Abstract
This paper reviews selected developments from the last ten years which argue that the stripe phase observed in the manganites is, in fact, an emergent charge density wave ground state. The paper’s main focus is directed towards two recent papers on this subject. The first is a theoretical treatment using Ginzburg-Landau theory, and the second is an experimental work using resistivity measurements to find evidence for the collective charge transport mode known as charge density wave “sliding.”
1. Introduction

The manganites exhibit a rich diagram of equilibrium phases resulting from the simultaneous interplay between charge, spin, orbital, and lattice degrees of freedom [1, 2]. These complex systems have the potential to advance our understanding of condensed matter physics on a number fronts, including high-temperature superconductivity. In fact, this is one of the main attractions for studying manganites: to research the stripe/checkerboard phases they exhibit, which are thought to play an important role in high-temperature superconductivity.

Although the study of manganites began in 1950 [3], and central pieces of our current understanding were introduced as early as 1951 with Zener’s double exchange, forming a complete picture of the physics of the manganites still remains a challenge.* One of the current points of contention is the nature of the stripe, or charge-ordered, phase itself. The traditional view is that the charges localize to form a “stripe” pattern. However, a different view started developing not more than ten years ago around the start of the new millennium. This view argued that the stripe phase is in fact a smoothly varying superstructure known as a charge density wave (CDW). This paper will outline the more recent interpretation with a summary of a couple of theoretical and experimental results/assertions, but first we provide a background† on CDWs and the manganites.

2. Background

2.1. Charge Density Waves. In a one-dimensional metal, conduction electrons occupy states below the Fermi surface (see Figure 1). The opening of an energy gap at the Fermi surface \((k = \pm k_F)\) would lower the energy of the occupied states, resulting in a reduced total electronic energy. In 1930, Rudolph Peierls showed that periodic lattice distortions with wave vector \(Q = 2k_F\) would open such an energy gap.

Of course, real metals are not one dimensional. Nonetheless, certain materials can still form CDW states due to high electronic anisotropy; such materials are termed “quasi-one-dimensional.” These quasi-one-dimensional metals have a CDW ground state when the temperature is low enough that the tradeoff between the elastic energy to modulate the lattice and the change electronic energy is favorable. At high enough temperatures the metallic state is stable due to thermal excitations. The second-order phase transition that occurs between these two states is known as the Peierls transition [7].

*For a historical review see [4].
†The information presented on CDWs comes from [5, 6, 7]. Information on the manganites is taken from [4] and from sources cited in the body of the paper.
The CDW state is characterized by a complex order parameter

\[ \psi(r) = \rho(r)e^{i(Qr + \phi(r))}. \]  

The magnitude \( \psi \) is associated with the amplitude of the atomic displacements that make up the charge modulations. The phase \( Qr + \phi(r) \) determines the position of the CDW relative to the underlying lattice. Written in this way, the phase has been broken into two parts, the first for the commensurate part, and the second for any incommensurate part. (Being commensurate simply means having the same periodicity as the underlying lattice.) Thus, \( Q = a^*/n \), where \( a^* \) is the lattice wave vector, and \( n \) is an integer. Technically, vectors should be used, but here we only consider the one-dimensional problem.

The charge modulation typically minimizes its energy by aligning in a special way with the lattice (if the modulation is commensurate), or by “pinning” to impurities (in the incommensurate case). When an electric field is applied which overcomes any pinning potential that may exist, the CDW can “slide” relative to the lattice as shown in Figure 2. The lattice atoms are sent into oscillation, producing a traveling potential, which the conduction electrons follow to produce a current [7].

2.2. Manganites. The manganites have a perovskite structure with general form \( \text{R}^{3+}_{1-x}\text{A}^{2+}_x\text{MnO}_3 \), where the divalent alkaline earth (A) dopant substitutes for the trivalent rare earth (R) element at the center of the cubic unit cell.

The interpretation of the stripe phase in the manganites resulting from a localization of charge at atomic sites was derived from transmission electron microscopy (TEM) and neutron diffraction measurements [9]. The introduction of the alkali earth
dopant allows the manganese ions to have either 3+ or 4+ valence, and so the charge modulations were seen as an ordering of Mn\(^{3+}\) and Mn\(^{4+}\) ions. However, neutron and x-ray studies came out that argued the difference in charge between atomic sites was much less than one, and the conclusions of the original TEM results came under question [9]. In a search for explanations, several authors have found that a charge density wave picture of the charge modulations in the manganites is in order; we now review two of these arguments and their conclusions.

3. A Ginzburg-Landau Theory

In seeking an explanation for experimental evidence showing the coexistence of ferromagnetism and charge-ordering, Milward et al. [2] showed that this and related findings can be described by a Ginzburg-Landau theory, utilizing an “extended ‘charge-density wave’ picture.”

Milward honed in on the discrepancy in the form of the change modulation’s averaged wave vector \(q\) (still only working in one-dimension). In a picture built from an ordering of Mn\(^{3+}\) and Mn\(^{4+}\) ions, it is expected that \(q \approx (1 - x) \ a^*\), where \(x\) is the doping fraction and \(a^*\) is the reciprocal lattice vector. In contrast to this, it is found that for underdoped \((x < 0.5)\) samples, \(q = 0.5 \ a^*\), independent of temperature (see Figure 3).
Figure 3. Wave Vector Dependencies. The wave vector temperature and doping dependencies for La$_{1-x}$Ca$_x$MnO$_3$ and Pr$_{1-x}$Ca$_x$MnO$_3$ at various dopings are plotted. The charge-ordering temperature and the Néel temperature have been indicated by $T_{CO}$ and $T_{AF}$, respectively. The important features to take away from this plot are: (1) For $T < T_{AF}$, where the ground state is commensurate and charge modulated, $q/a^* \approx (1 - x)$ applies. (2) For $T > T_{AF}$, where the charge-ordering is now incommensurate, the wave vector magnitude decreases with increasing temperature. (3) The data for underdoped Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ is clearly disparate from the rest of the data, both in its (lack of) temperature dependence, and its low-temperature contradiction of $q/a^* \approx (1 - x)$. From [2].

To describe the involvement of the different phases and phase transitions in the empirically determined behavior of the manganites, Milward lays out a Ginzburg-Landau theory starting with an expression for the free energy in terms of the order parameters and their gradients. The free energy can be broken into three parts: magnetization, charge modulation, and coupling terms. For the magnetization and charge modulation,

$$\mathcal{F}_M = \frac{1}{2} a_M (T - T_c) M^2 + \frac{1}{4} B_M M^4 + \frac{1}{2} \xi_M^2 (\nabla M)^2$$

$$\mathcal{F}_\psi = \frac{1}{2} a_\rho (T - T_{CO}) \rho^2 + \frac{1}{4} B_\rho \rho^4 + \frac{1}{2} \xi_\rho^2 (\nabla \rho)^2 + \frac{1}{2} \xi_\rho^2 \rho^2 (\nabla \phi - q_0)^2 + \frac{1}{n} \eta \rho^n \cos(n\phi).$$
$M$ represents the spatially dependent magnetization, $\psi$ is the order parameter for charge modulation in one dimension, $\rho$ stands for the amplitude of the modulation, and $\phi$ is the phase of any incommensurate charge modulations, as explained previously. The quadratic and quartic order parameter dependencies are familiar, being common with Landau theory. The last two terms in Equation 3 battle to determine whether the system has incommensurate or commensurate charge modulations. In the $\frac{1}{2}\xi_{\rho}^2 \rho^2 (\nabla \phi - q_0)^2$ term, $q_0 = 1/2 - x$. Note that this term is minimized by the uniform incommensurate modulation $\nabla \phi = q_0$; also note that the last term in Equation 3 is pulling for a commensurate modulation (using $\eta < 0$) since $\cos(n\phi) = 1 \rightarrow n\phi = 2\pi j$, where $n$ and $j$ are integers, but the point is that $\nabla \phi = 0$ in this case. Thus the competition between these two terms determines the commensurability/incommensurability of the system. Critical to this analysis is the value of $n$ (which is related to the commensurate wave vector) and the ratio of $\eta$ to $\xi_{\rho}^2$.

More interesting, are the conclusions Milward draws from the coupling terms, specifically the one of the form $d_2 \rho^2 M^2 (\nabla \phi - q_0)$. He explains how this term can be incorporated into Equation 3 by the substitution

$$q_0 \rightarrow q_{\text{eff}} = \frac{1}{2} - x - \frac{d_2}{\xi_{\rho}^2} M^2.$$  

This has two profound consequences which are captured by the experimental data summarized in Figure 3. Firstly, this essentially makes $q_0$ dependent on $M$, so that any magnetism pulls $\nabla \phi$ away from zero, and hence creates a favoritism for incommensurability. Secondly, if we take $d_2 > 0$, we realize that $x = 1/2$ is a special value. For $x < 1/2$, $q_{\text{eff}}$ could potentially be zero, whereas that would be an impossibility for $x > 1/2$. Thus, magnetism coexisting with charge modulation tends to negate efforts to bring about incommensurability, which not only explains the “dog-leg” shape of the wave vector vs. doping plot inset in Figure 3, but also comes full circle by explaining the coexistence of ferromagnetism with charge modulation.

4. Evidence for CDW sliding

Just under two years ago, Cox et al. published a letter [8] describing “orientation-dependent resistivity . . . effects [in La$_{0.5}$Ca$_{0.5}$MnO$_3$] that are characteristic of CDW sliding” as a further indication beyond previous heat capacity work [9] that the manganites are capable of a CDW phase. In addition to the arguments already raised, they add the strong temperature dependence of $q/a^\star$ to the list of reasons why “a model in which the superstructure periodicity is derived from the sample stoichiometry cannot be valid.”

The following explanation comes from the [9]. The hysteretic resistivity features shown in Figure 4 are typical of CDWs in pinned and sliding states [6]. As the
Fig 4. TEM and Hysteresis Evidence. In each plot, red represents components parallel to the charge modulations, and blue represents the perpendicular components. (a) Line scans from a TEM diffraction pattern indicate a stripe superlattice periodicity only in the parallel direction. (b-f) Differential resistivity of $La_{0.5}Ca_{0.5}MnO_3$ versus d.c. bias with bias applied in the parallel and perpendicular directions at various temperatures. In each case, the upper curve is the differential resistivity obtained after cycling the temperature to 300 K, and the lower curve is the path followed by subsequent bias sweeps. From [8].

sample is cooled, the CDW settles into a minimum-free-energy pinned configuration, corresponding to maximum electrical resistivity (note how the zero-field resistivity value increases with decreasing temperature). On the application of electric field, the CDW initially undergoes local distortions that occur over longer and longer length scales as the field increases; eventually, the threshold field is reached and the CDW starts to slide. As the field is reduced again, the CDW freezes into a distorted state, characterized by a lower resistivity; the initial, minimum energy state cannot be regained without thermally cycling the sample, explaining the hysteresis in the data. The authors attribute the small hysteresis in the perpendicular direction to small misalignment of the biasing axes.

References