k-Dependent Electronic Structure, a Large "Ghost" Fermi Surface, and a Pseudogap in a Layered Magnetoresistive Oxide

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The k-dependent electronic structure of the low temperature ferromagnetic state of $La_{1.2}Sr_{1.8}Mn_2O_7$ was measured using angle-resolved photoemission spectroscopy and calculated using the local spin density approximation (LSDA). The measured near-Fermi energy states display E vs k and symmetry relationships which agree relatively well with the LSDA prediction through much of the Brillouin zone, and the locus of lowest energy excitations matches the predicted large Fermi surface quite well. However, the spectral features are too broad to be well described as Fermi-liquid-like quasiparticles, and they are strongly suppressed from the Fermi energy, i.e., there is a pseudogap in the excitation spectrum. We discuss the spectral properties in terms of strong coupling to a local effect such as a lattice distortion. [S0031-9007(98)06522-3]

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Colossal magnetoresistance (the CMR effect) has recently been observed [1] in doped manganese-oxide ceramics (manganites), sparking a great amount of effort aimed at understanding the electronic and magnetic properties of these materials. At low temperatures, properly doped manganites exhibit ferromagnetic metallic or nearly metallic behavior, while at high temperatures they exhibit a paramagnetic insulating behavior. The application of a magnetic field near the transition temperature lowers the resistivity by orders of magnitude, i.e., they exhibit colossal negative magnetoresistance. This generic behavior, as well as the magnetoresistive effect which occurs near the transition, is usually described to first order within the framework of double-exchange (D-E) theory, as developed in the 1950s and 1960s [2]. Recently, there has been an increasing realization that, although D-E is clearly important for understanding the behavior of the manganites, it is not enough. For instance, it has been shown that the insulating behavior above T_c cannot be understood solely with the spin-disorder scattering inherent in the D-E model [3]. It appears that an additional effect such as perhaps the creation of polarons due to strong electron-phonon coupling [3] is necessary to explain the observed behavior.

One major obstacle in gaining an understanding of the physics of the manganites has been a lack of information concerning their electronic structure. To try to correct this, we have performed the first set of high-energy resolution angle-resolved photoemission (ARPES) measurements on the critical near-Fermi energy (E_F) electronic structure of the manganites to determine the E vs k relationship and interaction effects of these materials. We have also performed the first set of band-structure calculations on a layered magnetoresistive oxide [4], allowing us to compare and contrast the experimental and theoretical data. We find the spectral properties of the low temperature ferromagnetic state of the manganites to be very different from that expected of a prototypical metal, indicating new and anomalous physics. A detailed analysis indicates that the very strange behavior is likely due to significant electron-lattice coupling even in the ferromagnetic state, the possibility of which had been mostly ignored previously.

Our experiments were performed on high quality single-crystalline samples of the bilayer manganite $La_{1.2}Sr_{1.8}Mn_2O_7$. This material has a nominal doping level of 0.4 holes per Mn site ($d^{3.6}$) and more than 2 orders of magnitude decrease in resistivity at the ferromagnetic T_c of 126 K [5]. The low temperature resistivity is unusually high—greater than $3 \times 10^{-3}\ \Omega$ cm and even has a slight upturn at the lowest temperatures. One of the key features of these layered samples for our experiments is that they cleave easily between the two ionically bonded (La,Sr)O planes, yielding a mirrorlike surface that should be representative of the bulk. High quality low-energy electron diffraction (LEED) patterns absent of superlattice spots are easily obtainable, confirming the high quality of the surfaces.

All spectra shown in this paper were measured at the Stanford Synchrotron Radiation Laboratory (SSRL) using a photon energy of 22.4 eV, an energy resolution of 40 meV FWHM (see the gold reference spectrum at the top left of Fig. 1), and an angular resolution of $\pm 1°$ (giving a k resolution better than 5% of the length of the first Brillouin zone edge). The chamber pressure was typically 4×10^{-11} torr, and the samples were cleaved and measured *in situ* at 10 K.

Figures 1a–1d show the near-E_F states along various k-space directions, measured at 10 K (ferromagnetic phase). Directions of these cuts in the two-dimensional Brillouin zone are indicated in Fig. 1f. Concentrating first on the spectra along the $(0,0) \rightarrow (\pi,0)$ line (Fig. 1a), we observe a strong feature first visible at $(0.27\pi,0)$ which disperses towards the Fermi energy as we progress

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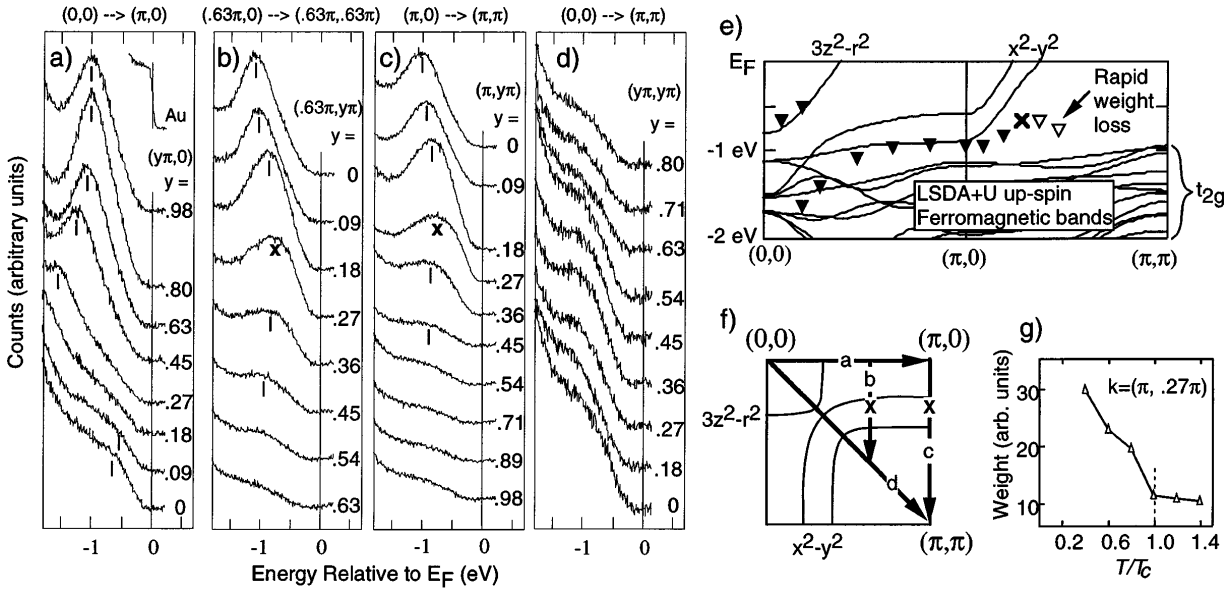

FIG. 1. (a)–(d) Low temperature (10 K) high resolution ARPES spectra of $T_c = 126$ K $La_{1.2}Sr_{1.8}Mn_2O_7$ along various high symmetry directions, as indicated at the top of each panel and by the arrows along the two-dimensional Brillouin zone of panel (f). (e) The up-spin bands in the LSDA + U band theory calculation vs experimentally determined peak centroids from (a) and (c) (tick marks). The three curved lines in (f) are the Fermi surfaces for the up-spin bands in the LSDA + U band theory calculation. The two $\times$s are the experimental locations of the closest approach to E_F. (g) Temperature dependence of the near-E_F spectral weight integrated over the energy range from -0.3 to 0.05 eV, for $k = (\pi, 0.27\pi)$ (the "$\times$" of cut c).

towards $(\pi, 0)$. In addition, there is a weak and broad feature at about -0.6 eV which is strongest near the $(0, 0)$ point (at higher photon energies this feature evolves into a clearly resolvable peak). Figure 1c shows a continuation of the dispersion along the $(\pi, 0) \rightarrow (\pi, \pi)$ direction. In the first part of this cut the peak continues to disperse towards the Fermi energy, but surprisingly never reaches E_F. Instead, it attains its minimum energy near $(\pi, 0.27\pi)$, at which point it rapidly loses intensity as if weight was transferred above the Fermi energy. Beyond this point, the spectra, in addition, exhibit some evidence of bending back away from E_F. A very similar result is seen for the cut shown in Fig. 1b, with the minimum energy at $(0.63\pi, 0.27\pi)$.

Figure 1e shows a plot of the peak centroids (indicated by the tick marks in Figs. 1a and 1c) vs crystal momentum along $(0, 0) \rightarrow (\pi, 0) \rightarrow (\pi, \pi)$ compared to the up-spin dispersion predicted by our local spin density approximation (LSDA) band-structure calculations [4]. The calculated band crossing E_F near the $(0, 0)$ point is predicted to have principally $d_{3z^2-r^2}$ out-of-plane character, while the two bands (because there are two Mn-O planes per unit cell) crossing between $(\pi, 0)$ and (π, π) are predicted to have primarily $d_{x^2-y^2}$ in-plane character. We find that there is a correspondence between certain aspects of the experimental and theoretical data. (1) The agreement in both energy position and dispersion rate between the experiment and theory along the $(0, 0)$–$(\pi, 0)$ line is reasonably good [6], especially considering that we have not rescaled or shifted the energy scales to account for the often observed renormalization effects. (2) By taking advantage of the polarization of the incident photons in the spirit of that done by Gobeli *et al.* and Dietz *et al.* [7], we have performed a symmetry analysis on the main dispersive features [the ones predicted to cross E_F along $(\pi, 0)$–(π, π)] and found them to have primarily $d_{x^2-y^2}$ character [8], in agreement with the band theory prediction. The predicted $d_{3z^2-r^2}$ symmetry of the band crossing E_F near the $(0, 0)$ point was not determined by these measurements. (3) The locations of the experimental minima in binding energy as well as the locations where the spectral weight is rapidly being depleted agree well with the predicted Fermi surface crossings. In other words, there is a locus of points in k space where critical spectral behavior occurs, and this locus is found to closely resemble the band-structure Fermi surface. This indicates that Luttinger's theorem [9] is obeyed for these compounds.

Despite these agreements there are clear deviations between the experiment and theory, signaling additional physics not contained in the calculation. These deviations can tell us many of the details of the interactions responsible for the very unusual properties of the manganites. In particular, (1) the width of the ARPES features are anomalously broad, and do not sharpen up as they approach the Fermi momentum k_F. This indicates that the dispersive peaks can not be described as single Fermi-liquid-like quasiparticle (qp) excitations. (2) The spectral behavior at the locus of critical k points discussed above is different from that expected at a real Fermi surface. This is why we call the locus a "ghost" Fermi surface. Specifically, we find (a) the centroids of the experimental peaks never approach closer than approximately 0.65 eV to E_F, while

theoretically they are expected to reach E_F. (b) There is never more than a vanishingly small spectral weight at E_F, even though the measurements were made in the ferromagnetic "metallic" state of the compound. To make sure that we simply didn't miss a Fermi crossing, we have made measurements along all of the high symmetry directions as well as along many off-symmetry points (not shown), have used a variety of photon polarizations and photon energies, and have repeated the measurements on more than ten samples.

We term the above depression of spectral weight a pseudogap. We find that this pseudogap affects *both* the ferromagnetic and paramagnetic states, although it affects the paramagnetic states more severely, i.e., the pseudogap is larger above T_c. The temperature dependence of the near-E_F weight is briefly indicated in Fig. 1g. The fact that the temperature-dependent changes begin at T_c gives much added confidence that the photoemission spectra we present are representative of the bulk properties of the samples, and also indicates that the pseudogap should be responsible for the drastic changes in the conductivity across the magnetic ordering temperature.

It is very surprising that the spectral weight at E_F could be so severely depressed in the low temperature metallic state of this material. However, the low temperature resistivity for this material is unusually high (approximately the inverse of Mott's minimum metallic conductivity) and is even increasing at the lowest temperatures, i.e., the ferromagnetic state of these samples is right on the border of what could be considered a metal or an insulator. The low frequency optical conductivity of the doped bilayer manganites has recently been measured, and it has been found that the Drude peak is absent for these materials, even at the lowest temperatures [10]. We believe that the pseudogap we have observed is responsible for all of this unusual behavior. The three-dimensional (infinite layer) manganese perovskites measured at low temperature do show finite photoemission spectral weight at E_F [8,11] and do show a clear Drude peak in the optical measurements [12]. In both cases, however, the weight of these peaks is reduced by at least a factor of 10 from expectations. We believe that this reduction of spectral weight is also due to the pseudogap, but with reduced strength compared to the layered manganites (the pseudogap is probably stronger in the layered compound because the one-electron bandwidth is smaller, due to dimensionality effects). We also note that certain one-dimensional compounds have also shown broad ARPES peaks and very little weight at E_F [13]. In those cases, the one-dimensional nature is expected to dominate, either from Luttinger liquid behavior or from a Peierls transition.

We now explore a couple of possible explanations for the anomalous spectral and physical properties of the manganites. Mechanisms that should be considered include gap formation due to static or fluctuating charge, spin, or orbital order; a Mott-Hubbard-type gap; a splitting of the levels due to the Jahn-Teller effect; a Coulomb gap; and strong electron-lattice coupling.

One of the important clues to help us distinguish the mechanism is the k-space dependence of the gap. We have found that the pseudogap affects the entire Fermi surface to a similar degree (including the data shown here and unpublished data along other k-space cuts). While we can not yet say that there is zero anisotropy to the gap, the general lack of k-space dependence makes it unlikely that charge, spin, or orbital ordering should play a dominant role in the gap opening, as these ordering phenomena should occur with a wave vector which will affect certain parts of the Brillouin zone more strongly than others. An example of this is the recently observed pseudogap effect in the high-T_c superconductors which has a pronounced k-space dependence [14]. In those materials, the maximal gapping effect is near the $(\pi, 0)$ point of the Brillouin zone, signaling a possible origin from the antiferromagnetic fluctuations with wave vector near (π, π).

Although it is expected that correlation effects will play a role in these materials, the Mott-Hubbard-type gap is expected to be centered at E_F only for samples of integral electron filling and so cannot be responsible for the observed pseudogap. The splitting of the e_g symmetry levels due to the Jahn-Teller effect should also only be centered at E_F at special doping levels. A Coulomb gap is usually discussed in terms of localized (impurity) states [15]. The large amount of dispersion observed in Fig. 1 is in opposition with such localized states.

An analytically solvable example that we believe contains much of the relevant physics is the classic problem of the coupling of a single electron to a bath of bosons (e.g., phonons) of energy ω_0 [16]. The electron spectral function for this problem is an envelope of many individual peaks separated by ω_0, as illustrated in Figs. 2a and 2b. The multiple peaks indicate that a single electron is not an eigenstate of the system—therefore the removal of an electron from the system occurs with a probability of shaking off a certain number of bosons. The qp peak or "coherent" part of the spectrum is the one with zero bosons shaken off and is the peak closest to the Fermi energy. In the strong coupling case the envelope function is broad and the qp peak will have very little spectral weight. An important point about this result is that, irrespective of the strength of the coupling, the centroid or first moment of the distribution is equal to the energy of the electron in the absence of the coupling [16]. A known example of this type of distribution is the measured photoemission spectrum of gaseous hydrogen, which shows a clear progression of many peaks, corresponding to the many different vibrational levels [17].

In contrast with the usual interpretation, we argue that the dispersive peaks we have measured should not be considered to be a single qp peak but should be considered to be an envelope of many individual peaks, in the spirit of the strong coupling arguments above (the individual peaks are probably not resolved due to lifetime, solid-state, and

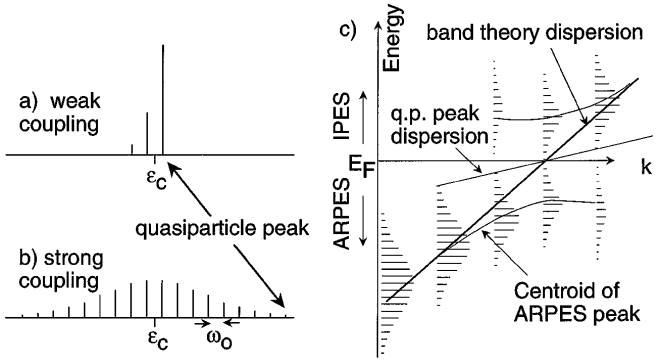

FIG. 2. Spectral function of a single electron coupled to a bath of Einstein phonons of frequency ω_0, for (a) weak and (b) strong coupling (see Ref. [16]. (c) A schematic of the dispersion of a strongly coupled photoemission (and inverse photoemission) peak across E_F. The low-energy portion of the spectrum (quasiparticle), if distinctly observable, would be expected to have less dispersion and cross E_F at the k value predicted by band theory.

resolution effects). Also, in analogy to the single-electron calculation above, we argue that the centroid of the ARPES spectrum should have an energy equal or similar to the energy in the absence of the coupling, which in this case is the LSDA band energy. This explains the relatively good agreement [6] of the experiment and theory through much of the zone (see Fig. 2c). The qp peak would correspond to the portion of the spectrum nearest E_F, and is found to have an almost vanishingly small weight for this material, indicating that the coupling is strong (this is also seen by the large width of the peaks). By Luttinger's theorem [9], we expect the qp peak to cross E_F at the location predicted by the band theory calculation (noninteracting limit). A key point here is that when the qp peak crosses E_F the entire photoemission peak must rapidly lose weight because the excitation can no longer be created (Fig. 2c). The centroid of the envelope therefore always stays well below E_F with a minimum binding energy equal to the distance between the centroid of the distribution and the qp peak, e.g., there should be a pseudogap in the spectral function. An important question then is what is the origin of the boson the electrons are coupling to. The lack of k dependence of the pseudogap in the manganites points towards important contributions from *local* effects such as strong electron-phonon or electron-lattice coupling.

The above scenario is in strong contrast with our usual findings and expectations, and, we believe, represents a new paradigm in the k-dependent electronic structure of a solid. Our results also indicate that the low temperature ferromagnetic state of the manganites are very strange metals with a very low (three-dimensional compounds) or vanishingly small (bilayer compounds) spectral weight at E_F, most likely due to strong electron-lattice interactions. The strong electron-lattice coupling (and the creation of polarons) has been widely discussed in the paramagnetic state, although it has been widely assumed that this coupling should not be important below T_c. We argue that for the layered samples the electron-lattice coupling critically affects the electronic structure even below T_c, and probably is also important below T_c for the three-dimensional manganites. This is in qualitative agreement with some recent structural data obtained from pulsed neutron diffraction experiments [18].

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