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LETTER TO THE EDITOR

Direct measurement of the charge ordering gap in $Nd_{0.5}Sr_{0.5}MnO_3$ using vacuum tunnelling

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Abstract. We have used tunnelling spectroscopy (TS) to probe the density of states (DOS) of the rare earth manganate $Nd_{0.5}Sr_{0.5}MnO_3$, which shows a transition to a charge ordered (CO) antiferromagnetic insulating state from a ferromagnetic metallic state. We find that a gap opens up in the DOS around the Fermi level, E_F, as the solid is cooled below the charge ordering temperature T_{CO}. The charge ordering gap (Δ_{CO}) was found to be strongly temperature dependent for $T \approx T_{CO}$ and for $T/T_{CO} < 0.6$ it reaches a limiting value of nearly 0.27 eV. Above T_{CO} the temperature dependence of the DOS at E_F was found to be similar to that of the solids such as $La_{0.8}Ca_{0.2}MnO_3$ which show colossal magnetoresistance but no charge ordering.

Novel electronic transport properties of perovskite oxides of the type $Re_{1-x}M_xMnO_3$ (where Re is La, Nd, Pr etc and M is Ca, Sr, Ba etc) have attracted much interest [1, 2]. These compounds contain a mixed valency of Mn ions with the Mn^{4+}/Mn^{3+} ratio $\approx x/(1-x)$, depending on the exact value of the oxygen stoichiometry. These oxides belong to the ABO_3 perovskite class of structure where the A site is occupied by the Re or M ions and the B site by the Mn ions. For a certain value of x $\approx$ 0.2–0.3 these materials show colossal magnetoresistance (CMR) close to the ferromagnetic transition temperature T_C when fields of a few tesla are applied. These solids show interesting transport properties even without the applied magnetic field [3–6]. An example is the observation of an insulator to metal-like (I–M) transition near the ferromagnetic Curie temperature, T_C. The stability of the ferromagnetic metallic state depends on the band width. When smaller ions are substituted in the A site, the packing of the MnO_6 octahedron changes leading to reduced overlap of the Mn and O orbitals which leads to reduced band width. This lowers the ferromagnetic T_C and makes the ferromagnetic state unstable [4, 7]. Under certain circumstances (particularly when $x \approx 0.5$) the unstable ferromagnetic state can make a transition to an insulating state when cooled much below T_C [8]. This transition occurs due to charge ordering which arranges the Mn^{3+} and Mn^{4+} ions in alternate sublattices. This particular transition is associated with large lattice distortions [8–10]. For the particular solid we have studied, $Nd_{0.5}Sr_{0.5}MnO_3$, 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 observed experimentally often depends on the radii of the Re and A cations. The tendency to charge order and the stability of the charge ordered (CO) state increases with a decrease in the

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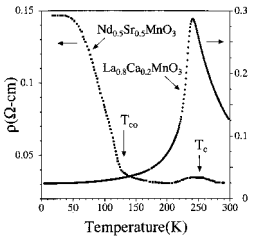

Figure 1. Electrical resistivity (ρ) of $Nd_{0.5}Sr_{0.5}MnO_3$ and $La_{0.8}Ca_{0.2}MnO_3$. T_C and T_{CO} are marked for the sample $Nd_{0.5}Sr_{0.5}MnO_3$.

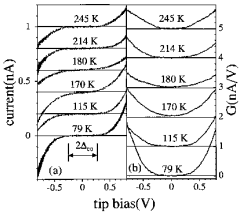

Figure 2. The I–V (a) and the dynamic conductance, $\mathrm{d}I/\mathrm{d}V$–V (b) curves for the sample $Nd_{0.5}Sr_{0.5}MnO_3$ at selected temperatures. Note the gap in the tunnelling data for $T < T_{CO}$ and $T > T_C$. The I–V curves are shifted by 0.2 nA and the $\mathrm{d}I/\mathrm{d}V$–V curves are shifted by 1 nA V^{-1} w.r.t. the curves at 79 K, for clarity. The as-observed gap is indicated in (a).

ionic radius of the above cations, which reduces the conduction band width. For solids such as $Nd_{0.5}Sr_{0.5}MnO_3$, the interesting question is whether a charge ordering gap (Δ_{CO}) opens up in the DOS around E_F as the solid is cooled below the charge ordering temperature T_{CO}. A measure of the value of Δ_{CO} is of great importance because it is needed to fix the scale of the energies involved in charge ordering. We sought to answer this question by direct measurement of the DOS near E_F using vacuum tunnelling spectroscopy (TS) in a variable-temperature scanning tunnelling microscope (STM). TS is particularly suitable for exploring the DOS at and close to E_F ($\mid E - E_F \mid \leqslant 1$ eV). We find that a gap indeed opens up below T_{CO} and we were able to fix its magnitude. This, to our knowledge, is the first direct measurement of the charge ordering gap using TS.

The material used in this work was prepared by the solid state method and is polycrystalline in nature. The samples were characterized by x-ray and titration methods to fix the exact Mn^{4+} concentration. The details of the sample preparation and characterization are given elsewhere [5]. We have also carried out similar TS measurements on the sample $La_{0.8}Ca_{0.2}MnO_3$, which shows the insulator–metal transition at the ferromagnetic transition temperature T_C ($\approx$240 K) but no charge ordering transition. In figure 1 we show the resistivity (ρ) as a function of T for both the materials. From the resistivity data on $Nd_{0.5}Sr_{0.5}MnO_3$ we find $T_C = 250$ K and $T_{CO} \approx 130$ K. This is close to the values $T_C = 255$ K and $T_{CO} = 158$ K found for the single-crystalline samples of the same material [8]. In the single crystal the charge ordering transition was found to be extremely sharp with the resistivity rising to a large value well within 1 K. As we will see below the somewhat smeared nature of the transition for the polycrystalline sample (mostly arising due to disorder) will not affect our 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 TS investigation was carried out with a home made low-temperature STM using

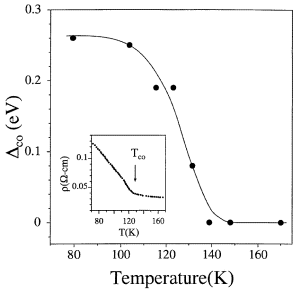

Figure 3. The temperature dependence of the charge ordering gap Δ_{CO} in $Nd_{0.5}Sr_{0.5}MnO_3$. The solid line is a guide to the eye. The inset shows the resistivity ρ close to T_{CO}. The gradual decrease of the gap to zero makes it difficult to find the exact temperature where $\Delta_{CO} \to 0$.

a platinum–rhodium tip [11]. The tip–sample separation (tunnelling distance), for a fixed bias, was kept constant using a feedback loop. For a given set of tip and sample, the tip–sample distance determines the value of the tunnel current I for a given bias. In our experiment, at each temperature the tunnel current $I \approx 1.5$ nA was first established at a bias ≈ 1.4 V. Since the observed Δ_{CO} is much 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}. After stabilizing the current the feedback loop was put to hold mode using a sample and hold circuit, so that the tunnelling distance did not change when the bias was changed. The bias was then swept across a certain range and a set of I–V curves was recorded. From the stored curves an average I–V curve was obtained by taking an average of typically five curves. The time taken to record an I–V curve is around 150 ms. The dynamic conductance ($G = \mathrm{d}I/\mathrm{d}V$) was obtained by taking the numerical derivative of the stored I–V data. A typical I–V curve contains 2000 points. (Note that fixing I and V at a predetermined value ensures that the tunnel junctions at each temperature have similar characteristic parameters. This makes comparison of the tunnelling data at different T physically meaningful.) We baked the sample to 400 K *in situ* in vacuum before starting the experiment. During cool-down the temperature of the rest of the cryostat was lowered first, keeping the sample at high temperature to ensure that condensation of the residual gases occurred on the cryopumped sorption element and not on the sample surface.

The I–V and the G–V curves for a range of temperature 77 K $< T <$ 300 K are shown in figure 2. The data are shown at a few selected temperatures. The evolution of the tunnelling curves as T is lowered below T_{CO} is evident from both the I–V and G–V curves. When there is a finite DOS at and around E_F we find that the G–V curve shows nearly a parabolic dependence on V. This is what is expected in a system with a finite $N(\epsilon = 0)$ [12], where we denote the DOS by $N(\epsilon)$ with $\epsilon = (E - E_F)$. The I–V curve shows a finite slope at zero bias. (In tunnelling experiments the zero bias corresponds to the Fermi level and bias $V = \epsilon/e$.) When a gap Δ_{CO} opens up at the Fermi level, we can clearly see a suppression of G nearly to zero for $| V | < \Delta_{CO}/e$. In figure 3 we have plotted the observed value of the gap (Δ_{CO}) as a function of T. At or near T_{CO} the gap opens up in the DOS and Δ_{CO} rises as T is reduced. However, for $T/T_{CO} < 0.6$, the gap reaches a limiting value of nearly 0.27 eV. We take this as $\Delta_{CO}(T = 0)$.

In figure 4 we have shown the zero-bias conductance G_0 (normalized by $G_{0.5}$, the tunnelling conductance at $V = 0.5$ V) as a function of T. For comparison we have shown in the same figure the ratio $g = G_0/G_{0.5}$ measured for the sample $La_{0.8}Ca_{0.2}MnO_3$ (which does not show charge ordering) in an identical experiment. This ratio can be taken as

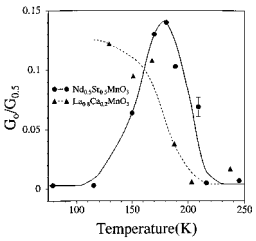

Figure 4. The temperature dependence of scaled zero-bias conductance, $G_0/G_{0.5}$, in the temperature range $T < T_C$. The circles are data points for $Nd_{0.5}Sr_{0.5}MnO_3$, which shows charge ordering, and the triangles are for $La_{0.8}Ca_{0.2}MnO_3$, which does not show charge ordering. The solid and dashed lines are guides to the eye. A typical error bar in evaluating $g = G_0/G_{0.5}$ is shown.

a scaled measure of the value of DOS at E_F. In both the materials $G_0/G_{0.5}$ increases rapidly as T is reduced below the ferromagnetic transition temperature T_C. For the sample $La_{0.8}Ca_{0.2}MnO_3$, which does not show charge ordering, the ratio remains finite as T is lowered much below T_C, indicating existence of the metallic state down to low temperatures. For the charge ordering sample $Nd_{0.5}Sr_{0.5}MnO_3$ the ratio g shows a turn-around below 175 K as $T \to T_{CO}$. Interestingly this is the temperature range where the value of ρ is the least in the temperature range $T_{CO} < T < T_C$. Below this temperature there is a very shallow rise of ρ. This is reflected in g, which shows a drop. Eventually, as the metallic state is lost below T_{CO}, ρ rises rapidly as T is reduced and the ratio $g = 0$. Below 140 K we see a measurable gap opening up as shown in figure 3. The strong temperature dependence of the DOS at E_F (as measured by the ratio g) is thus a hallmark of these manganates. This is unlike conventional metals where the ratio remains T independent in the range of measurement [11]. From our data, as discussed below, it is very difficult to ascertain the correct value of the temperature where $\Delta_{CO} \to 0$, because it goes rather smoothly to zero as opposed to a sudden drop to zero.

The tunnelling data need to be normalized in order to account for the bias dependence arising from the tunnelling barrier alone [11, 13]. In general, when the barrier factor is removed by suitable normalization, the tunnelling conductance $G(V) \propto N(\epsilon)$ where $\epsilon/e = V$. The normalization of the zero-bias tunnelling conductance G_0 by the tunnelling conductance value at a certain bias ($V > \Delta_{CO}/e$) is one such procedure which provides a relative measure of the value of $N(\epsilon \approx 0)$.

There are two issues that we would like to address in our observation: first, the limiting magnitude of the charge ordering gap $\Delta_{CO}(T = 0)$, and second, the order of the transition. Below we discuss these two issues. One likely way the charge ordering takes place is due to Coulomb repulsion U_{nn} of the charges sitting on nearest-neighbour sites. This is the suggested model for the charge ordering in magnetite (Fe_3O_4) [14]. In that case $\Delta_{CO}(T = 0)$ should have values comparable to U_{nn}. The exact value of $\Delta_{CO}(T = 0)$, however, depends on a number of details such as the band width and the strength of the lattice distortion. Assuming absence of any screening in the CO state, we find $U_{nn} \approx 0.38$ eV using a lattice constant of 0.38 nm for these solids and the dielectric constant ≈ 10. Thus $\Delta_{CO}(T = 0)$ as estimated from this experiment and U_{nn} are comparable. Recently a model for charge ordering based on nearest-neighbour Coulomb interaction has been proposed [15]. It was found that for a sufficient strength of U_{nn} (relative to the band width) the CO insulating state will have a lower energy than the ferromagnetic non-CO state and there is a first-order transition leading to a charge ordering gap $\Delta_{CO} \approx 0.45$ eV. This value is close to what has

been seen in our experiment.

The order of the transition is an important issue related to charge ordering. Electronic transport studies on a single crystal of $Nd_{0.5}Sr_{0.5}MnO_3$ have shown that the transition is a first-order transition. However, we find a smooth variation with temperature of the as-observed gap close to T_{CO}. There are two reasons for this observation as we explain below. Our sample, being polycrystalline, will have more local disorder than the single-crystalline samples. Close to T_{CO} when Δ_{CO} is small ($\leqslant$0.1 eV) the disorder energy can be large enough to smooth the transition. This is the likely reason why the transition as seen by ρ is also somewhat smeared compared to that seen in the single crystal. In fact both ρ and the density of states as measured by g show some precursor of the transition starting below 175 K. We have plotted in figure 3 the 'as-observed' value of Δ_{CO} as seen directly from the G–V curve without making any correction to the tunnelling data due to finite temperature. When the gap is small this can lead to smearing of the gap. To remedy this point it will be necessary to analyse both I–V and G–V data using expressions which contain the finite-temperature effects through the Fermi function [11, 12]. However, estimation of a temperature dependent DOS from the tunnelling data is not trivial and requires the use of a model DOS, particularly for the CO phase below T_{CO}. Such modelling needs details which are beyond the scope of the letter, where we report the essential and basic results. These calculations for removing the thermal smearing effects at finite T are expected to remove the uncertainties of Δ_{CO} near T_{CO}, where it is small, and are not going to affect significantly our estimate of the limiting value of the gap as $T \to 0$. In short, close to T_{CO} when the gap is small we cannot definitively determine from our experimental results, directly, whether the transition is continuous or first order and we cannot exactly locate the temperature at which Δ_{CO} becomes zero.

Another important point that we observe in our data is the opening of a small gap above T_C in both the samples. Again the exact magnitude of the gap can be determined after the thermal smearing effects are taken care of, but the estimate from the observed data is around 0.1–0.15 e.V for $Nd_{0.5}Sr_{0.5}MnO_3$. The value of the gap for $T > T_C$ is quite constant with T. This is the value of the gap in the charge excitation spectra above T_C.

To summarize, we have measured the charge ordering gap Δ_{CO} in the compound $Nd_{0.5}Sr_{0.5}MnO_3$ below T_{CO}. At zero T the gap has a limiting value of 0.27 eV. The magnitude of the gap is of the same order as expected from Coulomb interactions of nearest neighbours.

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