T = 4.2$ K ($T/T_{CO} = 0.028$) and 112 K ($T/T_{CO} = 0.747$). The data are taken for an FC sample.The H–T phase diagram obtained by us agrees qualitatively with the H–T

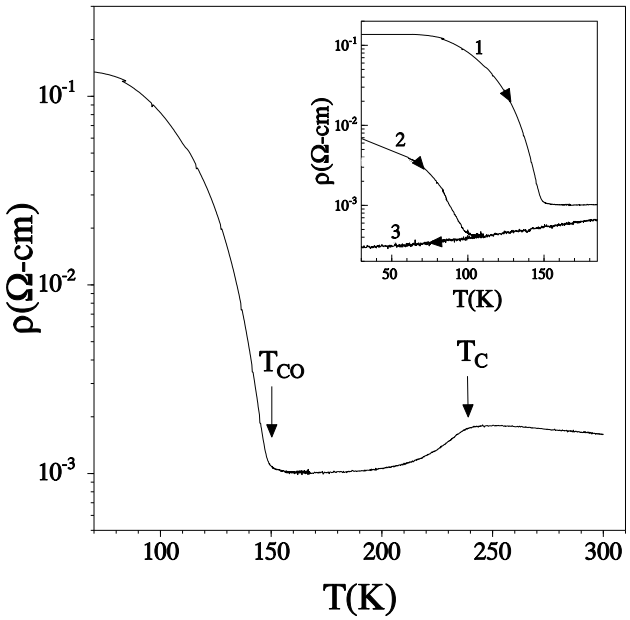

Figure 1. The ρ against T plot for $Nd_{0.5}Sr_{0.5}MnO_3$ for a zero field warming cycle on a zero field cooled sample. The inset shows the effect of a magnetic field on the resistivity behaviour of $Nd_{0.5}Sr_{0.5}MnO_3$. The arrows indicate the direction of the change in temperature. The zero field cooled sample was first warmed in zero field (curve 1), then the zero field cooled sample was warmed in a 6 T field (curve 2) and then the sample was field cooled in 6 T (curve 3).

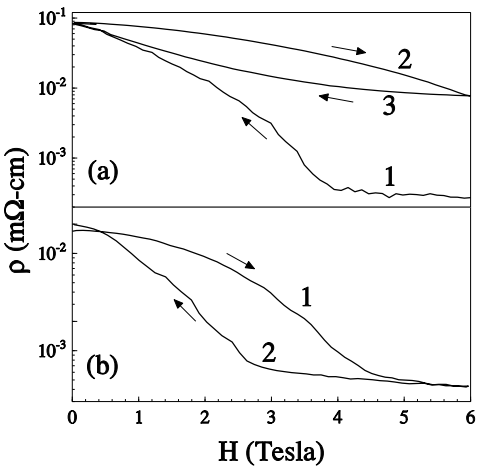

Figure 2. The ρ against H plots at two temperatures (a) 4.2 K and (b) 112 K. In (a), the sample was field cooled to 4.2 K in 6 T. The sequence of the the ρ against H data taken thereafter is marked by the numbers. The sample was then heated in zero field to 112 K and another set of ρ against H data were taken. The sequence is marked by the numbers on the curves.

diagram obtained for the single crystal of the same material [7]. The measurement of Δ_{CO} in a magnetic field follows the same history as in the resistivity measurement.

Steps followed for measuring the variation of Δ_{CO} with the applied magnetic field are

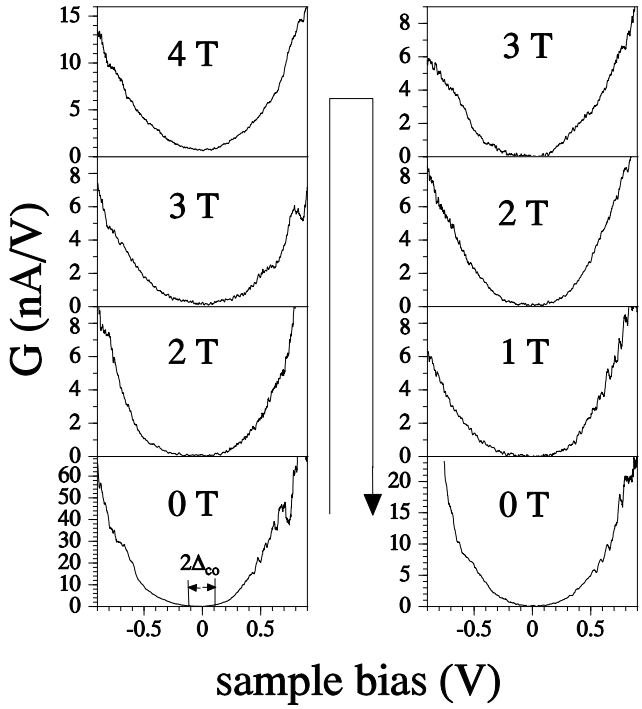

Figure 3. The evolution of $G - V$ curves with magnetic field at 109 K. $2\Delta_{CO}$ is marked for one curve. The sequence of the experiment is marked by the arrow.

described below. The temperatures at which the variation of Δ_{CO} with H are measured, are chosen carefully so that different regions of the H–T plane are probed. We mainly probed two regions in temperature, one deep inside the CO state ($T \ll T_{CO}$) and other close to T_{CO}. The temperature is then stabilized at one such chosen temperature. The tunneling current is established as described earlier and the I–V curves are recorded at different values of H. From the I–V curves the G–V curves are obtained. To move in the other direction of the H–T phase diagram, i.e. to measure the change of Δ_{CO} with temperature in the presence of a constant magnetic field, the field was set at a particular value and the temperature was stabilized at different values where the I–V data were acquired as described earlier. For all these measurements the direction and sequence of the change in T and H was chosen carefully to account for the history dependence of the charge ordering transition.

Figure 3 shows a set of I–V and G–V curves taken on a ZFC sample. The sample was cooled to 109 K ($T/T_{CO} = 0.71$) in zero field. After the temperature stabilization the magnetic field was ramped up to 4 T and down to zero again. One can clearly see from the tunneling curves that the gap in DOS at E_F in zero field collapses in a field of 4 T and reappears again when the field is reduced. This variation of Δ_{CO} with H is shown in figure 4. For field ramped up and down, we observe nearly the same value for Δ_{CO}. The corresponding ρ against H curve is shown in figure 2 where one sees a 'hysteresis' when field is ramped up and down. In the field increasing cycle the ρ collapses at 4.5 T while in field reducing cycle the CO state reappears at 2.5 T. In case of Δ_{CO} the collapse and the onset of the gap takes place at the same field of $H \approx 4$T. In figure 4 we also show the variation of the gap for a ZFC sample at 34 K. Even at a field of 6 T, though the gap is reduced substantially, it does not collapse. This

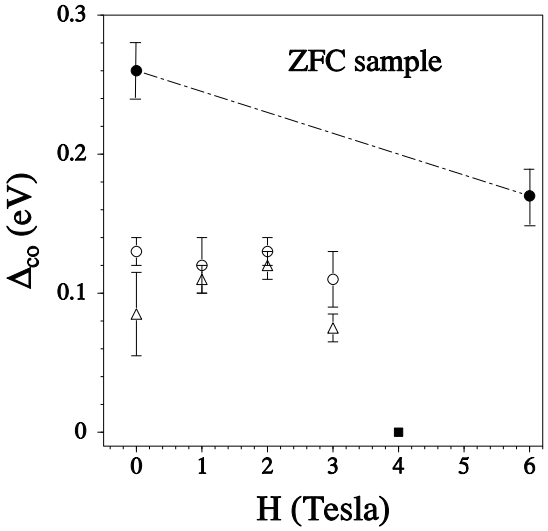

Figure 4. The variation of Δ_{CO} with field at 109 K. The open triangles denote the field increasing run and open circles are the data points obtained during the field decreasing run. The filled square denotes the collapse of Δ_{CO} at 4 T. The filled circles are the values of Δ_{CO} for $T = 34$ K.

corresponds to the resistivity data on a ZFC sample. Probably at a higher field than accessible to us we can melt the CO gap at low temperatures.

The data on FC samples are shown next. In figure 1 it can be seen that for the sample field cooled in 6 T there is no CO state. We also find that no gap opens up in the DOS at E_F in a field of 6 T down to 4.2 K in an FC sample. But we make a very interesting observation regarding the zero bias conductance G_0 which shows a gradual a decrease in a 6 T field as T is reduced below 150 K (the zero field T_{CO}). The zero bias conductance, G_0 is a proportional measure of the DOS at E_F, $N(E_F)$. In order to compare it at different T we normalize it by the tunneling conductance for a bias value far away from the Fermi level (in our case $V = 0.9$ V). The normalized tunneling conductance $G_0/G_{0.9}$ is shown as a function of T in a field of 6 T for the field cooling run, in figure 5. We find that though the CO gap does not appear even down to 4.2 K, there is a big reduction in the normalized DOS at E_F on cooling. The DOS is small but finite at the lowest T. The temperature dependence of $G_0/G_{0.9}$ down to $T = 120$ K is such that a smooth extrapolation (shown by the dotted line in figure 5) will give zero DOS at E_F at $T = 100$ K which is the CO temperature for the ZFC sample, in a field of 6 T (see figure 1). The main difference between the FC and the ZFC samples is that for the former there is a finite but small DOS at E_F even down to the lowest T which stabilizes the metallic state as seen from the ρ against T curves for the FC sample. This is a clear indication that the CO state can only be stabilized in the presence of a gap in the DOS. Even a small DOS at E_F can stabilize the metallic phase as in the FC sample in a field of 6 T. Specific heat measurements have shown that the DOS at E_F is very small for a field cooled sample of the CO compound $La_{0.5}Ca_{0.5}MnO_3$ which has a metallic behaviour of the ρ against T [16]. When the field is reduced to a lower value (staying at low temperatures) the charge ordering sets in at a field of 4 T as per the resistivity data (see figure 2). But the resistivity at the lowest temperature is less than that of of the ZFC sample. This may imply that in the FC sample the CO is incomplete even when the field is reduced to zero. The variation of Δ_{CO} as the field is reduced in a FC sample at low temperatures is shown in the inset of figure 5. One can clearly see the onset of

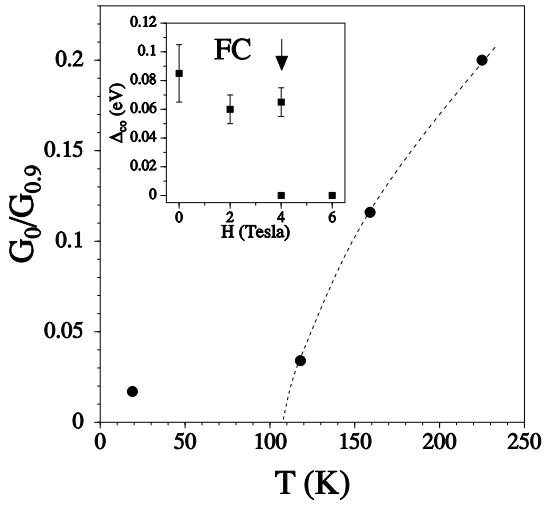

Figure 5. The variation of $G_0/G_{0.9}$ as the temperature is reduced in an applied field of 6 T. The dotted line is a guide to the eye (details in text). The inset shows the variation of Δ_{CO} with magnetic field at 25 K of the sample field cooled in 6 T. Note the two-phase behaviour at 4 T as marked by the arrow.

the CO gap at $H \leqslant 4$ T. Interestingly the value of Δ_{CO} at $H = 0$ is much less than that seen in the ZFC sample. This also points to an incomplete CO in the FC sample, when the field is removed.

In the FC sample we make yet another observation. When the field is reduced at low temperature and the CO state sets in, there is a clear existence of two phases as we can make out from the TS data as shown in the inset of figure 5. At a field of 4 T the measured gap is zero at some positions on the sample and finite at other positions. This behaviour is denoted by the two values of Δ_{CO} at $H = 4$ T and is marked by an arrow.

Our experiment in both FC and ZFC samples clearly establishes that the stability of the CO state under a magnetic field depends on whether there is a gap in the DOS at E_F. In a recent experiment on the compound $(NdLa)_{0.5}Ca_{0.5}MnO_3$ we found that a lattice instability can lead to a collapse of the incipient CO state [17]. In that case also we find that a gap in the DOS at E_F closes when the CO state collapses. We can thus conclude that in these compounds a gap in the DOS at E_F (Δ_{CO}) is a necessary condition for the stability of the CO state.

When a CO state melts in a magnetic field, ρ changes substantially. This can arise either from changes in the mobility, μ, or in the the free carrier density, n, or both. In the specific case of $Nd_{0.5}Sr_{0.5}MnO_3$ the CO state is also a spin ordered AFM state. In a magnetic field it undergoes a metamagnetic transition and becomes ferromagnetic. In the ferromagnetic state (which is stabilized by double exchange interaction) the spin alignment will definitely lead to an enhancement of μ leading to a decrease in ρ. However, if there is a gap in the DOS at E_F which closes in the magnetic field, it will lead to an enhancement of n when the CO state melts. This in turn will reduce the ρ substantially. Our experiment suggests that a substantial contribution in the reduction in ρ on melting of the CO state arises from the gap closing. Independent experimental tests like Hall measurement can establish whether there is indeed an enhancement of n when the CO state melts in a magnetic field.

To summarize we have shown that when a CO state melts in a magnetic field the gap in the DOS at E_F collapses. We have concluded that a gap in the DOS at E_F is needed for

stability of the CO state. As result of the gap closing the free carrier density n should increase on melting of the CO state, leading to a reduction in ρ by orders of magnitude. The magnitude of Δ_{CO} is large compared to the thermal scale $k_B T_{CO}$. At $T/T_{CO} \approx 0.7$ the CO state melts in a field of ≈ 4 T. The scale of magnetic energy required to collapse the CO gap is an order of magnitude less than the scale of Δ_{CO}. In our opinion this anomaly of the energy scales remains an open and relevant issue and it is a feature characteristic of the charge ordering phenomenon in manganites.

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References

[1] von Helmholt R, Weckerg J, Holzapfel B, Schultz L and Samwer K 1993 *Phys. Rev. Lett.* **71** 2331
[2] Chahara K, Ohno T, Kasai M and Kozono Y 1993 *Appl. Phys. Lett.* **63** 1990
[3] Urushibara A, Moritomo Y, Arima T, Asamitsu A, Kido G and Tokura Y 1995 *Phys. Rev.* B **51** 14103
[4] Mahendiran R, Tiwary S K, Raychaudhuri A K, Ramakrishnan T V, Mahesh R, N, Rangavittal and Rao C N R 1996 *Phys. Rev.* B **53** 3348
[5] Hwang H Y, Cheong S-W, Radaelli P G, Marezio M and Batlogg B 1995 *Phys. Rev. Lett.* **75** 914
[6] Mahendiran R, Mahesh R, Raychaudhuri A K and Rao C N R 1996 *Phys. Rev.* B **53** 12160
[7] Kuwahara H, Tomioka Y, Asamitsu A, Moritomo Y and Tokura Y 1995 *Science* **270** 961
[8] Lees M R, Barratt J, Balakrishnan G, Paul D McK and Yethiraj M 1995 *Phys. Rev.* B **52** 14303
[9] Vogt T, Cheetham A K, Mahendiran R, Raychaudhuri A K, Mahesh R and Rao C N R 1996 *Phys. Rev.* B **54** 15303
[10] Amlan Biswas, Raychaudhuri A K, Mahendiran R, Guha A, Mahesh R and Rao C N R 1997 *J. Phys.: Condens. Matter* **9** L355
[11] Chainani A, Kumigashira H, Takahashi T, Tomioka Y, Kuwahara H and Tokura Y 1997 *Phys. Rev.* B **56** R15513
[12] Mishra S K, Pandit R and Satpathy S 1997 *Phys. Rev.* B **56** 2316
[13] Calvani P *et al* 1998 *Phys. Rev. Lett.* **81** 4504
[14] Kumar N and Rao C N R 1997 *J. Solid State Chem.* **129** 363
[15] Biswas A, Suja E, Raychaudhuri A K and Bhat H L 1999 *Phys. Rev.* B **59** 5368
[16] Smolyaninova V N, Ghosh K and Greene R L 1998 *Phys. Rev.* B **58** R14 725
[17] Arulraj A, Biswas A, Raychaudhuri A K, Rao C N R, Woodward P M, Vogt T, Cox D E and Cheetham A K 1998 *Phys. Rev.* B **57** R8115