

The pseudogap regime revisited *

Questions which have been raised concerning the “pseudogap” region of the cuprate phase diagram since the earliest days include: (1) Does the system undergo, as a function of doping p and temperature T , one or more phase transitions? If so, is it (they) first- or second-order? (2) If the answer to (1) is yes, what is the nature of the low-temperature phase(s), and in particular, which symmetry(ies) is broken? (3) Is the (pseudo)gap seen in the single-fermion excitation spectrum in this regime a relic of the superconducting gap? If not, what is its origin? (4) More generally, are the unusual phenomena occurring in this regime helpful or harmful to the occurrence of superconductivity, or just irrelevant to it? By Nov. 2015, we can probably say that we have been able to obtain answers to some though not all of the above questions.

Let's start by noting a few reasons why it has taken 30 years even to get to our current limited understanding. In the first place, as noted earlier in the course, (and explained further below) many of the experimental techniques available can only be used on one or a few cuprates (e.g. neutron scattering requires large crystals, so mainly done on LSCO or YBCO; ARPES requires clean surfaces, so mostly done on BSCCO; etc.). The effect of such restrictions is further complicated by the fact that the various cuprates differ, in some cases qualitatively, in their crystallographic characteristics: the most obvious example of this is the different layer multiplicities, but in addition e.g. YBCO is strongly anisotropic in the ab -plane, and some of the La compounds undergo at low temperatures a transition between tetragonal and orthorhombic symmetries. Particularly when one is considering the possibility of types of order (“nematic”) which break the tetragonal symmetry, this consideration may be important.

Secondly, it is necessary to remember that in addition to the obvious variables p and T , the behavior of the system may be a function of other thermodynamic variables, in particular of pressure and magnetic field: contrary to what one might perhaps infer from “back-of-envelope” arguments, the evidence is that fields as low as 50T can change the phase diagram qualitatively, and it is necessary to remember this when comparing the conclusions from different types of experiment.

Thirdly, not only are the error bars on some of the experiments of the same order of magnitude as the signal (this particularly applies to the neutron scattering data), but even when the raw data is clear-cut its interpretation may not be immediate or unambiguous; in several cases (e.g. the quantum oscillation data) the usually accepted interpretation has only been derived rigorously within a Fermi-liquid picture which may not be applicable over the whole of the regime in question.

With those caveats in mind, let's turn first to the question of the existence or not of one or more phase transitions in the pseudogap regime. Generally speaking, one expects that a first

* A fairly good picture of the situation in mid-2012 can be obtained from the collection of papers in the Nov. 2012 issue of *Physica C* (hereafter referenced as $\phi C12.11$). Later developments are referenced individually in the text. (A few of the papers in the March 2015 issue of *Physica B* [sic!] are also of interest: this is referenced as $\phi B15.3$)

(second) order phase transition should, barring pathology, lead to a discontinuity (derivative discontinuity) in the thermodynamic and transport properties of the system. Until recently, the problem has been that while many properties of the cuprates, such as spin susceptibility, resistance, etc., show fairly sharp changes across the so-called T^* line, there has been no clear observation of either a discontinuity or even a slope discontinuity in any measured quantity. This has left it unclear whether (a) the T^* line does not in fact correspond to a thermodynamic phase transition but to a smooth “crossover” (such as is e.g. realized in the dissociation of diatomic molecules in the gas phase), or (b) a true thermodynamic transition exists, but its effects are obscured by the presence of disorder, which tends to smooth out any discontinuity.

This issue appears to have been resolved in June 2013, at least as regards one particular cuprate (YBCO), by the experiment of Shekhter et al.* on ultrasound velocities and absorption. They fixed the doping[†] to a value (~ 0.12) corresponding to $T_c = 61 \cdot 6\text{K}$, at which other measurements give a value of $T^* \sim 250\text{K}$. They calibrated the measurements by observing a small ($\Delta f/f \sim 10^{-4}$) discontinuity[‡] in the US velocity, and a more noticeable derivative discontinuity, at the superconducting phase transition. At a temperature of approximately 245K they observe a $\sim 5\text{K}$ wide slope discontinuity (but no discontinuity in the velocity itself); they also found a marked increase in absorption around this temperature. Although the slope discontinuity (shown in the crucial figure of their paper (see fig. 1)) is only $\Delta\{d/dT(\Delta f/f)\} \sim 10^{-6}/\text{K}$ and so not very spectacular to the naked eye, it has been very widely accepted as conclusive evidence for a second-order phase transition which, at least at this doping value, seems to occur at the T^* line. Whether there is one or more additional phase transitions (e.g. at the T_K line to be discussed below) is left open by this experiment, but if so it leaves no signature at the level of a few parts per million which is its sensitivity.

If one or more symmetries are broken in the pseudogap regime, what are they? If for simplicity we think about a strictly tetragonal system such as Hg-1201, then at higher temperatures the symmetries which are unbroken include: time reversal (\hat{T}), space inversion (\hat{P}), translation (modulo lattice vectors) (call it \hat{Z}) and $\pi/2$ rotation in the ab-plane (call it $\hat{R}_{\pi/2}$)[§]. A phase which breaks both \hat{Z} and $\hat{R}_{\pi/2}$ (as in fig. 3) is called a “one-dimensional stripe phase”: one which breaks \hat{Z} but not $\hat{R}_{\pi/2}$ (as in fig. 4) is a “2D stripe phase” (or “checkerboard” phase); one which breaks $\hat{R}_{\pi/2}$ without breaking \hat{Z} is “nematic”; one which breaks \hat{P} but not \hat{T} is “gyrotropic”. (There appears to be no special name, other than TRSB, for a phase which breaks \hat{T} with or without breaking \hat{P}). All of these possibilities have been seriously considered as states of the cuprates in the pseudogap regime.

Next, let’s review a few of the experimental probes available to investigate this question. **STM** and **ARPES** are both surface probes, and hence have been mainly conducted on these

* Nature **498**, 75 (2013)

[†] Shekhter et al. repeated the experiment at overdoping corresponding to $T_c \sim 88\text{K}$ getting similar results well inside the superconducting dome.

[‡] This is probably due to the onset of the Meissner effect.

[§] Also inversion in an ab-plane crystal axis, but there’s no evidence that this is broken in the pseudogap regime.

cuprates which are easily prepared with clean surfaces, that is BSCCO and to a lesser extent YBCO. STM can be regarded for our purposes* as measuring the total (surface) electron (charge) density $\rho(\mathbf{r})$ as a function of position, while ARPES measures the corresponding quantity in \mathbf{k} -space, i.e. the single-electron occupation factor $n(\mathbf{k})$. In both cases, spin-polarized variants are available (but have not to my knowledge been widely used in the present context). Turning to bulk probes, **neutron scattering** requires large pure crystals, so has been done mostly on LSCO (or LBCO) and YBCO; the neutrons effectively “see” the electron spin density and the nuclear density (hence are sensitive to crystallographic distortions); they do not see the charge density directly. By contrast, **X-ray scattering** is directly sensitive to the electronic charge distribution. As well as the traditional Bragg (elastic) scattering technique, there are now available a number of variants, of which one in particular, the so-called **RSXS** (resonant soft X-ray scattering) has played a major role in work on the pseudogap regime and thus deserves a little discussion, which I now give.

RSXS[†] (or REXS, “resonant elastic X-ray scattering”) is essentially a special case of Raman scattering, in which a single photon is incident and a single phonon emerges; however, in this case (a) the scattering is elastic, i.e. the energy transfer $\omega = 0$ but the momentum transfer $\mathbf{q} \neq 0$. (b) the frequency of the incident photon is tuned close to an atomic transition, e.g. in cuprates, the Cu L or O K edges (hence typically $400 \text{ eV} - 1 \text{ keV}$). The theory of what exactly is measured by the RSXS cross-section is complicated and not all that well-developed, but Abbamonte et al. (ref. cit.) argue convincingly that it may be considerably simplified in the case of a K transition in the cuprates, where the hole created by absorption of the incident photon is in the 1s shell and may not interfere with the propagation of the electron created, which is in the 3d shell. Because the outgoing phonon must refill the hole, i.e. return the electron to the same atomic site, the RSXS scattering amplitude is proportional to the expression

$$S(q\omega) = \sum_{jn} \frac{|\langle n | d_j^+ | 0 \rangle|^2}{\hbar\omega - (\epsilon_n - \epsilon_{case} - \mu) + i\eta} \exp i\mathbf{q} \cdot \mathbf{r}_j$$

where the sum over j is over atomic sites. Note that this expression is zero for $\mathbf{q} \neq 0$ for any uniform state. For a nonuniform state, and for given ω , it is proportional to the F.T. of the probability of being able to create an electron on site j , i.e. of $1 - n_j$. Following this line of argument, Abbamonte et al. conclude that the RSXS scattering intensity is given, apart from a constant involving the detailed form of the matrix elements, etc., by

$$I_{RSXS}(q\omega) \sim \left| \int -d\mathbf{r} \int d\omega' \frac{A_{STM}(\mathbf{r}\omega)}{\omega - \omega' - i\eta} \exp i\mathbf{q} \cdot \mathbf{r} \right|^2$$

* Actually both STM and ARPES measure more than this, but to discuss this we would need to go into the question of energy-dependence, which is unnecessary for present purposes.

[†] Abbamonte et al, in ϕ C12.11

where $A_{STM}(\mathbf{r}, \omega)$ is the quantity measured in an STM experiment. (Or more accurately, what would be measured at point \mathbf{r} (in bulk) if one could do the experiment there!)

One other bulk probe which has been important in recent work on the cuprates is NMR. As is well-known, independently of the (nonzero) value of the nuclear spin I , the frequencies and linear widths of the NMR peaks give information on the magnetic environment of the nuclei in question. However, for $I > 1/2$ (e.g. ^{63}Cu and ^{65}Cu , both with $I = 3/2$) the nucleus also has an electric quadrupole moment, and this “sees” the electrical environment; in particular, by studying the anisotropy (or not) of the electric quadrupole shifts and linear widths we can infer the presence or not of nematic order on the intra-cell scale.

Among the many optical probes which have been used on the cuprates, the ones most relevant in the present context are those which detect optical rotation, namely the **Faraday effect** (rotation of the plane of polarization of light transmitted through the medium) and the **Kerr effect** (rotation of the plane of polarization of light reflected from the surface). The Faraday effect as such can occur in a medium which is optically anisotropic but does not break P or T symmetry, if the plane of polarization of the incident light is not parallel to a crystal optical axis, thus by itself it is not very useful; however, this effect can be eliminated by reversing the path traversed, and the situation is then closely connected to the Kerr effect. The significance of a nonvanishing Kerr effect has been somewhat controversial in the recent literature: some authors have argued that it can occur as a result of gyrotropy (breaking of P but not T), but Kapitulnik* has argued, to my mind convincingly, that it requires (what I would call†) genuine breaking of time-reversal symmetry.

Now let’s turn to what is perhaps the area in which most progress has been made over the last three years, namely the existence of spin and charge “stripes”. Let’s start with a bit of history: Since very early days in the story of cuprate superconductivity, it has been appreciated that the original “Bednorz-Müller” compound $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, has a very deep minimum ($< 5\text{K}$) in T_c at a value of x equal to 0.125 (“1/8 doping”). A similar minimum is observed in the related compounds $\text{La}_{1.8-x}\text{Eu}_{0.2}\text{CuO}_4$ (“LESCO”), and $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$, again at or close to $x = 0.125$, but **not** in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (cf. Jie et al., *Physica* **481**, 48 (2012), fig. 2a). What the three compounds which show the minimum have in common, and is missing in plain LSCO, is a subtle “tilt” in the oxygen octahedral. In the LTO phase this is uniform throughout the sample, while in the LTT phase it alternates between (“naïve”) unit cells along the c -axis, thus giving an overall tetragonal symmetry. In any case, in the present context what is interesting is that already 20 years ago LBCO (and subsequently the other compounds showing the deep minimum) were found, by neutron and X-ray scattering experiments, to display both spin and charge ordering, below a transition temperature T_{CO} which peaks close to $x = 0.125$ at around 60K^\ddagger (and appears to be associated with the onset of the LTT phase) (see fig 2). The in-plane periodicity of the charge order is about $4a$, and that of the spin order (as superimposed on the regular AF

* $\phi\text{B15.3}$

† in Kapitulnik’s language, “breaking of reciprocity” (the distinction is necessary only in the presence of dissipation)

‡ The temperature below which spin ordering is detected is somewhat lower, see Hücker, $\phi\text{C12.11}$

periodicity) about $8a$, but there is no commensuration; the data appear to be consistent with the picture shown in fig. 3. The direction of the “stripes” is staggered along the c -axis (as might be expected from the nature of the local orthorhombic anisotropy in the LTT phase). A very important observation is that the linear ab -plane conductivity remains fully metallic throughout the charge-ordered regime (contrast the behavior of more “traditional” CDW systems such as NbSe_3 , which are near-insulating in weak electric fields).

For many years it was debated whether the occurrence of spin and charge stripe order in LBCO and the related LSCO systems was a specific consequence of the peculiar crystallographic properties of these systems or whether it was a more general characteristic of the cuprates, and whether, if the latter is true, the ordering is always locally “1-dimensional” as in fig. 3 or “2-dimensional” (“checker-board”, see fig. 4). A flurry of experiments, particularly using resonant soft X-ray spectroscopy (RSXS), over the last three years seem to have answered these questions: See E. Blackburn, *Physica B* **460**, 132 (2015).

The most extensive experimental data is on YBCO (which, recall, is untypical in being strongly orthorhombic): they show a modulation of electron density which onsets below a temperature $T_{\text{CO}}^{(p)}$ which depends on doping and has a maximum of $\sim 150\text{K}$ ($< T^*$) close to $p=0.125$ (which we recall does **not** correspond to a local minimum in $T_c(p)$ for YBCO); the intensity in these subsidiary Bragg peaks gradually disappears in the superconducting state. With the usual convention that the components of the wave vector \mathbf{q} are measured in units of $2\pi/a_i$ when a_i is the relevant lattice constraint, the characteristic wave vectors \mathbf{q}_1 and \mathbf{q}_2 at which the subsidiary peaks appear are $(q_h, 0, 0 \cdot 5)$ and $(0, q_k, 0 \cdot 5)$, where $q_h \sim q_k \cong 0 \cdot 31$, corresponding to a periodicity of approximately 3 lattice constraints in both a and b directions (but q_h is not exactly equal to q_k , and neither is commensurate). It may be significant that q_h and q_k correspond, at least approximately, to nesting vectors associated with the “flat” parts of the (hole) Fermi surface. This is the behavior which would be expected at a more traditional Peierls instability; however, see below.

Because of the untypical orthorhombic anisotropy of YBCO, it is important to confirm these results on other cuprate superconductors. Over the last three years qualitatively similar results on other cuprate superconductors. Over the last three years qualitatively similar results, again mostly using RSXS, have been obtained on Bi-2201, Bi-2212, BiPbSrCaCuO; LSCO and, most importantly, on Hg-1201 which is exactly tetragonal in crystal structure. Thus the orthorhombic anisotropy of YBCO does not appear to be playing an important role. As far as I know, however, there is no hard evidence at present for any static spin ordering in any of these materials (or in YBCO), and which there are certainly strong low-energy spin fluctuations their characteristic wave vector appears to scale differently with doping than that of the charge stripes.

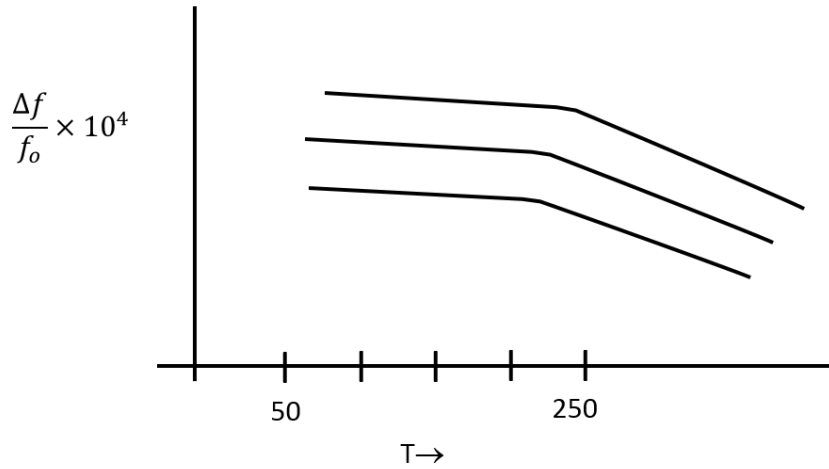


Fig 1 Dependence of ultrasound velocity of various modes in temperature (schematic, after Shekhter et al.)

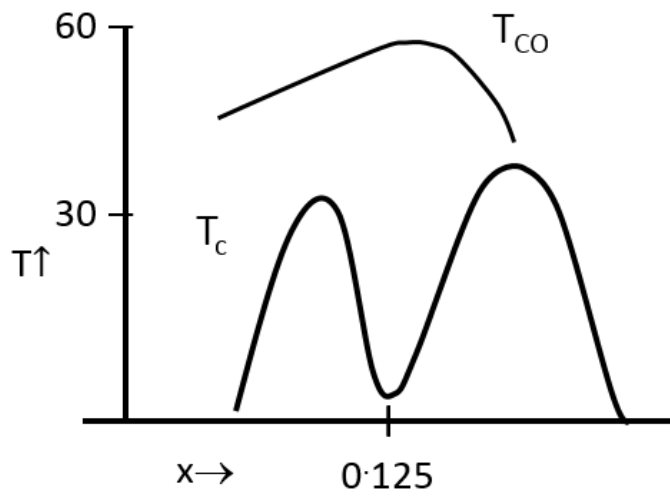


Fig 2 Doping-dependence of charge-ordering temperature T_{CO} and superconducting transition temperature T_c in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$.

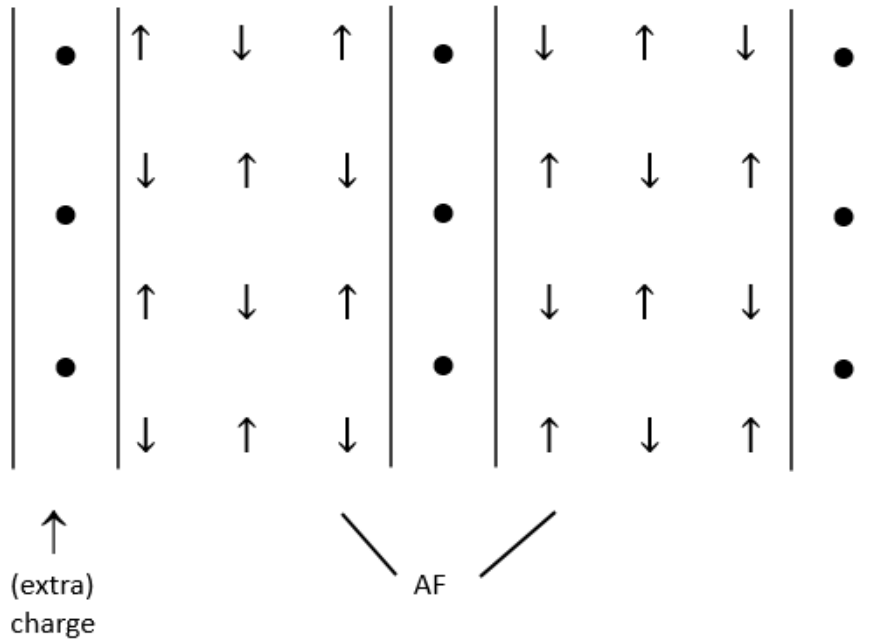


Fig 3 “2-dimensional” (“stripy”) order in LBCO (schematic)

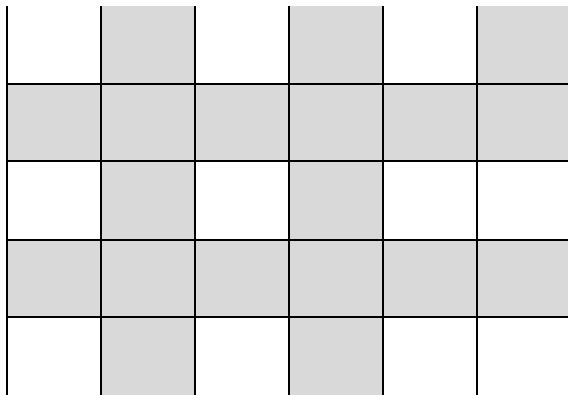


Fig 4 “1-dimensional” (“checkerboard”) charge order (schematic)

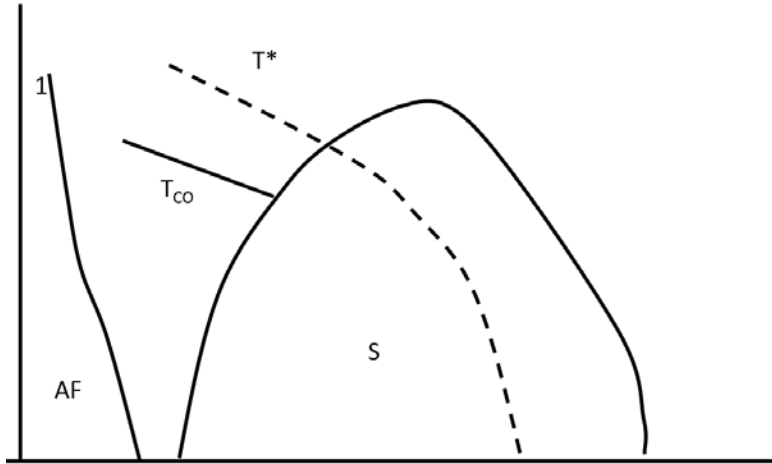


Fig 5 Tentative cuprate phase diagram

Until very recently, it has been unclear whether the charge ordering in YBCO and the other non-LA-based compounds is of the 1-dimensional (“stripe”) or 2-D (checkerboard”) type. (In the La-based compounds it is certainly “stripy”, but this could be due to their special crystallographic characteristics). In March 2015, Comin et al.* were able to resolve this question by a very ingenious RXS technique: they examined the behavior of the component of the structure factor $S(Q)$ which peaks around (say) Q_a as a function of the difference $q \equiv Q - Q_a$. A very distinct anisotropy was found (see their fig. 1.c-e†, demonstrating unambiguously that the ordering is 1D. However, the correlation length is only $\sim 20 - 30 \text{ \AA}$, so that the system “looks” 2D from a macroscopic point of view. Further work showed that the charge order primarily resides on the $0.2p$ orbitals and has a d-wave character.

By combining RSXS, STM and ARPES measurements on the same sample of YBCO, Comin et al.‡ were able to draw a very important conclusion concerning the single-electron states which go into the formation of the CDW: If we look at the variation with doping of the “pitch” of the latter (that is, the q -value at which the peak in the RSXS data appears) it does **not** correspond to the “nesting” vector on the Fermi surface (i.e. the vector connecting the nearly-flat portions) but rather to the vector connecting the ends of the Fermi arcs (recall that these appear at a higher temperature than that for the onset of CDW order). Thus it appears that the existence of a

* Science **347**, 1335 (2015)

Comin et al. Nature Materials **14**, 796 (2015)

† Wu et al., Nature **477**, 191 (2011)

‡ Science **343**, 390 (2014)

pseudogap (terminating the arcs) is a necessary condition for the appearance of a CDW, rather than vice versa.

Further information on the nature of the anisotropy is given by NMR experiments. One important finding* is that in magnetic fields sufficient to suppress superconductivity in YBCO, true CDW long-range order appears below about 50 – 70 K. In further work in lower fields†, the same group observed an onset of electronic quadrupole broadening (indicating intra-cell nematicity) below an onset temperature which apparently coincides with the onset of peaks in the RSXS data and of a nonzero Kerr angle. On the other hand, they put an upper limit on the **magnetic** field of 0.8G at the apical O sites and 4G at the O(2) (in-plane) sites, a much lower value than required by most theories of the violation of T symmetry. They raise two important questions: (1) is there a relation between the (short-ranged) nematic order observed in those experiments and the long-range CDW order seen at high fields and low temperatures in earlier experiments, or are they two unrelated phenomena? (2) (since the static short-ranged order now observed appears to be associated with (static) crystalline disorder, what would be the situation in a perfect crystal? Would it be (a) static long-range order (b) fluctuating short-range order? (c) something else?

Yet another input to the puzzle comes from the Kerr-effect experiments. Using a novel experimental arrangement, Kapitulnik et al.‡ observed the onset of a small but nonzero Kerr effect ($\Theta_K \sim 0 \cdot 5 \mu$ rad) in YBCO below a temperature which appears to coincide with that of the onset of a peak in the RSXS data. It is very interesting that this effect seems to be independent of the magnetic field applied to the sample, indeed it occurs with full strength even in zero-field-cooled samples (see fig. 6 of K. et al.). If the analysis of Kapitulnik (in ϕ B15.3) is right, this indicates that **time reversal symmetry is spontaneously broken below T_{onset}** .

Where does all this leave us? It now looks reasonably certain that the phase diagram in the p–T plane for zero magnetic field looks approximately as in fig. 5: there are two characteristic lines, which we may call T^* and T_{CO} . The T^* line corresponds to a genuine second-order phase transition and, approximately to the appearance of a nonzero pseudogap. By contrast, the line T_{CO} appears to correspond to the onset of (a) short-ranged charge order (but in general **not** spin order, at least at a level observable by current techniques) (b) intra-cell nematicity (c) breaking of time-reversal symmetry. However, to date there is no observable signature of a phase transition! At high magnetic fields, when inter alia the superconductivity is suppressed, things are even more complicated: we appear to get (long-range) charge order at low temperatures, but it is not at all clear how, if at all, this is related to the small Fermi surface observed in the quantum-oscillation experiments.

* Wu et al., Nature **477**, 191 (2011)

† Wu et al., Nature Comm. **6**, 7438 (2015)

‡ NJP **11**, 055060 (2009)