Work function changes in the double layered manganite La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$

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We have investigated the behaviour of the work function of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ as a function of temperature by means of photoemission. We found a decrease of 55 ± 10 meV in going from 60 K to just above the Curie temperature (125 K) of the sample. Above $T_C$ the work function appears to be roughly constant. Our results are exactly opposite to the work function changes calculated from the double-exchange model [1], but are consistent with other data. The disagreement with double-exchange can be explained using a general thermodynamic relation valid for second order transitions [2] and including the extra processes involved in the manganites besides double-exchange interaction.

I. INTRODUCTION

Doped manganese oxides containing a significant proportion of Mn$^{4+}$ ions exhibit colossal magnetoresistance (CMR), an effect whereby the resistivity around the Curie temperature ($T_C$) of the material dramatically diminishes when a magnetic field is applied. This effect was first discovered in the cubic perovskite manganese oxides [3] and later extended to other manganites from the same family, containing one or more MnO$_2$ layers [4]. Within this so called Ruddlesden-Popper series, the double layered (n=2) branch has received tremendous interest as the CMR effect is even stronger than in the 3D compounds (n=∞) [5]. The strong anisotropy in these layered materials, rendering the materials quasi two-dimensional, is responsible for this increased effect. Another important discovery was made with poly-crystalline films without GB’s. This difference in work function between the PM and FM phases arises naturally from the double-exchange (DE) model [6], which is the traditional starting point for explaining the MR phenomenon in the manganites, and in the following section we will take a more in-depth look at this model. Although the simplified DE model alone can by no means fully account for the rich and diverse properties of the actual compounds, it is widely accepted as a good basis for their explanation. In real materials, other aspects play a role, such as the influence of the competing antiferromagnetic super exchange interaction [7], or the strong interplay between electrons and lattice [8], to name but a few. However, in view of the experiments by Klein et al. it remains essential to investigate whether this work function difference predicted by the DE model does indeed exist.

II. THE DOUBLE-EXCHANGE MODEL

In this section we will review parts of the DE model, in order to present a complete picture. In Fig. 1 we qualitatively demonstrate the idea of this form of direct exchange. According to Hund’s rules, each separate Mn$^{3+}$ or Mn$^{4+}$ ion will be in high spin configuration, and this will be our starting point. In fact, the DE model assumes that the intra-atomic exchange integral $J_x$ can be considered infinite. When placed in octahedral surroundings (Fig. 1a) the Mn 3d orbitals splits up further into a $t_{2g}$ and an $e_g$ level. In the layered manganites the symmetry is further reduced to tetragonal, because of the slight difference in Mn-O distances within the MnO$_2$ bilayer plane compared to those directed out of it [9,10]. In Fig. 1c this complete 3d orbital splitting is drawn, and also the localized $t_{2g}$ spin $S = 3/2$ and the itinerant $e_g$ spin $\sigma$ are indicated. Although in $D_{4h}$ symmetry the $t_{2g}$ level theoretically splits up into a $b_{2g}$ $(xy)$ and an $e_g$ $(xz, yz)$ level, $O 1$s XAS measurements have indicated that a splitting...
between these two levels was not clearly observed and thus the \( t_{2g} \) level remains basically unchanged \[13\]. In the same measurement an effective splitting of 0.4 eV was observed between the two \( e_g \) orbitals, which has turned out to be very important in understanding our measurements, as will become clear later on.

The lowest unoccupied level for a Mn\(^{4+}\) ion is now the \( 3z^2-r^2 \) majority spin orbital, which can contain at maximum one electron. At this point we would like to stress that this level diagram is valid for on-site excitations only. If we want to look at electron hopping between adjacent Mn ions, the energy needed for transfer will also depend on the number of initial 3d electrons on both ions. In the DE model larger charge fluctuations are neglected: electron transfer from a 3+ to 3+, or from a 4+ to 4+ ion is costlier in energy by a factor \( U \), the on-site Coulomb repulsion energy, than hopping from a 3+ to a 4+ ion. Therefore, these processes are not taken into consideration in the double-exchange model, effectively this means that one assumes \( U \) to be infinite. Furthermore the assumption \( J_{ex} \rightarrow \infty \) excludes the low spin configuration of \( \sigma \) and \( S \) and will also not allow electron transfer to an ion with \( t_{2g} \) spin \( S \) anti-parallel to the initial one. These assumptions concerning \( U \) and \( J \), combined with the crystal field splitting, lead again to a description of the charge carriers in terms of a single electron, band picture. The only ingredient remaining is the spin-correlation between adjacent manganese ions. This is reflected in the dependence of the effective hopping integral \( t_{eff} \) on the angle \( \theta \) between neighbouring \( t_{2g} \) spins \( S_i \) and \( S_j \) (see Fig. 1b).
and a coolable Janis cryostat. The temperature was measured using a calibrated Pt-thermocouple. The pressure inside the vacuum chamber was always $3 \cdot 10^{-11}$ mbar or better. In order to see the low kinetic energy cutoff of the spectrum, which gives us the work function, we have to bias the sample by a few volts, in order to push the ‘zero’ kinetic energy electrons out of the energy region where the analyzer can no longer respond linearly to counts (roughly the region from 0 to 1 eV). It is, however, important to keep the bias as low as possible to avoid distortion of the spectra due to the build up of electric fields.

We note here that this method can not provide accurate absolute values of the work function, but as we are only interested in changes in the work function, this method is applicable, provided of course, that the changes are large enough compared to the energy resolution and statistics of the measurements. In order to determine the accuracy of our system, we performed a cyclic temperature dependent test measurement on a polycrystalline silver sample (see Fig. 2), which was sputtered and annealed twice in situ. Fig. 2a shows an example of the Fermi edge and Fig. 2b shows the low energy cutoff, both at 2 volt bias and T=50 K. In Fig. 2c we show the work function as a function of temperature. At each temperature the cutoff position was also determined as a function of bias to monitor the optimum bias voltage range. We assumed that the cutoff is defined by a step-function convoluted with a Gaussian describing the broadening of the cutoff in energy, due to the finite energy resolution of the analyzer and temperature. We noticed, from fitting, that measurements with a bias between 1.5 and 3 volt were trustworthy on all accounts. At each measured temperature, the reproducibility is remarkable (less than 5 meV difference), but over the entire temperature range of 50 K to 150 K, we observed an average value of $4.403 \pm 0.013$ eV, assuming the work function of silver should not show a temperature dependence. The apparent contradiction between reproducibility at a particular temperature and dissimilar values at different temperatures can be due to slight movements of the measuring spot with temperature, caused by expansion and contraction of the cryostat. On a polycrystalline sample this can mean a difference in average value of the work function over the various exposed crystal faces within the spot, and should therefore not give any problems on a single crystal. We also performed the silver measurements to obtain an accurate value for the Fermi edge, since on La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ a clear edge is not observed in ARPES measurements [7]. The numerical value of the work function is obtained through

$$\Phi = 21.22 - (E_F - CO)|_{bias} + bias. \quad (1)$$

Where 21.22 (eV) stands for the energy of the incoming UV light. The Fermi energy $E_F$, and the cutoff energy CO, are both measured with a bias voltage applied.

Before discussing the results it is important to stress that these very surface sensitive measurements need to be performed quickly, because the surface of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ deteriorates rapidly [8], probably resulting in a more lanthanum rich compound at the surface [11].

IV. RESULTS

In Fig. 3 we show the results of the measurements on the La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ single crystal. Fig. 3a shows an example of a low energy cutoff at 2 volt bias and 60 K. In Fig. 3b we show three broad spectra, one taken at the start of the measurements right after the cleave (black, solid), one just after finishing the work function measurements (grey, dashed) and the last one taken 9 hours after the cleave (black, dotted) all at 60 K. The spectrum taken just after the last work function measurement shows an increase in the 9 eV peak, but this is still small compared to the “fully aged” sample. After this point in time we found the values of the work func-
other recurrent behaviour we found in different measurements is the increase of the work function with time, i.e. with surface degradation. This is not surprising considering the low starting value of the work function: ± 3.56 eV at 60 K, which is almost a full eV lower than that of silver.

Quantitatively we find Φ to decrease by ≈ 55 ± 10 meV, going from 60 K (≈ 1/2 T_C) to 180 K (≈ 3/2 T_C), which is in the same order of magnitude as the 0.1 eV predicted by Furukawa. Qualitatively, on the other hand, we find Φ_{FM} > Φ_{PM}, which is exactly opposite to his conclusion (and to our intuitive band picture of Fig. 1).

V. DISCUSSION

A number of explanations can be put forward to explain this latter disagreement. The most simple solution would be to infer from this measurement that the tetragonal distortion is not large enough to split the e_g level into x^2 − y^2 and 3z^2 − r^2 levels. In that case, the e_g majority spin band, which can contain a maximum of two electrons, is only 30% filled, and one would indeed expect to find Φ_{FM} larger than Φ_{PM}. This however, would put us in disagreement with the experiments by Park et al.

To find a general constraint for the solution to this problem, let us look at it from the more general point of view of thermodynamics. In the beginning of the nineties a universal relation was deduced for the behaviour of the chemical potential at the transition temperature of any second order phase transition. It states that there will be a change Δ in slope of μ versus temperature at T_C, provided that T_C depends on particle density n:

$$\Delta \left( \frac{d\mu}{dT} \right) = \Delta C \frac{d\ln T_c}{dn_e}$$  \hspace{1cm} (2)

In which the subscript e indicates that we are dealing with the electronic part of both μ and n. Since this formula was derived for constant pressure as well as for constant volume conditions, the specific heat C can be taken to be either C_V or C_p, as long as the chemical potential measurement is performed under the same conditions. We hereby define the difference Δ (both in C and in dμ/dT) as the value above T_C (the disordered state) minus the value below T_C (ordered state). In our experiments we have measured the work function, which means that the change at T_C will have the opposite sign compared to μ. From our data set we can only get a rough estimate (assuming dμ/dT = 0 above T_C) of Δ(dμ/dT) = −Δ(dΦ/dT) ≈ −4 · 10^{-4} eV/K. The change in the specific heat was obtained from figure 2b in the paper of Gordon et al. We find a change ΔC = −54 J mol⁻¹ K⁻¹ or −8 · 10⁻⁵ eV/K referred to a unit of MnO_2, since the chemical potential is influenced (mainly) by the processes within the MnO_2 layers. To
find the slope of $T_C$ versus particle density for the double layered manganites, we used the data taken from three different papers \cite{21,22,23} and averaging the slopes we found for $x = 0.4$ that $d\ln T_C/dx = -3.3 \pm 0.4$ (see Fig. 4). This is, however, the slope depending on the concentration of holes, for electrons we should therefore use the theoretical DE prediction. We therefore expect that a sample with a hole concentration $x$ smaller than 0.36 will show an increase in $\mu$ in the ferromagnetic phase, in accordance with Furukawa’s prediction for the DE model. Before concluding, we would like to comment on the fact that our sample is quasi two-dimensional, and that the predictions made by Furukawa are based on a simple three dimensional picture. The consequence of this is mainly that short-range magnetic correlations can remain above $T_C \simeq 36$ in bilayered samples like ours, almost up to room temperature, and they tend to smear out the effect in $\mu$ at the phase transition over a larger temperature range. Since we still observe a clear change comparing measurements below and above $T_C$, we claim that these short range correlations are not strong enough to obliterate the effects of the 3D long range order setting in at $T_C$. Lastly, there has been some debate regarding the precise nature of the phase transition in $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ \cite{23,24}, but since no dependence on heating rate was observed in the measurements of Gordon et al. we believe the phase transition to be at least of second order, which is an important ingredient in our explanation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig.png}
\caption{Top panel: Curie temperature as a function of hole doping for the layered manganites taken from ref. 15, 16 and 17 respectively. Bottom panel: $d\ln T_C/dx$ versus hole doping.}
\end{figure}

VI. CONCLUSION

From photoemission measurements on slightly biased $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ we found a decrease in the work function with increasing temperature below $T_C$, and a roughly constant value above $T_C$. The quantitative decrease is $55 \pm 10$ meV, going from 60 K to 180 K. Although the number of measured temperatures is small, we are confident that our measurements do show the true dependence on temperature, based on a number of reasons: 1) All our successful cleaves (always performed at 60 K) on $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ show the same downward trend with temperature, irrespective of the low absolute value of the work function at 60 K, 2) The presented measurement is self-consistent within the two temperature cycles, 3) As a function of increasing surface degradation the work function increases, opposite to the temperature trend, 4) The measured effect in $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ is far more substantial than the deviations with temperature measured on a poly-crystalline silver sample. Our measurements show the opposite trend to that predicted by Furukawa. We believe this stems from the fact that in the real $\text{La}_{2-2x}\text{Sr}_{1+x}\text{Mn}_2\text{O}_7$ system, the behaviour of $T_C$ with doping $x$ is different than that inferred from a simple double-exchange picture. The reason for this is that, in the DE model, the influence of the intra-atomic exchange interaction $J_{zz}$, and the on site Coulomb repulsion energy $U$, although initially taken into account for selecting the dominant processes, are from there on neglected. It is however obvious that, neither $U \approx 4$ eV \cite{23} or 7 eV \cite{24} nor $J_{zz} = 3J_H \approx 2.7$ eV \cite{25}, in Mn$^{4+}$ can be considered infinite with respect to the bandwidth.
W (∼1 − 1.5 eV). Therefore the continuing influence of \(U\) and \(J − \alpha r\) on the charge dynamics of the manganites is not to be discarded. In strongly correlated electron models where these parameters, together with hybridization, are kept in play, one generally finds asymmetrical doping behaviour of physical properties, such as the spectral weight function in photoemission, a direct link to the kinetic energy per particle [20]. Consequently, it is then no surprise that for the manganites the transition temperature also does not peak at half-filling as the DE model predicts, but rather at lower hole doping \(x \approx 0.36\) (analogous to the perovskite manganites: \(x \approx 0.31\), and the high Tc cuprates: \(x \approx 0.2\)). In order to come to a full understanding of the manganites, we want to emphasize therefore that it is crucial to retain the electron correlation parameters in the description of the charge dynamics and thus to go beyond the effective single electron approximation of double-exchange.

Our findings are furthermore consistent with a general thermodynamical relation for the difference in \(\Phi\) across a second-order phase transition. It validates the observed trend in our measurements and links it to the difference between the simple DE model and the real complexity of the manganites. It would be interesting to further test this hypothesis by performing a work function measurement on a \(\text{La}_{2−2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7\) sample with \(x < 0.36\), where the slope of \(dT_c/dx\) is opposite to ours and agreement with the DE model would be expected. Our quantitative value for the work function change is in accordance with the order of magnitude inferred by the double-exchange model, suggesting \(J_{ex}\) and \(U\) are large enough, compared to the bandwidth \(W\), for double-exchange to be the right starting point. Most importantly, the observed chemical potential difference is large enough for the explanation put forward by Klein et al., regarding the way grain boundaries affect (magneto)-resistive properties in films, to be valid.

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