Structural compliance, misfit strain, and stripe nanostructures in cuprate superconductors

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Structural compliance is the ability of a crystal structure to accommodate variations in local atomic bond lengths without incurring large strain energies. We show that the structural compliance of cuprates is relatively small, so that the short, highly doped, Cu-O-Cu bonds in stripes are subject to a tensile misfit strain. We develop a model to describe the effect of misfit strain on charge ordering in the copper-oxygen planes of oxide materials and illustrate some of the low-energy stripe nanostructures that can result.

The existence of charge stripes in high-$T_c$ superconductors and their relevance to the high-$T_c$ property are highly debated subjects at present. The tendency towards stripes implies that regions of the CuO$_2$ plane that are heavily doped, and therefore have short bonds, coexist with those that are lightly doped. The tendency towards stripes makes with the plane.

FIG. 1. The angle $\alpha$ that describes the buckle in the copper (solid circle)-oxygen (open circle)-copper bonding.
shortens from $r_s = 1.904 \text{ Å}$ to $r_s = 1.882 \text{ Å}$, i.e., by $\sim 0.022 \text{ Å}.^{17}$ For illustration purposes, we take this bond-length difference to be an estimate of the difference in length of the short and long Cu-O bonds in the Cu-O planes. In order for structural compliance to accommodate this bond-length mismatch we need $\delta_r = 0.022/1.89 = 0.012$, which requires a tilt angle of 8.9° in the LTT symmetry and of 12.6° in the LTO system. However, in the La$_{2-x}$(Sr,Ba)$_x$CuO$_4$ system tilts have LTO symmetry with a tilt angle of $\sim 3.5^\circ$ resulting in a structural compliance of only $\delta_r \sim 0.001$. There is therefore insufficient structural compliance to accommodate the short Cu-O bonds in these materials, resulting in a misfit strain if charges localize, for example, in stripes. Note that these numbers represent rough estimates and the precise value for the crossover will depend on the charge density and the degree of delocalization of the charge in the stripe as well as details of whether the stripes are site or bond centered. Nevertheless, it is evident that in cuprates, stripe formation will lead to misfit strain, but that materials with moderate tilts could accommodate short bonds with little or no misfit strain.

We now consider what happens to the microstructure of the charge stripes in the case where a misfit strain is present. We expect to show that the presence of strain results in a breakup of the stripes into short segments. Lattice strain therefore prevents the stripes from ordering over long range; a situation that is a prerequisite for most stripe theories of high-temperature superconductivity.\textsuperscript{2,3,24–28} This has implications for superconductivity by producing an electronic microstructure\textsuperscript{29} of domains of broken stripes that results in a high density of topological stripe defects.\textsuperscript{25,30,31} The ends of the stripes are in a state of high stress, making them especially susceptible to charge fluctuations.

We assume that the neighboring doped Cu sites in a stripe have a separation $l_0$ that is shorter than, but approximately equal to, the average separation $a$ dictated by the crystal structure and the average doping level. In this case, as the stripes form and increase in length, strain energy will build up. The basic competition is between the length scale of the periodic potential $a$ due to the lattice structure and the natural length of the short bonds due to near-neighbor doped sites, as illustrated in Fig. 2. The breakup length scale of the stripes is approximated by comparing the strain energy gain $[\sim k_{nn}N(a-l_0)^2/2]$, which occurs when a strained stripe of length $L \ll Na$ breaks up, to the formation energy per bond of an unstrained stripe ($\sim J_{nn}$). This yields (dropping the constant prefactors)

$$N_c \approx \left( \frac{J_{nn}}{k_{nn}} \frac{1}{a-l_0} \right)^2.$$  

The key parameters setting the scale of the energies in Eq. (1) are $k_{nn}$, which are proportional to the stiffness of the Cu-O bonds and $J_{nn}$, the energy gain (per bond) in forming stripes. The spring constant $k_{nn} = V_0/a^2$, where $V_0$ is of the order of an ionic bond energy ($\sim 5$ eV). $J_{nn}$ is of the order of the stripe formation temperature, e.g., the temperature where the pseudogap appears $\sim 400 \text{ K} \sim 40 \text{ meV}$. As discussed above, the misfit strain for cuprates is of order $(a-l_0)/a \sim 0.01$. Use of these numbers in Eq. (1) indicates that for cuprates, the characteristic length of stripe domains, $N_c$, should be of the order of 100 lattice spacings. The stripe length diverges quadratically [see Eq. (1)] as the misfit strain approaches zero leading to long-range stripes in oxides with no misfit strain, as appears to be the case, for example, in La$_{2-x}$Nd$_x$Sr$_x$CuO$_4$.

We now develop a model to test whether the simple prediction (1) holds when there are many stripes, and to study the stripe nanostructures produced once strain destabilizes long-range stripes. This model is as simple as possible while including the key aspects of doping, stripes, and misfit strain. Note that this model considers only stripe breakup and not stripe formation. We assume that magnetic effects and long-range Coulomb interactions play a key role in stripe formation,\textsuperscript{3,34,35} but that misfit strain leads to their breakup. Quantum fluctuations may also contribute to stripe breakup, however, we consider here only the misfit strain that we assume is the dominant factor. The model is defined on a square lattice where each site is assigned an occupancy number $n_i$ where $n_i = 1$ indicates that the site is doped with a hole and $n_i = 0$ indicates that it is undoped:

$$H = -\sum_{ij} J_{nn} n_i n_j + \sum_{ij} J_{nnn} n_i n_j + \mu \sum_i n_i + \sum_{ij} k_{nn} (l_{ij} - l_0)^2 n_i n_j + \sum_i n_i V(r_i).$$  

Similar to the stripes seen in La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_4$ where a hole resides on every second site along the stripe, we can simplify the computation by considering a sublattice of every second Cu site and include an attractive nearest-neighbor interaction, $J_{nn}$ and $J_{nnn}$, respectively. These will result in stripe formation provided $J_{nn} > 0$ and $J_{nnn} > 0$. The third term in the Hamiltonian has the chemical potential $\mu$ and allows us to vary the doping in the model to some occupation density $\rho$. Note that our sublattice model only allows doping at every second copper site along the $x$ and $y$ directions so that $\rho$ is related to the doping fraction $\rho$ in the cuprates via $(\rho) \approx 4\rho$. The last two terms in Eq. (2) are the strain terms. The first term contains the misfit strain that occurs when two nearest-neighbor sites on the sublattice are occupied (this corresponds to next-nearest-neighbor sites in the cuprates). The parameter $l_0$ is the natural length of this bond, i.e., the length that the bond would have in the absence of stress. The sec-
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ond term $V(r_i)$ is the periodic potential imposed on the copper oxide layers by the crystal structure. In our model we take this potential to be modulated along both of the in-plane axes of the CuO$_2$ planes with a wavelength $a$ and having an amplitude $V_0$. These terms in the Hamiltonian result in a finite stress energy unless $l_0 = a$, as can be seen in the schematic in Fig. 2. The strain energy is long range and has to be relaxed self-consistently using a gradient or Newton’s method.

It is difficult to find the ground state of the strained lattice gas (2), however, it is easy to demonstrate that long-range stripes are unstable in the presence of misfit strain and to test the general form (1). To illustrate this, consider the three-stripe nanostructures of Fig. 3. From the lattice-gas model (2), it is evident that the long-range stripe has the lowest energy, provided there is no misfit strain. However, in the presence of misfit strain, the lower two nanostructures of Fig. 3 have lower strain energy, though they do incur an energy cost proportional to $J_{nn}$ due to breaking up the long range stripes. The strain energy in the long stripes is simply

\[ k_{nn}(l_0-a)^2/2 \]

per bond. For a strain of 0.01 and $V_0 = 1 = k_{nn}$ (in lattice units), this leads to a strain energy of 0.0152 for the structure of the top panel in Fig. 3. In contrast, the

interleaved stripe and weave structures (bottom two panels in Fig. 3) have strain energies of 0.0100 and 0.00765, respectively. These calculations were carried out using simple gradient descent on the unit cells of Fig. 3, with the periodic cell shape fixed, and the boundary atoms fixed and excluded from the total-energy calculation. Tests using free and periodic boundaries and other nanostructures indicate that the state of lowest energy does depend on a variety of factors, including doping, boundary conditions, and cell size. However, in all cases, the strain energy of the long-range stripes is of the order twice that of the stripe domain states and this is not sensitive to the modeling details. It is thus reasonable to find the breakup length scale of the long-range stripe array (top panel of Fig. 3) by comparing the strain energy of long-range stripes with the nearest-neighbor energy cost incurred in breaking the stripes. This leads to $N_s k_{nn}(l_0-a)^2 = J_{nn}$, which is consistent with the simple estimate (1). In general, the ground-state structures of discrete strained systems are extremely rich and we expect a similar richness in the ground structure of the Hamiltonian (2) as a function of doping and temperature, as will be described elsewhere. However, the main point emphasized here is that misfit strain destabilizes long-range stripes in cuprates at a length scale well approximated by Eq. (1).

Now we briefly comment on a number of experimental observations that can be explained by the strain-induced stripe nanostructures. The most important point is that the presence of strain will prevent the stripes from ordering over long range resulting in broken stripes even at moderately high dopings. Broken stripes will have significant quantum fluctuations. More structural compliance in the form of enlarged octahedral tilt distortions will reduce the misfit strain and cause the stripes to grow in length, presumably slowing their dynamics. Systems where the CuO$_2$ plane is in tension, or nearly in tension, such as the Hg and Tl systems will have faster stripe dynamics and therefore better superconducting properties and higher $T_c$’s as observed. Similarly, the increase in $T_c$ with decreasing tilt distortions have an explanation here. The strained stripes will also tend to stabilize the LTT phase over the LTO phase because this results in greater structural compliance, as we discussed, and therefore a decrease in the misfit strain. Stripe microstructures, such as those shown in the third panel of Fig. 3 will result in local LTT symmetry tilts but averaging over the two 90° rotated LTT variants will lead to an effective LTO behavior, as observed in La$_{2-\delta}$Ba$_{\delta}$CuO$_4$. Also, highly misfitting ions will give rise to large amplitude tilts locally, resulting in locally varying structural compliance that will tend to pin the stripes. This explains the observation that superconductivity can be suppressed by increasing the mean-square dopant-ion size at fixed average dopant-ion size. Finally, we note that ferroelastic effects, the observation of tweed microstructures, as well as the sensitivity of $T_c$ on dopant ordering in YBa$_2$Cu$_3$O$_{6.5+\delta}$ and La$_{2-\delta}$CuO$_{3+\delta}$, might have an explanation in strained stripe induced microstructures.

In summary, we point out that doping shortens the Cu-O bond length and that inhomogeneous doping in the form of stripes results in a tensile misfit strain. This breaks up the

FIG. 3. Stripe nanostructures in cuprates. In systems with tensile misfit, the static stripe (top panel) has a high-strain energy. Interleaved stripes (middle panel) and the weave microstructure (bottom panel) reduce this strain energy as they can accommodate strain relaxation. One unit cell of each microstructure is shown. Only copper atoms are shown. Concentric circles indicate doped sites, while sites indicated by crosses are excluded from the strain relaxation. For illustration purposes the natural length of bonds between doped sites are 10% shorter than bonds between undoped sites.
stripes and results in, presumably fluctuating, domains of broken stripes where the domain size depends on the misfit strain. Structural compliance in the form of buckling modes can reduce the misfit strain and result in long-range ordered and static or quasistatic stripes reducing or destroying superconductivity.

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