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LETTER TO THE EDITOR

Tunnelling spectroscopy and the density of states of $La_{0.8}Ca_{0.2}MnO_3$

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Abstract. We have used tunnelling spectroscopy (TS) to probe the density of states (DOS) near the Fermi level (E_F) of $La_{0.8}Ca_{0.2}MnO_3$, which shows giant magnetoresistance (GMR). The tunnelling current–voltage (I–V) curves and their derivatives (dI/dV) show significant changes for temperatures above and below the ferromagnetic Curie temperature (T_C). We have estimated the energy dependence of the DOS near E_F from the tunnelling spectroscopy data, and this shows a strong temperature dependence, for temperatures above and below T_C.

Observation of giant magnetoresistance (GMR) in perovskite oxides of the type $La_{1-x}A_xMnO_3$ (where A is a divalent metal, Ca, Sr, Ba etc) has recently attracted much interest to the structural, magnetic and electronic transport properties of these materials [1, 2]. These compounds show interesting transport properties even without the applied magnetic field [3–6]. An example is the observation of an insulator to metal-like transition (I–M) near the ferromagnetic Curie temperature, T_C. One of the crucial questions that one would like to answer is the nature of the electronic density of states (DOS) close to the Fermi level (E_F). Since these states are the ones involved in the dc transport, a knowledge of these states is an essential ingredient in our understanding. There is evidence from previous photoelectron spectroscopy [7] as well as optical conductivity studies on the La–Sr–Mn–O system [8] that the DOSs of these solids are somewhat unusual; in particular the DOS near E_F seems to be very low . Optical conductivity studies on the Sr substituted system ($La_{1-x}Sr_xMnO_3$) [8] have shown evidence that the DOS is temperature dependent. We report in this letter an investigation of the DOS using tunnelling spectroscopy (TS). TS is particularly suitable for exploring the DOS at and close to E_F ($|E - E_F| \leqslant 1$ eV). Our aim is to see whether the DOS near E_F, and particularly its energy dependence close to E_F, show any clear dependence on temperature for $T > T_C$ and $T < T_C$. This, to our knowledge, is the first investigation of the DOS of these materials using TS.

The material used in this work has been 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 electrical resistivity and ac susceptibility were also measured to obtain the electrical and magnetic characteristics. The details of the sample preparation and characterization are given elsewhere [5]. The TS investigation was carried out with a home-made low-temperature scanning tunnelling microscope (STM) using a platinum–rhodium tip. The tip–sample separation (tunnelling distance) was kept constant using a lock-in amplifier based feed-back loop. The details of this technique are given in [9].

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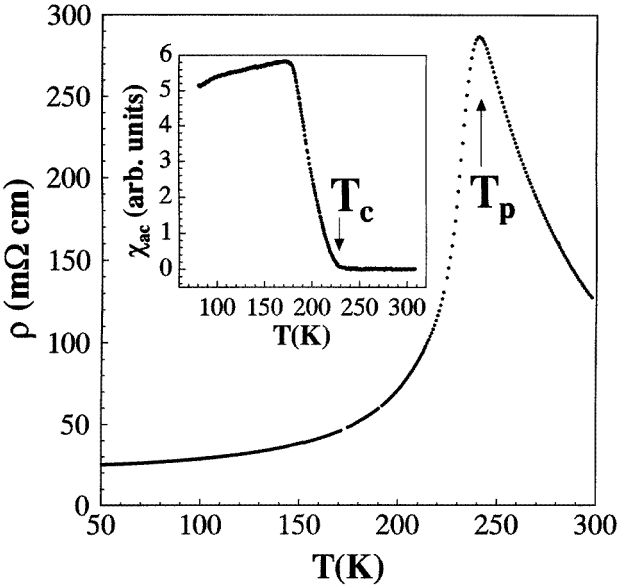

Figure 1. Electrical resistivity (ρ) and ac susceptibility (χ_{ac}) of the $La_{0.8}Ca_{0.2}MnO_3$.

Data were taken for different tunnelling distances and at different points on the surface. The data taken for different tunnelling distances give the same DOS if the tip–sample distance s is properly taken care of as described below. Also we obtain similar TS data on different points of the surface. For a fixed tunnelling distance the bias was swept up and down at a frequency of 12 Hz and the I–V curves thus obtained were stored. From the stored curves an average I–V curve was obtained by taking an average of five curves. The dynamic conductance ($\mathrm{d}I/\mathrm{d}V$) and the scaled dynamic conductance ($\mathrm{d}\ln I/\mathrm{d}\ln V$) were obtained by taking the numerical derivative of the stored I–V data.

In figure 1 we show the resistivity ($\rho(T)$) and ac susceptibilities of a sample of $La_{0.8}Ca_{0.2}MnO_3$, on which we carried out the TS investigations. The material has a slight oxygen excess and an Mn^{4+} content of 25%. The ferromagnetic T_C and the peak in resistivity (T_p) both occur at around 240 K. The close proximity of T_p and T_C is a sign of a good material with proper oxygenation [10]. The material has a saturation magnetization of 3.8 μ_B, which is close to the theoretically expected value and is also another sign of a well characterized material. The average grain size is in excess of 4 μm.

The I–V and the $\mathrm{d}I/\mathrm{d}V$–V curves for two temperatures, 77 K ($< T_C$) and 300 K ($> T_C$), are shown in figure 2. The differences between the tunnelling curves taken at the two temperatures are evident. In particular note the relatively sharp dip in the tunnelling conductance ($\mathrm{d}I/\mathrm{d}V$) at 300 K near the zero bias for $|V| < 0.15$ V. The differences in the two curves taken at two temperatures most likely arises (as shown below) from the differences in the DOS ($N_s(E)$) near the Fermi level, implying that in this class of materials the $N_s(E)$ is strongly dependent on temperature. This is unlike the case in a conventional metal, where the DOS is more or less temperature independent.

The voltage dependence of the tunnelling conductance arises essentially from two sources: (i) the energy dependences of the DOS of the sample ($N_s(E)$) and the tip ($N_t(E)$) and (ii) the energy dependence of the quantum mechanical barrier penetration factor $\tilde{t}$. As the tunnelling conductance is a convolution of $\tilde{t}$ and both $N_s(E)$ and $N_t(E)$, a quantitative

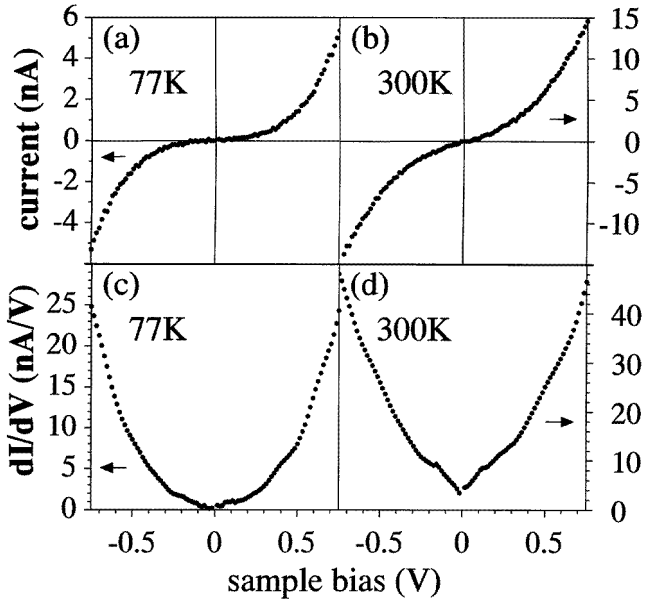

Figure 2. The I–V ((a), (b)) and the dynamic conductance, $\mathrm{d}I/\mathrm{d}V$–V ((c), (d)) curves for the sample $La_{0.8}Ca_{0.2}MnO_3$ at two temperatures, 77 K ($< T_C$) and 300 K ($> T_C$).

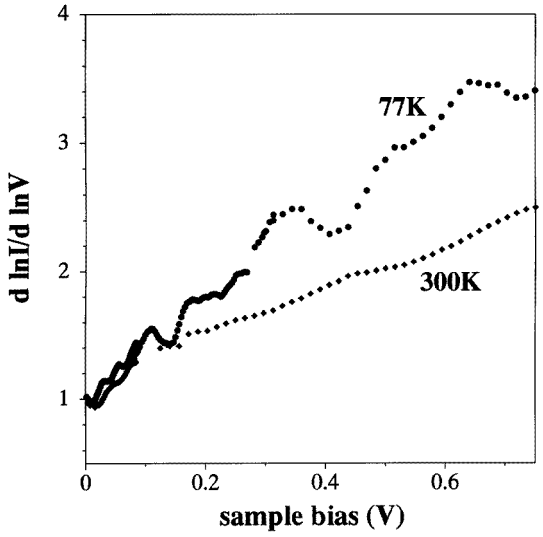

Figure 3. The $\mathrm{d}\ln I/\mathrm{d}\ln V$–$V$ curves for $La_{0.8}Ca_{0.2}MnO_3$ at 77 K and 300 K.

evaluation of $N_s(E)$ requires a knowledge of both $N_t(E)$ and $\tilde{t}$. The estimation of $N_s(E)$ from the tunnelling data thus requires certain approximations to factor out the barrier parameter $\tilde{t}$ by a suitable normalization procedure.

A commonly used normalization procedure often followed in the field of STM-based tunnelling spectroscopy is to use the scaled dynamic conductance $\mathrm{d}\ln I/\mathrm{d}\ln V$ [11] as a

function of V where the dynamic conductance $\mathrm{d}I/\mathrm{d}V$ is normalized by the conductance I/V in order to factor out the energy dependence arising due to $\tilde{t}$. $\mathrm{d}\ln I/\mathrm{d}\ln V$–$V$ curves at the two different temperatures are shown in figure 3. The fact that $\mathrm{d}\ln I/\mathrm{d}\ln V$ is more or less independent of the barrier parameter was confirmed by taking data for different values of the junction conductance and hence different values of tip–sample separation (s). The $\mathrm{d}\ln I/\mathrm{d}\ln V$–$V$ curves at the same temperature, for different values of junction conductance (and hence different values of s) coincide with each other. Since $\tilde{t}$ is a function of s, the coincidence of these curves would imply independence of the quantity $\mathrm{d}\ln I/\mathrm{d}\ln V$ from the barrier parameter $\tilde{t}$. The $\mathrm{d}\ln I/\mathrm{d}\ln V$–$V$ curve thus represents, approximately, the energy dependence of the DOS, $N_s(E)$, where $V = E/e$ and the energy is measured with respect to the Fermi level. (As explained below, the presence of the barrier parameter $\tilde{t}$ weights preferentially the unfilled states of $N_s(E)$ for $V > 0$ and the unfilled states of $N_t(E)$ for $V < 0$ when the bias is applied so that $V > 0$ implies electrons going from the tip to the sample. We therefore show only the data with positive bias, which shows the unfilled DOS for the sample.) The curves, as can be seen, have a strong dependence on the temperature. The curve at 77 K, which is for the ferromagnetic metallic state, rises more sharply as the bias is increased beyond $V = 0.1$ V than the curve at 300 K (the non-metallic state). Also the curve at 77 K shows peak-like features which are not present in the 300 K curve. The most prominent features occur at approximately 0.1, 0.35 and 0.6 V. It is interesting to note that such low-energy features have also been seen in a closely related manganite showing GMR (La–Sr–Mn–O [8]) in optical conductivity measurements. Noting that DOS is the common connection between these two experiments, it is likely that these features arise from the DOS itself.

The scaled dynamic conductance, $\mathrm{d}\ln I/\mathrm{d}\ln V$, does give an approximate energy dependence of the DOS and shows its important qualitative features. However, it does not give a strict quantitative estimate of the energy dependence of the DOS, because the normalization procedure of dividing $\mathrm{d}I/\mathrm{d}V$ by I/V does not eliminate the effect of the barrier parameter $\tilde{t}$ completely [12]. As an alternative procedure we have also used the method suggested in [12] to normalize the data and obtain an estimate of the DOS. The method is described briefly in the following. The tunnelling current between the tip and sample (in the symmetric form) is given by

$$I(s, V, W, T) = c\int_{-\infty}^{\infty} N_s\left(E + \frac{eV}{2}\right) N_t\left(E - \frac{eV}{2}\right)\tilde{t}(s, E, W)\left[f\left(E - \frac{eV}{2}\right) - f\left(E + \frac{eV}{2}\right)\right]\mathrm{d}E \tag{1}$$

where the barrier penetration factor $\tilde{t}$ is given by

$$\tilde{t}(s, E, W) = \exp\left(-2ks\sqrt{2(W - E)}\right) \tag{2}$$

where E is the energy of the electron, c is a constant dependent on the tip–sample effective junction area, s is the tip–sample distance, W is the average work function of the tip and sample surface, V is the bias between tip and sample, T is the temperature, $N_t(E)$ and $N_s(E)$ are the tip and sample DOS, $k = \sqrt{m}/\hbar$ and $f(E)$ is the Fermi function at temperature T. In the above expression all the energies are measured with respect to E_F which is the zero of the energy scale. The tunnelling current I and the dynamic conductance $\mathrm{d}I/\mathrm{d}V$ thus depend on the contributions of the barrier transmission factor $\tilde{t}$, the DOS of the tip and sample and the temperature. From (1) the tunnelling current at very low temperatures ($k_B T \ll eV$) for

a constant tip and sample DOS ($N_t(E) = N_t$ and $N_s(E) = N_s$ are constants) is given by

$$I^0_{\text{const}}(s, V, W) = cN_tN_s \int_{-\frac{eV}{2}}^{\frac{eV}{2}} \tilde{t}(s, E, W)\,\mathrm{d}E \tag{3}$$

$$\frac{\mathrm{d}I^0_{\text{const}}}{\mathrm{d}V} = \sigma^0_{\text{const}}(s, V) = \frac{c}{2}N_tN_s(\tilde{t}(s, eV/2, W) + \tilde{t}(s, -eV/2, W)) \tag{4}$$

where the subscripts on I^0_{const} and σ^0_{const} signify that this is the expected tunnelling current and tunnelling conductance, respectively, for constant N_t and N_s and the superscript denotes the temperature at which they were calculated. The voltage dependence of I^0_{const} and σ^0_{const} thus arises solely from the barrier function $\tilde{t}$. (Due to the presence of the strongly energy dependent barrier parameter, $\tilde{t}$, in the tunnelling equation (1), the DOS obtained by the above procedure gives correct $N_s(E)$ only for $E > 0$, i.e. for the unfilled states of the sample. The same argument also applies for the method using $\mathrm{d}\ln I/\mathrm{d}\ln V$. This has been described in detail in [12].) The barrier parameters W and s are estimated by fitting (4) to our experimental $\mathrm{d}I/\mathrm{d}V$–V curves. We then calculate the tunnelling current for $T = 300$ K and $T = 77$ K, using (1) and the barrier parameters estimated from the fit above and the same constant $N_s(E) = N_s$ and constant $N_t(E) = N_t$. From the tunnelling current thus obtained for $T = 300$ K and $T = 77$ K we obtain $\sigma^{300}_{\text{const}}$ and $\sigma^{77}_{\text{const}}$ (by differentiating the current with respect to V). $\sigma^{300}_{\text{const}}$ and $\sigma^{77}_{\text{const}}$ are the background voltage dependencies of the $\mathrm{d}I/\mathrm{d}V$–V curves at $T = 300$ K and $T = 77$ K respectively, which contain the effect of $\tilde{t}$ only and have to be removed from our experimental data to evaluate the energy dependence of the DOS. So we divide our experimental $\mathrm{d}I/\mathrm{d}V$ at $T = 300$ K and $T = 77$ K by $\sigma^{300}_{\text{const}}$ and $\sigma^{77}_{\text{const}}$ respectively to obtain the DOS at the particular temperature. We have fitted our data taken at different values of the junction conductance (i.e. for different values of s) to the (4) and we obtained an average value of $W \approx 1.9 \pm 0.1$ eV. This is expected since W is a property of the tip and the sample and should not change with junction conductance in the vacuum tunnelling regime. We obtain similar DOS curves from tunnelling data obtained at different values of s. Figure 4 shows the DOS of $La_{0.8}Ca_{0.2}MnO_3$ at 77 K (curve A) and 300 K (curve B), estimated by the method outlined above, for $E > 0$ (for reasons mentioned above). It may be noted that the above procedure is strictly valid when the energy dependences of $N_s(E)$ or $N_t(E)$ are weaker than that of $\tilde{t}$. As a result some quantitative limitations to obtain DOS from the tunnelling data still persist. This method of analysis gives almost a flat DOS near the Fermi level for metals such as platinum, as shown in figure 4 (curve C) which we have evaluated from the tunnelling data, taken in the same apparatus on platinum. In comparison $La_{0.8}Ca_{0.2}MnO_3$ has a much stronger energy dependence of DOS. This method of evaluating the DOS is still semi-quantitative in the sense that we do not obtain an absolute value of the DOS, but we do obtain the correct energy dependence. (This is because we have obtained the $\sigma^{77}_{\text{const}}$ and $\sigma^{300}_{\text{const}}$ independently for a given temperature, so the normalizing factors are different at different temperatures.) Therefore, all the curves have been normalized by the DOS at E_F ($N(0)$). The estimated DOS (for $La_{0.8}Ca_{0.2}MnO_3$) has features similar to those observed in the $\mathrm{d}\ln I/\mathrm{d}\ln V$–$V$ curves given in figure 3. This shows that despite limitations in obtaining an exact quantitative value for the DOS from the tunnelling data, both procedures give an approximate DOS which contains the main qualitative features. The important conclusion from our analysis is that there is a rapid rise of the DOS at 77 K for $E > 0.1$ eV whereas this rise is much slower at 300 K. The sharp dependence of DOS on E, below T_C, implies that a large number of states are available to take part in the conduction process. The data for the energy range $E \leqslant 0.1$ eV, however, are not very clear and a careful look using data of higher resolution is needed.

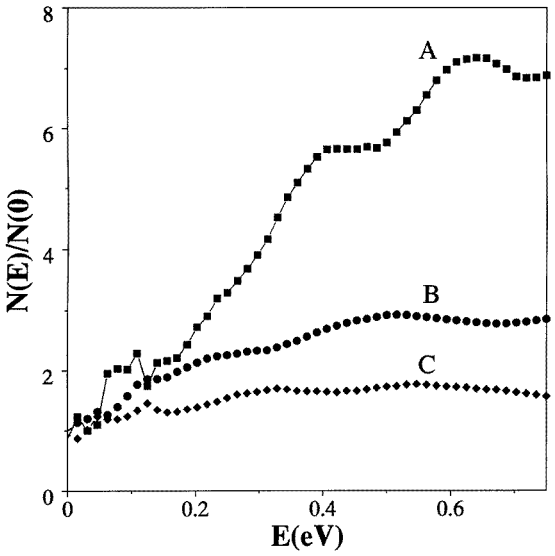

Figure 4. The DOS of the sample $La_{0.8}Ca_{0.2}MnO_3$ estimated from the TS data at two temperatures. Curve A is for $T = 77$ K and curve B is for $T = 300$ K. Curve C is the DOS of platinum at 300 K. Note the negligible variation of the DOS with energy for platinum, compared to that of the oxide. For these data the tip–sample separation was around 14–18 Å. $E = 0$ corresponds to the Fermi level.

There is one particular observation in our data that we cannot explain. This is the symmetric nature of the tunnelling data (see figure 2). It is expected that in a junction of this type the tunnelling barrier will be of a trapezoidal type, which will not give symmetric tunnelling curves. We are currently investigating this particular issue.

In conclusion, we have shown here that the DOS of $La_{0.8}Ca_{0.2}MnO_3$ near E_F, measured using TS, has a strong dependence on temperature. We have shown this only for the unfilled states (above E_F) of the sample for reasons explained above. We have used two methods to normalize the tunnelling conductance and obtain an estimate of the DOS. The estimated energy dependence of the DOS agrees well with that deduced from x-ray absorption and photoelectron spectroscopy studies [7]. Further work is in progress to study the change in the TS spectra over a wider temperature range and as the temperature is continuously changed across the T_C and also to determine the absolute value of the DOS at E_F which is not possible with the present set of data.

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