Temperature-Dependent Pseudogaps in Colossal Magnetoresistive Oxides

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Direct electronic structure measurements of a variety of the colossal magnetoresistive oxides show the presence of a pseudogap at the Fermi energy \(E_F\) which drastically suppresses the electron spectral function at \(E_F\). The pseudogap is a strong function of the layer number of the samples (sample dimensionality) and is strongly temperature dependent, with the changes beginning at the ferromagnetic transition temperature \(T_c\). These trends are consistent with the major transport trends of the CMR oxides, implying a direct relationship between the pseudogap and transport, including the “colossal” conductivity changes which occur across \(T_c\). The \(k\)-dependence of the temperature-dependent effects indicate that the pseudogap observed in these compounds is not due to the extrinsic effects proposed by Joynt.

The colossal magnetoresistance (CMR) effect recently discovered in the manganese oxides (La\(_{1-x}\)B\(_x\)MnO\(_3\) (B=Sr, Ca, Ba) and Li\(_{2-2x}\)Sr\(_{1+2x}\)Mn\(_2\)O\(_7\)) is a phenomenon which dramatically displays the strong correlation between magnetism and electronic conduction \(\llbracket3\rrbracket\). At low temperatures \(T\), properly doped manganese oxides exhibit ferromagnetic metallic behavior, while at high \(T\) they exhibit paramagnetic insulating behavior. If one starts at \(T\) slightly above \(T_c\), the application of a magnetic field can play a similar role as \(T\) by driving the material through the insulator-metal transition. This is the CMR effect.

Traditionally, the starting point for understanding the electronic and magnetic properties of the CMR oxides is the double exchange (DE) model originally studied by Zener, de Gennes, and Anderson and Hasegawa \(\llbracket3\rrbracket\). DE says that the hopping probability \(t\) for an \(e_g\) symmetry (conduction) electron to hop from one site to the next is \(t = t_0 \cos(\theta/2)\), where \(t_0\) is the bare hopping probability and \(\theta\) is the relative angle between two \((12g)\) spins (see Fig. \(\llbracket3\rrbracket\)). A ferromagnetically ordered sample has \(\theta = 0\) and so a full hopping probability, while an antiferromagnetically ordered sample has \(\theta = 180^\circ\) and no probability of hopping. The paramagnetic case corresponding to \(T > T_c\) can be approximated by \(\theta = 90^\circ\), i.e. \(t\) should be reduced to \(\cos(90^\circ/2)\) or about 70% of its original value. A calculation of the bandwidth \(W\) change with temperature is done more precisely by Kubo \(\llbracket1\rrbracket\), with the result coming out very similarly to our simple explanation. Directly associated with the change in hopping probability is the effect on the \(E\) vs. \(k\) relations and \(N(E_F)\), which is schematically illustrated in Fig. \(\llbracket3\rrbracket\) vs. \(\llbracket4\rrbracket\). The roughly 30% changes in \(t\) and \(W\) expected across the transition will contribute to similar changes in the electronic mobility \(\mu\) and conductivity \(\sigma\). Since the conductivity changes across the transition may be many orders of magnitude instead of just a 30% effect (see Fig. \(\llbracket4\rrbracket\) and reference \(\llbracket4\rrbracket\)), it has been argued that additional physics must be necessary to explain the conductivity changes in the manganites \(\llbracket5\rrbracket\). The results presented here confirm these ideas but go one farther, indicating that at least for the layered samples, DE is probably not even the dominant mechanism but is instead supplementing some other more important physics.

We performed Angle Resolved Photoemission (ARPES) experiments on cleaved single crystalline samples of the layered and pseudocubic manganites at the Stanford Synchrotron Radiation Laboratory (SSRL) using a 50 mm hemispherical analyzer. The energy resolution was about 40 meV FWHM and the \(k\) resolution was better than \(\pm 0.05\pi\) in the 1st Brillouin zone of the photon energy of 22.4 eV. The samples were grown by the floating-zone method \(\llbracket6\rrbracket\). The surfaces of the layered samples were mirror-like and high quality low energy electron diffraction patterns were easily obtainable, with no evidence of extra superlattice spots. Other indications of the quality of the surfaces are the large amount of \(E\) vs. \(k\) dispersion observed and the \(T\) dependence, which as we will see has many similarities to the Drude part of optical conductivity measurements whose probing depth is typically several thousands of Å \(\llbracket5\rrbracket\). We note that the recent claim that the surface magnetism of the manganites is different from that of the bulk \(\llbracket5\rrbracket\) is on strained thin films which have undergone a complicated surface cleaning procedure. We consider these films to have a non-ideal surface, which is further confirmed by a lack of \(E\) vs. \(k\) dispersion from these surfaces.

Figure \(\llbracket1\rrbracket\) shows the full valence band spectra of La\(_{1.2}\)Sr\(_{1.8}\)Mn\(_2\)O\(_7\) along the \((0,0) - (\pi,0) - (\pi,\pi)\) symmetry line at 200 K (paramagnetic state) and at 50 K (ferromagnetic state). Figure \(\llbracket2\rrbracket\) shows the near-\(E_F\) data from the same sample taken under identical conditions. All the spectra have been normalized by the total area of the main valence-band spectra at the highest \(T\) at each \(k\)-space point. The procedure for the angle-integrated spectra of cubic compounds is the same. All 200K data were taken first, immediately after the sample cleave which was also performed at 200K. At each emission angle the
valence band and near-$E_F$ spectra were taken concurrently without a sample reoptimization or realignment. After all 200K data were finished the sample was cooled to 50K and the measurement procedure was repeated. Therefore the low temperature spectra are more aged than the high temperature spectra, accounting for the slightly higher (but still very small) “dirt” peak at -10 eV observed in the low temperature spectra. We note that with continued ageing the dirt peak continues to grow and the emission intensity near $E_F$ is found to decrease. The fact that our low temperature spectra show the same or even more weight than our high temperature spectra implies that the temperature dependent reduction in the spectral weight at high temperatures discussed here is not due to an ageing effect. We also checked the reproducibility of the $T$-dependent changes by several cleaves including warming runs and have confirmed that the qualitative changes were much larger than the ageing effects.

Figure 3(A) shows two major features, labeled $\alpha$ and $\beta$, the centroids of which are plotted as a function of $k$ in Fig. 3(B) which also includes the $e_{g\uparrow}$ bands from our LSDA+$U$ band structure calculations [11]. According to the calculation as well as our polarization-dependent photoemission experiments [11], $\alpha$ has primarily $d_{x^2-y^2\uparrow}$ symmetry and $\beta$ has primarily $d_{3z^2-r^2\uparrow}$ symmetry. We see that the dispersion and energy position of the centroids of the ARPES features is in relatively good agreement with the calculations except near $E_F$, where a pseudogap suppresses the weight at $E_F$. Additionally, the experiment shows a $k$-space locus of lowest energy excitations forming a large "ghost" Fermi surface (FS), [11] which is in rough agreement with FS calculated by the LSDA band theory. This large hole FS is also consistent with recent Hall effect measurements. [12]

Robert Joynt has recently argued that the pseudogap observed in photoemission experiments in the manganites and possibly many other compounds may be due to extrinsic loss effects [13]. It is important that we can exclude this possibility before analyzing our data in more detail. In Joynt’s proposal, the electric field created by the outgoing photoelectron produces ohmic losses, lowering the kinetic energy of the ejected photoelectron. This would show up in the spectra as a pseudogap, even if there was not one in the true density of states, and should be most important for highly resistive samples.

The data of figure 3(A) can directly address this question. Some of the curves (for example $\vec{k} = (\pi, 28\pi)$) show a significant shift away from $E_F$ with temperature, while other curves (for example $\vec{k} = (46\pi, 0)$) show a minimal effect. The minimal temperature-dependent changes observed at $(46\pi, 0)$ put an upper limit on the magnitude of the effects that could be due to Joynt’s extrinsic losses, and so the dramatic changes observed at $\vec{k} = (\pi, 28\pi)$ should be of intrinsic origin. Additionally, since there is no effect at some angles from a two-order of magnitude change of resistivity, it should also be clear that the weaker pseudogap observed at $(\pi, 28\pi)$ at 50K in the spectra is not due to ohmic losses (the pseudogap should be measured at the $k$ where the peak is closest to $E_F$, which occurs at $(\pi, 28\pi)$). In a recent comment and reply, [11][13] Joynt agrees that the spectral weight suppression in these compounds appears to be intrinsic.

We discuss two main aspects of the $T$-dependence of the data of Fig. 3 and 3: (1) The data shows only a very small change in $W$, in contradiction with the DE prediction. (2) There are large changes in the spectral intensity at $E_F$ for $k$ near $(\pi, 0.28\pi)$, which is due to the opening of a pseudogap.

(1) DE tells us that $W$ should decrease by about 30% when going from the ferromagnetic to the paramagnetic phases (see Fig. 2). In our measurement, the highest binding energy occupied states that are clearly resolvable are at $(0.18\pi, 0)$ and a binding energy near 1.6 eV. Upon going to the high $T$ paramagnetic state, DE theory predicts that these states should show a significant (~30%) energy shift towards $E_F$, i.e. they should appear centered around 1.1 eV. Instead, we observe a small energy shift of approximately 0.06 eV, or a change in $W$ of just a few percent (0.06/1.5=4%). This lack of a change in $W$ should imply that a short-range (in-plane) ferromagnetic correlation still exists above $T_c$. This is consistent with a recent neutron scattering measurement from the same sample source which showed in-plane short-range ferromagnetic order as high as $T=284$ K [16].

(2) In contrast to the small $T$ dependent changes at $(0.18\pi, 0)$, there are dramatic $T$ dependences near $k=(\pi, 0.28\pi)$, which corresponds to a predicted FS crossing point as well as the point of closest approach of the peak centroid to $E_F$. The spectra at the higher $T$ is pushed farther away from $E_F$ and the spectral intensity near $E_F$ is reduced. This behavior represents the opening of a (pseudo)gap centered at $E_F$ with $T$. In particular, a gap centered at $E_F$ is expected to affect the states near $k_F$ strongly and those away from $k_F$ much more weakly, as observed in our data. We call this gap a pseudogap because the edges of the gap are “soft” and because the spectral weight at $E_F$ is not always completely suppressed.

We note that even at low $T$ the spectra at $(\pi, 0.28\pi)$ remain pulled back from $E_F$, and the spectral weight reaching $E_F$ is vanishingly small. This indicates that the pseudogap is active at low as well as at high $T$, although it is stronger at high $T$. Figure 3(A) shows this $T$ dependence in more detail from a different La$_{1.2}$Sr$_{1.8}$MnO$_3$ sample, also measured while cooling. The triangles indicate the spectral weight found very near $E_F$ obtained over two different energy integration windows, and the diamonds show the energy shift of the leading edge (at two different positions on the edge) as a function of $T$. It is seen that both the near-$E_F$ weight and the position of the leading edge begin increasing at $T_c$ and then rise.
monotonically without saturation as the $T$ is lowered.

Figure 4(B) shows that a similar $T$-dependent behavior is found for the perovskite samples, although this time the $T_c$ is very different and we plot the angle-integrated DOS $[17]$. As in figures 2 and 3, the high temperature data was measured prior to the low temperature data, negating the possibility that the trends observed here are due to ageing. A portion of the raw data is shown in the upper right hand corner of Fig. 3(A), with similar raw data being presented by other groups $[13,14]$. The high $T$ data does not exhibit any weight right at $E_F$, while the low $T$ data exhibits a clear Fermi-edge cutoff indicating a finite DOS at $E_F$.

The left vertical scale of Fig. 4(B) corresponds to the ratio of the observed weight to the weight deduced from the band structure calculations $[21]$. The way in which this ratio was determined is shown more clearly in figure 5, which shows a comparison of low temperature (22K) experimental angle-integrated valence band data to a photoionization cross-section-weighted band structure density of states $[2]$. To make this comparison, a small ($\sim 15\%$) background due to inelastically scattered electrons was removed from the experimental photoemission data, and the integrated spectral area under the two curves from 0 to 8 eV was made to match.

While the agreement between the theory and experiment is nowhere very good, it is worst near $E_F$, where the experiment shows a greatly reduced weight compared to theory. The left axis of figure 4 shows that the near-$E_F$ weight always remains at least a factor of 10 lower than the predicted weight, even at the lowest $T$, even though a clear Fermi edge is observed in the perovskite spectrum of Fig. 3(A). As shown in the figure, a similar $T$ dependence and reduction in low frequency spectral weight is observed in the Drude portion of optical conductivity experiments of a very similar ($x=0.175$) sample $[8]$.

Figure 5 shows near-$E_F$ photoemission data and DC resistivity from the three different families of the manganites, all with the same doping level of 0.4 holes per Mn site. At the low $T$ of the measurements, the cubic sample has a finite $N(E_F)$ and is metallic, the $n=1$ sample has a clear gap and is insulating ($n=1$ samples are insulating for all doping levels and $T$ $[22]$), while the $n=2$ sample has a vanishingly small weight at $E_F$ and is barely metallic. The trends in the data again indicate the significance of the pseudogap in explaining the transport properties of the manganites. Our data indicates a direct and possibly causal relationship between $N(E_F)$ and conductivity $\sigma$. Considering the very small $W$ changes that are observed across $T_c$, it appears that the changes in $N(E_F)$ due to the pseudogap are more important for the metal-insulator transition than is the DE effect.

It may be tempting to attribute the decrease in spectral weight at $E_F$ to be due to a decrease in mobile carriers. For instance, on the basis of transport measurements Jaime et al. have proposed a two-fluid model where the reduced conductivity of the manganites is due to a $T$-dependent reduction in the number of otherwise normal high mobility carriers $[24]$. Such a situation should lead to a small FS with normal (i.e. non-gapped) behavior. Here, we have a large “ghost” FS enclosing a large number of carriers $[14]$, although each of these carriers gives a drastically reduced spectral weight at $E_F$ due to the pseudogap. The large size of this observed ghost FS is consistent with the recent Hall effect experiments which indicated a large FS $[12]$.

A few theoretical works are able to predict gaps or pseudogaps in the electron spectral function. In particular, the Jahn-Teller (J-T) effect has been heavily discussed in the context of the manganites. Strong coupling between the electrons and the J-T phonons will break the degeneracy of the $e_g$ orbitals, opening a gap between them. $[24]$ However, $E_F$ will only lie in this gap for a doping level of $x=0$, i.e. for the $d^4$ compounds such as LaMnO$_3$. Our work clearly shows that there is a gap at $E_F$ for filling levels far away from $x=0$, so coupling to Jahn-Teller phonons can not explain the pseudogap. The inclusion of other phonons such as breathing-mode phonons may be relevant, although it is unclear if the electron-phonon coupling to these modes can be strong enough to open a gap as large as what we have experimentally observed. If so, then the pseudogap as well as the broad ARPES peaks may be explainable within the context of strong electron-phonon coupling $[10]$. Other interesting possibilities are the recent works by Alexandrov et al $[25]$ and Moreo et al $[26]$, both of which predict the gap to exist at $E_F$ irrespective of the doping level, as observed experimentally. Alexandrov’s pseudogap is due to the formation of bipolarons, while Moreo’s is due to strong electron-phonon coupling in the presence of phase separation. Other effects that should be considered are the charge/orbital ordering tendencies $[27]$ as well as long-range Coulomb interactions which may open a Coulomb gap $[28]$.

Finally, we briefly contrast the physics between the pseudogap discussed here and the pseudogap in the high temperature superconductors (HTSC’s) $[29]$. In the HTSC’s the pseudogap occurs below the temperature $T^*$ and corresponds to a reduced resistance state, while in the manganites the pseudogap is most active above the temperature $T_c$, and corresponds to an increased resistance state. We suggest that this can be understood by assuming that in the HTSC’s only the spin excitations are gapped, while for the manganites the charge excitations are gapped as well. The elucidation of the pseudogap origin will likely be a crucial step in our progress to understand the physics of both of these families of compounds.

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FIG. 1. (A) The relevant Mn-O derived electronic orbitals for the manganites. According to DE theory t from one site to the next is a strong function of the relative angle (θ) between the t(2g) spins on the two sites. (B) Schematic drawing of the E vs. k relations expected within DE theory. The paramagnetic states should have a dispersion about 70% of that in the ferromagnetic state. (C) Total electronic density of states N(E) expected within DE theory. Concomitant with the reduced dispersion and bandwidth, the paramagnetic phase is expected to have a slightly higher N(E) at EF.

FIG. 2. (A) ARPES spectra from hν=22.4 eV of the full valence band region from La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ along the (0,0)—(π,0) (left panel) and (π,0)—(π,π) (right panel) symmetry lines at 200K (red) and 50K (blue). The square panels at top show the location of the cuts in one quadrant of the two-dimensional Brillouin zone.

FIG. 3. (A) Near-EF spectra taken under identical conditions as the spectra of figure 2. The red × shows the predicted FS crossing point. In the right panel, the La$_{0.82}$Sr$_{0.18}$MnO$_3$ spectra at two T and the gold spectrum are shown. (B) Comparison between the experimental dispersion of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ from Panel A (red: 200 K, blue: 50 K) and the LSDA+U bands (green).

FIG. 4. (A) Integrated spectral weight of La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ in two different windows and relative energy shifts of the peak and the edge at -0.3 eV at (π,0.28π). (B) Comparison of the integrated spectral weight of La$_{0.82}$Sr$_{0.18}$MnO$_3$ in two different windows between the experimental spectra and the band-structure calculations [24]. The Drude weight of x=0.175 sample is also shown for comparison.

FIG. 5. Angle integrated valence band data from La$_{0.82}$Sr$_{1.8}$MnO$_3$ (red) versus the cross-section corrected band structure density of states, courtesy of W. Pickett.
FIG. 6. (A) Normal emission photoemission data in the near $E_F$ region for the layered ($n=1,2$) and cubic ($n=\infty$) systems, all with doping $x=0.4$. For the layered samples, this $k$-point mostly samples the $d_{3z^2-r^2}$ out-of-plane bands ($\beta$ in Fig. 2). The photon energy was 48 eV for $n=1,2$ and 36 eV for $n=\infty$ and for Au. At these high photon energies these states have a higher cross section than shown in Fig. 2. Spectra taken at $k$ near $(\pi,0.28\pi)$ show a similar layer-number dependence (not shown). (B) Resistivity as a function of $T$ for the same samples 2.
(A) \[ t = t_0 \cos \left( \frac{\theta}{2} \right) \]

(B) 

(C) 

\[ t = t_0 \]

\[ t \sim 0.7t_0 \]

Ferromagnetic

Paramagnetic

\[ \nu(E) \]

\[ E \]

\[ k_F \]

\[ k \]

\[ N(E) \]

\[ \sim 70\% \]

Ferromagnetic (\( T < T_c \))

Paramagnetic (\( T > T_c \))

Saitoh et al.
Figure 2  Saitoh et al.
(A) Figure 3

(B) Saitoh et al.
Figure 4  Saitoh et al.
La$_{0.82}$Sr$_{0.18}$MnO$_3$ 22 K (Mn62b) $h\nu=36.0$ eV

Original Band Structure Calculation by Pickett and Singh

Saitoh et al.
Figure 6

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