Very weak electron-phonon coupling and strong strain coupling in manganites

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We describe transmission electron microscopy experiments that demonstrate the validity of the charge density wave (CDW) Landau theory in describing the so-called stripe phase of the manganites and that permit quantitative estimates of some of the theoretical parameters that describe this state. In polycrystalline Pr$_{0.48}$Ca$_{0.52}$MnO$_3$ a lock-in to $q/a^* = 0.5$ in a sample with $x > 0.5$ has been observed. Such a lock-in has been predicted as a key part of the Landau CDW theory of the stripe phase. Thus it is possible to constrain the size of the electron-phonon coupling in the CDW Landau theory to between 0.08% and 0.50% of the electron-electron coupling term. In the thin film samples, films of the same thickness grown on two different substrates exhibited different wave vectors. The different strains present in the films on the two substrates can be related to the wave vector observed via Landau theory. It is demonstrated that the elastic term, which favors an incommensurate modulation, has a similar size to the coupling between the strain and the wave vector, meaning that the coupling of strain to the superstructure is unexpectedly strong.

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I. INTRODUCTION

The properties of the manganites comprise a zoo of delicately balanced phases in which changes in temperature, magnetic field, chemical composition, and strain (among other parameters) yield a rich tapestry of phase coexistence. The stripe phase, which forms at low temperatures on the insulating side of the manganite phase diagram, was long thought to be driven by strong electron-phonon coupling, since the materials are insulating at all temperatures. However, recent experimental work has led to the conclusion that the stripe phase is actually a charge density wave (CDW) subject to a high level of disorder. The CDW model of the stripe phase was described theoretically using a Landau theory, which successfully reproduced the observed variation of the wave vector $q$ with composition $q/a^* = 1 - x$, where $a^*$ is the reciprocal lattice vector. This theory made the prediction that for $x$ slightly greater than 0.5, there should be a lock-in of the wave vector to $q/a^* = 0.5$, though no such lock-in had ever been observed. Measurements of the wave vector of manganites with $x \geq 0.5$ always found $q/a^* \leq 1 - x$. Here we report an observation of such a lock-in, in Pr$_{0.48}$Ca$_{0.52}$MnO$_3$. In addition, the values of the wave vector that we observe can be used to constrain the Landau theory parameter for the electron-phonon coupling relative to the electron-electron coupling to the range 0.08%–0.50%, suggesting that the electron-phonon coupling in the manganites is extremely weak. This supports the model of a prototypical CDW, which is only weakly tied to the lattice, for the manganite stripe phase.

Landau theory also predicts that it should be possible to tune the low-temperature superstructure of the manganites by altering the strain in a small area of a thin film. Thus far it has not been possible to measure the changes in strain, and so it has not been possible to quantitatively link such changes in property to theoretical work. Here we measure the properties of the low-temperature superstructure in different known strain states using thin films of La$_{0.50}$Ca$_{0.50}$MnO$_3$, and provide a quantitative analysis of the results, allowing us to compare the size of the strain coupling and electron-electron coupling via the Landau theory.

For the thin-film experiments, the composition La$_{0.50}$Ca$_{0.50}$MnO$_3$ was chosen since it has been well characterized in both thin film and polycrystalline forms. Previous work on La$_{0.50}$Ca$_{0.50}$MnO$_3$ found a $q/a^*$ of around 0.48, whereas in Pr$_{0.5}$Ca$_{0.5}$MnO$_3$, $q/a^*$ is around 0.45. In polycrystalline La$_{0.50}$Ca$_{0.50}$MnO$_3$, $q/a^*$ exhibits values between 0.46 and 0.50 at 90 K (the intergranular variation is up to 9%; the intragranular variation is less than 1%). Below the Néel transition temperature $T_N = 135$ K (on cooling), the positions of the superstructure reflections appear to stabilize, and it is assumed that in the absence of extrinsic factors, $q/a^*$ would take the value 0.5. The superstructure persists up to the Curie temperature of $T_C = 220$ K, and for $T_N < T < T_C$, $q/a^*$ is hysteretic and incommensurate. Polycrystalline La$_{0.48}$Ca$_{0.52}$MnO$_3$ shows similar behavior to La$_{0.50}$Ca$_{0.50}$MnO$_3$, except that $q/a^*$ does not lock in to 0.5 in any grains (low-temperature values lie between 0.43 and 0.475), and the variation of $q/a^*$ with temperature does not show a hysteresis loop. The compound Pr$_{0.48}$Ca$_{0.52}$MnO$_3$ was investigated here because it is predicted to have stronger electron-phonon coupling than La$_{0.48}$Ca$_{0.52}$MnO$_3$, since the Pr ion is smaller than the La ion. Stronger electron-phonon coupling should be associated with a stronger bias toward the stripe phase as opposed to the ferromagnetic (FM) phase. This is because $q/a^* = 0.5$ is always observed if the stripe phase exists below $x = 0.5$. Stronger electron-phonon coupling means a larger energy gain when the superstructure locks into the lattice. This effect can be observed in the phase diagrams for the two materials, in which the Pr$_{1-x}$Ca$_x$MnO$_3$ stripe-phase region extends down to $x = 0.3$, whereas for La$_{1-x}$Ca$_x$MnO$_3$ it extends only to $x = 0.5$. Thus it should be more energetically favorable for the superstructure to lock...
into the lattice in \(Pr_{0.48}Ca_{0.52}MnO_3\) than in \(La_{0.48}Ca_{0.52}MnO_3\).

It is also important to consider the effect of the oxygen stoichiometry on the stripe-phase wave vector. Samples annealed in conditions expected to give lower oxygen doping are found to lock in to \(q/a' = 1 - x\), whereas samples expected to have higher oxygen doping exhibit \(q/a' < 1 - x\) (for various \(x = 0.5\) samples).\(^{10}\) However, there is no method of measuring oxygen stoichiometry with sufficient accuracy to detect the variation between samples. Here we use polycrystalline samples prepared under the same conditions as samples used another extensive study,\(^7\) giving us a high degree of confidence that the grain to grain variation in oxygen stoichiometry should be the same as in the other samples, and the results should therefore be comparable. In particular, this allows us to determine that the lock-in observed in \(Pr_{0.48}Ca_{0.52}MnO_3\) is unlikely to be due to variations in the oxygen stoichiometry, since if it was, a similar lock-in should have been observed during the extensive measurements of \(La_{0.48}Ca_{0.52}MnO_3\).\(^7\) In addition, all thin films are grown under the same conditions to control the oxygen stoichiometry to as great a degree as possible.

The paper is organized as follows: Sec. II gives a description of the sample preparation and experimental setup and Sec. III describes the results of the experiments on thin film \(La_{0.48}Ca_{0.52}MnO_3\) and polycrystalline \(Pr_{0.48}Ca_{0.52}MnO_3\), while Sec. IV discusses these results in the context of the Landau theory for manganites. A summary is given in Sec. V.

II. EXPERIMENTAL DETAILS

Films were grown by pulsed laser deposition on NdGaO\(_3\) and SrTiO\(_3\) substrates.\(^8\) Three films were grown on NdGaO\(_3\), with thicknesses of 44 ± 2 nm, 80 ± 3 nm, and 123 ± 3 nm as measured by high resolution x-ray diffraction. One film of thickness 44 ± 2 nm was grown on SrTiO\(_3\). The 44 nm thickness is sufficiently low to preserve cube-on-cube epitaxy. Magnetization was measured using a vibrating sample magnetometer, with measurements being made for the films of 44 nm, 80 nm, and 123 nm grown on NdGaO\(_3\), and a bare substrate. The measurements for the films were obtained by subtracting the substrate measurement from the thin-film measurement, after correcting for the different volumes. The polycrystalline sample of \(Pr_{0.48}Ca_{0.52}MnO_3\) was prepared as described in Ref. 17. The macroscopic stoichiometry of the samples was assessed by measuring the oxygen content using iodometric titration,\(^8\) which found the oxygen stoichiometry to be the desired value within experimental error (0.1%), and using energy dispersive x-ray analysis,\(^7\) which found the La/Ca ratio to be at the predicted level within the error of the measurements (2%).

All the samples were prepared for transmission electron microscopy by conventional grinding and dimpling, and were thinned to electron transparency (~100 nm) by argon ion milling. Measurements were taken in a Philips CM30 transmission electron microscope (TEM) with a 90 K liquid nitrogen stage. Each diffraction pattern was taken over a time scale of seconds. Conventional imaging of the polycrystalline sample indicated that the grain size was ~2 µm.

III. EXPERIMENTAL RESULTS

A. \(La_{0.48}Ca_{0.52}MnO_3\) thin films

The films grown on NdGaO\(_3\) gave a uniaxial superstructure, i.e., at 90 K the superstructure reflections appear along only one axis [see Fig. 1(b)]. The strength of the magnetization and of the superstructure reflections were monitored for different film thicknesses (see Fig. 2). The magnetization increased with decreasing temperature in all samples, as has previously been observed.\(^19\) It can be seen that the magnetization at low temperatures decreases in amplitude with increasing film thickness (from 0.5µ\(_B\)/Mn ion at 44 nm to 0.2µ\(_B\)/Mn ion at 80 nm to 0.1µ\(_B\)/Mn ion at 123 nm). In addition, the temperature at which magnetic hysteresis appears decreases from 250 K in the 44 nm-thick film to 175 K in the 80-nm-thick film, while no hysteresis appears in the 123-nm-thick film. However, the superstructure is strongest and most distinct for the 44-nm-thick film, being much fainter in the 80-nm-thick film and not detectable in the 123-nm-thick film. Thus both the superstructure and the magnetization become stronger with decreasing film thickness. This has two implications. First, since the strain would be expected to decrease with increasing film thickness, it suggests that decreasing the level of strain in the film suppresses the superstructure, and that in fact in the absence of any strain, the superstructure cannot exist. Second, it suggests that rather than being in competition, the FM and stripe phases coexist; if the stripe phase is destroyed, a FM phase is not formed, but rather a paramagnetic insulator (PMI).
NdGaO$_3$ because of the different symmetries of the substructure in the two types of films. The diffraction patterns at 90 K for each film are also displayed, with the superstructure reflections being visible for (a) and (b). The three diffraction patterns have been enhanced to the same degree by high-pass filtering and saturation.

is supported by a recent work, which has found that for thin films there is an area of the phase diagram ($x > 0.42$, limited by the maximum $x$ of 0.45 measured) for which the low-temperature phase is a PMI, i.e., there are no signs of the FM or stripe phases. In addition, this result strongly suggests that the oxygen stoichiometry is unlikely to be driving the variations of the wave vector seen in thin films, since in this case all the films were grown on the same substrate under the same conditions, and therefore would be expected to have the same oxygen stoichiometry.

In contrast with films grown on NdGaO$_3$, films grown on SrTiO$_3$ gave diffraction patterns in which superstructure reflections appeared along both axes (see Fig. 1). By taking dark field images using superstructure reflections from each of the two directions (see Fig. 3), it was shown that the two superstructure orientations did not coexist. Instead, the images revealed small complementary regions of the different ordering orientations for the superstructure. The region of each twin extends over a length scale of 50–100 nm. The twinning occurs for films grown on SrTiO$_3$ but not on NdGaO$_3$ because of the different symmetries of the substrate: NdGaO$_3$ has an orthorhombic structure, as does La$_{0.5}$Ca$_{0.5}$MnO$_3$, and so it is always most favorable for the a axis of La$_{0.5}$Ca$_{0.5}$MnO$_3$ to align with the a axis of NdGaO$_3$. However, SrTiO$_3$ is cubic, and thus it is equally favorable for the a axis of La$_{0.5}$Ca$_{0.5}$MnO$_3$ to align along either the a or c axis of SrTiO$_3$.

A further difference between the properties of the La$_{0.5}$Ca$_{0.5}$MnO$_3$ superstructure in the two types of films was the value of the wave vector. Diffraction patterns of a large area were taken using a selected area aperture of 500 nm diameter, as measured in the sample plane. The selected area diffraction patterns were analyzed using software which measured the position of many superstructure reflections in one pattern. The film on NdGaO$_3$ had a wave vector of $q/a^* = 0.475$ in regions away from the edges, whereas the film grown on SrTiO$_3$ had a wave vector of $q/a^* = 0.50$.

**B. TEM measurements of Pr$_{0.48}$Ca$_{0.52}$MnO$_3$**

We now turn to the TEM measurements of Pr$_{0.48}$Ca$_{0.52}$MnO$_3$. Selected area diffraction patterns were taken using an aperture of 500 nm diameter, as described above. The size of the aperture was much smaller than the grain size (2 µm). Therefore the diffraction patterns measure intrinsic properties of the grains, including strain. In all patterns q was found to be essentially parallel to a*. Three diffraction patterns [Figs. 4(a)–4(c)] have values of $q/a^*$ between 0.445 and 0.450, and the fourth shows $q/a^* = 0.5$ [Fig. 4(d)]. Therefore in Pr$_{0.48}$Ca$_{0.52}$MnO$_3$ the superstructure will lock into the lattice under certain conditions, supporting the idea that the electron-lattice coupling is stronger in this compound than in La$_{0.48}$Ca$_{0.52}$MnO$_3$.

The measurements of the wave vector in the grains in which no lock-in occurred are within the range one would expect from previous measurements of La$_{0.48}$Ca$_{0.52}$MnO$_3$. It should be noted that the nominal value of $q/a^* = 1 - x$ is never actually observed; in fact, $q/a^* < 1 - x$. This deviation and the variation of the wave vector from grain to grain are traditionally ascribed to different levels of strain in the grains. This can be described in the context of a Ginzberg-Landau theory (see Fig. 5).

Convergent-beam electron-diffraction patterns were obtained using a converged beam with a full width at half maximum of 3.6 nm, which corresponds to 6.7 room temperature unit cells in Pr$_{0.48}$Ca$_{0.52}$MnO$_3$. From the composition $x = 0.52$ in a one-dimensional model of charge ordering using Mn$^{3+}$ and Mn$^{4+}$, one would expect alternating Mn$^{3+}$ and Mn$^{4+}$, with an extra Mn$^{4+}$ every 13.6 unit cells on average. This would lead to a value of $q/a^* = 0.5$ being recorded in
structure is four times the room-temperature pseudocubic cell.\textsuperscript{11} The third term couples $\eta$ and $\nabla \phi$ with strength $c$, the fourth term is the strain energy density in terms of the bulk elastic modulus $\kappa$, and the fifth term gives the elastic energy due to the stress $\sigma$ on the film from the substrate. For ease of reference, these parameters are defined in Table II, which also summarizes the values obtained in the experiments described in this paper.

Minimizing $F$ in the plane-wave limit ($\nabla \phi=$constant and $\nabla \eta=0$), we find
\begin{equation}
\nabla \phi = \frac{\delta - \frac{c\sigma}{\kappa^2}}{1 - \frac{c^2}{\kappa^2}}. \tag{2}
\end{equation}

To calculate the approximate levels of stress in each film, the strain in the $a$ and $c$ directions must first be found. Let SrTiO$_3$ be substrate 1 and NdGaO$_3$ be substrate 2. Calculating the strain using the mismatch of the $a$ and $c$ lattice parameters for the substrate and La$_{0.50}$Ca$_{0.50}$MnO$_3$, we obtain $\eta_{1a}=0.012$, $\eta_{1c}=0.0066$, $\eta_{2a}=-0.0048$, and $\eta_{2c}=0.0035$ (see Table I). These values can be used to calculate the level of strain in the films, using $\sigma_a = E(\eta_a + r\eta_c)/(1-\nu^2)$, where $E$ is the Young’s modulus of the material. Using approximate values of the bulk modulus $\kappa$ (135 GPa) and shear modulus (31 GPa),\textsuperscript{11} we obtain a Young’s modulus of 86 GPa and a Poisson’s ratio ($\nu$) of 0.39, giving $\sigma_{1a}=0.00405E$ and $\sigma_{2a}=0.0172E$.

Considering the results for the film on SrTiO$_3$, with $\nabla \phi_1=0$,
\begin{equation}
\frac{\sigma_{1a}c}{\kappa^2} = \delta. \tag{3}
\end{equation}

To obtain an approximate value of $\delta$ we consider the results for polycrystalline samples, and assume that the extraneous effects which render $\delta$ finite have different values in

Table I. In-plane strains for La$_{0.50}$Ca$_{0.50}$MnO$_3$ on NdGaO$_3$ and SrTiO$_3$ at 90 K and 300 K. Positive numbers refer to the La$_{0.50}$Ca$_{0.50}$MnO$_3$ parameter being smaller than the substrate parameter, so the film is stretched. Data from Refs. 23–25.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\eta_a$ at 90 K</th>
<th>$\eta_c$ at 90 K</th>
<th>$\eta_a$ at 300 K</th>
<th>$\eta_c$ at 300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>NdGaO$_3$</td>
<td>0.0048</td>
<td>0.0035</td>
<td>0.0017</td>
<td>0.0119</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>0.0012</td>
<td>0.0066</td>
<td>0.0176</td>
<td>0.0157</td>
</tr>
</tbody>
</table>
TABLE II. Table showing the meaning and values of the parameters used and derived in this paper.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Meaning</th>
<th>Value/constraint</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>Strain due to substrate</td>
<td>See Table I</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Electron-electron coupling</td>
<td>Unknown, but see $v$ and $V$ below</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Deviation of $q$ from $0.5a^*$ in the absence of strain from a substrate</td>
<td>Positive-estimated value $0.0124a^*$</td>
</tr>
<tr>
<td>$\delta_c$</td>
<td>Deviation of $q$ from $0.5a^*$ in the absence of lock-in term</td>
<td>$0.03a^<em>-0.77a^</em> \ a$</td>
</tr>
<tr>
<td>$c$</td>
<td>Coupling between strain and superstructure</td>
<td>$c/\xi^2=-1.1, c/\kappa=-0.3$</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Coupling between commensurate periodicity and superstructure</td>
<td>$2v/\eta \xi^2 &lt; 0.0009$, or $v/\xi^2 &lt; 0.0018$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stress due to substrate</td>
<td>0.00405E on SrTiO$_3$, 0.0172E on NdGaO$_3$</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Bulk modulus</td>
<td>135 GPa</td>
</tr>
<tr>
<td>$S$</td>
<td>Shear modulus</td>
<td>31 GPa</td>
</tr>
<tr>
<td>$E$</td>
<td>Young’s modulus</td>
<td>86 GPa</td>
</tr>
<tr>
<td>$V$</td>
<td>Strength of electron-phonon coupling and electron-electron coupling</td>
<td>$=(2v/\eta \xi^2) = (v/2 \xi^2)$ where $v/\xi^2$ is the ratio between the strength of electron-phonon coupling and electron-electron coupling</td>
</tr>
</tbody>
</table>

where $V = 2v/\eta \xi^2 = v/2 \xi^2$. Here, $v/\xi^2$ is the ratio between the strength of the electron-phonon coupling and the electron-electron coupling. The ground state can be found by minimizing this quantity with respect to $\phi$, with the boundary condition that at $\phi = 0$, $\nabla \phi = \delta + t$, where $t \ll \delta$. In the limit of small $t$, this gives $F = V$. The free energy of this state can be calculated and compared to the energy of the lock-in state, which has $\phi = \pi/8$, $\nabla \phi = 0$, and thus $F = \delta^2$. So if the energy of the lock-in state is lower, the superstructure will lock in and $q/a^* = 0.5$ (see Fig. 5).

Since the wave vector does not lock into the lattice for $\delta = 0.05$, it follows that $V$ must be smaller than $\delta^2$, since above this level a lock-in should occur. However, we know that a lock-in does occur in one grain. Therefore in that grain $\delta$ is taken to be the smallest value previously observed in a manganite with $x=0.52$, which is $\delta = 0.02$. Therefore the lock-in provides a lower bound for $V$, since $V$ must be larger than $\delta^2$ in this case to allow a lock-in to occur. So $0.0025 < V < 0.0004$ for Pr$_{0.48}$Ca$_{0.52}$MnO$_3$ (Table II). This method can also be used to provide an upper bound for $V$ in Lao$_{0.48}$Ca$_{0.52}$MnO$_3$, since no lock-in is observed when $q/a^* = 0.03$, giving $V < 0.0009$ (Table II).
The significance of the value of the wave vector being the same at length scales of 3.6 nm and 500 nm was then investigated. The equations shown above were used to calculate the values of $q$ for an array of 925 room-temperature unit cells (equivalent to the diameter of the 500 nm aperture). From this array 90 nonoverlapping regions of 6.7 unit cells were chosen. The standard deviations of the average wave vectors of these regions were found for different values of $V$. The results are shown in Fig. 7, displayed as a percentage of the 925-cell average. Given the 1% standard deviation in the measurement of the wave vector for the selected area diffraction and convergent-beam electron-diffraction results, we wanted to know the probability of measuring large- and small-scale values close to each other for each value of $V$. We assume that both the measurement of the wave vector and the simulation of the areas of 6.7 unit cells have Gaussian distributions. The probability of the convergent-beam electron-diffraction result being within 4% of the selected area-diffraction result experimentally is then 95%. Then taking the distribution of the simulation, the probability of the small-scale results being within 4% of the large-scale result can be calculated from the standard deviation at each value of $V$. This indicates the probability of obtaining the result we did for each value of $V$. As can be seen, the probability decreases with increasing $V$, meaning that the values of $V$ close to 0.0004 are more likely to be correct. All parameters are summarized in Table II.

V. CONCLUSIONS

The CDW Landau theory of the manganites predicts that a lock-in should occur in the manganite superstructure when $x > 0.5$, for some range of $x$ close to 0.5. In this paper we report an observation of such a lock-in. It is also expected that the electron-phonon coupling parameter should be small relative to the electron-electron coupling parameter. Based on our data, we have used Landau theory to constrain the value of the electron-phonon coupling relative to the electron-electron coupling to between 0.08% and 0.50%, with the results indicating that the lower end of this scale has a higher probability. In addition, we have found that the coupling of the strain to the superstructure in the stripe phase is of the same magnitude as the electron-electron coupling, indicating that the coupling of the superstructure to strain is unexpectedly strong. This is particularly interesting since our results also suggest that the stripe phase cannot exist in the absence of strain. Therefore the properties of the manganite CDW can now be quantified to a reasonable extent (Table II). Our results also raise the possibility of using strain to manipulate the CDW, via the strong coupling of strain to the CDW and the possibility of destroying the CDW by releasing the strain.

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