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Pseudogap in $YBa_2Cu_3O_{6+\delta}$ is not bounded by a line of phase transitions: Thermodynamic evidence

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We discuss a recent resonant ultrasound spectroscopy (RUS) study of $YBa_2Cu_3O_{6+\delta}$, which infers a line of phase transitions bounding the pseudogap phase and argue that this scenario is not supported by thermodynamic evidence. We show that the anomalies in RUS, heat capacity, and thermal expansion at the superconducting transition temperatures agree well, but there are large discrepancies between RUS and thermodynamic measurements at T^* where the pseudogap phase transitions are purported to occur. Moreover, the frequency and temperature dependence of the RUS data for the crystal with $\delta = 0.98$, interpreted in terms of critical slowing down near an electronic phase transition, is five orders of magnitude smaller than what is expected. For this crystal the RUS data near T^* are more consistent with nonequilibrium effects, such as oxygen relaxation.

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Hole-doped, high-T_c superconducting (SC) cuprates have a partial gap in the electronic density of states (DOS), above and below T_c, in both underdoped and optimally doped regions of their phase diagram [1,2]. This partial gap is referred to as a "pseudogap" because its spectroscopic signatures involve loss of spectral weight near the Fermi level [3,4]. For many years debate focused on whether the pseudogap is a precursor or competitor to superconductivity [5]. More recently there has been a consolidation of support for the latter view—the pseudogap coexists with superconductivity and depletes spectral weight otherwise available for superconductivity [6–9]. As a consequence, ground-state properties such as superfluid density, quasiparticle weight, critical fields, and condensation energy become sharply diminished as p, the number of doped holes per Cu, falls below the critical doping p_{crit} at which the pseudogap opens [2,4]. This ground-state crossover from strong superconductivity in the overdoped region to weak superconductivity in the coexisting pseudogap region is remarkably abrupt [2,10].

This raises the further critical question as to whether this abrupt crossover is in fact a phase transition. Is the pseudogap state a thermodynamic phase bounded by a line of phase transitions? We have consistently argued that it is not—no specific heat anomaly at the boundary has been observed despite an intensive search [1,2,11]. However, there is evidence for anomalies in other properties; for example, He *et al.* [12] presented a combined study of angle-resolved photoemission spectroscopy, polar Kerr effect, and time-resolved reflectivity, all consistent with a mean-field-like vanishing of an order parameter at T^*. With hindsight it is probable [13] that many of these effects arise from the gradual onset of charge density wave (CDW) order in the pseudogap state. Hard x-ray measurements of $YBa_2Cu_3O_{6+\delta}$(YBCO) show that this sets in below 150 K for both the ortho-VIII ($\delta = 0.67$) [14] and ortho-II ($\delta = 0.54$) phases [13]. Recently, Shekhter *et al.* [15] conclude from resonant ultrasound spectroscopy (RUS) studies that $T^*(p)$ represents a line of phase transitions, and ascribe this to the onset of a pseudogap. We discuss their work in detail and show that the results for their overdoped crystal are not consistent with changes in equilibrium thermodynamics as might be found in the neighborhood of a phase transition, but are more consistent with nonequilibrium anelastic relaxation effects.

The conclusions advanced by Shekhter *et al.* were based on measurements of mode frequency f and resonance width Γ of various mode vibrations for two detwinned single-crystal samples of YBCO. One was fully oxygenated and slightly overdoped with $T_c = 88$ K and the other was underdoped with $T_c = 61.6$ K. For the latter sample they find a change in slope df/dT near 245 K, close to the doping-dependent $T^*(p)$ found in neutron scattering [16], where evidence for the onset of weak magnetic order was reported. Shekhter *et al.* also report broad peaks in Γ at somewhat higher temperatures for two modes and at a lower temperature for a third mode. More dramatic effects are observed for the fully oxygenated, overdoped sample, with $T_c = 88$ K. A clear break in slope in mode frequency is observed at $T^* = 68$ K, as reproduced below in Fig. 1(a). Further, as shown in Fig. 1(b), a strong peak in Γ is found at a slightly higher temperature which increases linearly with mode frequency. From these data Shekhter *et al.* infer the occurrence of a thermodynamic phase transition at the onset of the pseudogap at T^*. They further conclude that T^* falls to zero (possibly at a quantum critical point) within the SC dome. Their conclusions are endorsed in a commentary by Zaanen [18], who asserts that these results provide evidence for the current-loop model of the pseudogap due to Varma [19].

The fact that $T^*(p) \to 0$ within the SC dome is a feature we have noted for 15 years [2,4], though our investigations suggest that this occurs at a significantly lower hole doping than the value in Ref. [15]. We first address the claim [15] that the prominent RUS anomaly at 68 K in the overdoped crystal is caused by the onset of a pseudogap. Thermodynamic evidence suggests that there is no pseudogap in fully oxygenated YBCO. This is based on two observations: (i) If, as claimed in Ref. [15], a pseudogap opens at $T^* \approx 68$ K, which is only a little below T_c ($T^* \approx 0.76 T_c$), it would cause a large additional entropy loss. This would inevitably result in a specific heat anomaly at T^* that is a significant fraction of the one at T_c, contrary to observation [see Fig. 1(a)]; and (ii) key thermodynamic features of a pseudogap ground state are a strongly reduced SC condensation energy, superfluid density, and associated critical

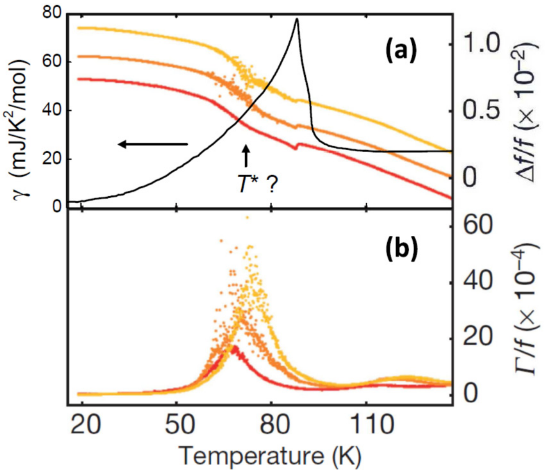

FIG. 1. (Color online) Adaptation of Figs. 2(b) and 2(d) from Shekhter *et al.* [15] showing (a) the relative change in RUS mode frequency $\delta f/f$ for their $YBa_2Cu_3O_{6.98}$ (YBCO) crystal superimposed on the electronic specific heat coefficient $\gamma \equiv C_V/T$ for YBCO at full oxygenation [1,2]. The right-hand scale has been corrected from units of 10^{-4} to 10^{-2}, consistent with Figs. 1(a) and 1(c) of the original article and as confirmed by the authors [17]. T^* marks where a change in slope of $\delta f/f$ is observed along with a peak in the resonance width Γ, which is shown in (b). No feature is observed in $\gamma(T)$ at T^* even though the relative scale for γ has been greatly amplified so that the jump $\delta\gamma$ at T_c is 90× the size of the jump in $\delta f/f$ at T_c.

fields [2] which all result from the partial gapping of the Fermi surface by the competing pseudogap. In YBCO these features are only present at lower hole doping, and at full oxygenation their full values are restored [2,8]. In other words, T^* is zero at full oxygenation, contrary to the findings of Shekhter *et al.*

As stated in the Supplemental Material (SM) of Ref. [15], the elastic moduli which determine the mode frequencies are related to the Helmholtz free energy F (proportional to the sample volume V). For an isotropic solid $dF = -SdT - PdV$, where S is the total entropy, T the absolute temperature, and PdV is the work done on the solid when application of pressure P causes a volume change $-dV$. Hence the isothermal bulk modulus $\kappa_T = -V(\partial P/\partial V)_T = V(\partial^2 F/\partial V^2)_T$. In the present case the crystal has many normal modes whose frequencies are determined by combinations of the elastic constants, such as c_{11}, c_{12}, and c_{44} in the usual notation. There are nine independent elastic constants for orthorhombic symmetry [20]. The crystal is a thermodynamic system and for every normal mode, whose frequency is measured by RUS, there will be a generalized force per unit area equivalent to P and a corresponding deformation equivalent to dV that relates the change in F to the work done on (or by) the crystal. For example, a uniform compression in the x direction gives a change in length $dL/L = -e_{xx}$, the force per unit area is $c_{11}e_{xx}$, the contribution to F (the work done on the crystal) is $\frac{1}{2}ALc_{11}e_{xx}^2$, where A is the area perpendicular to x, giving $c_{11} = V^{-1}(\partial^2 F/\partial e_{xx}^2)_T$.

The effect of a phase transition (i.e., the order parameter) on the elastic moduli can be calculated from the volume, or, more generally, the strain dependence of the transition temperature T_c. For any second-order transition described by Landau theory there is a jump $\delta\gamma$ in the specific heat coefficient $\gamma \equiv C_V/T$ at T_c, where $C_V = TV^{-1}(\partial S/\partial T)_V$ is the specific heat capacity at constant volume and $S = -(\partial F/\partial T)_V$. Integrating twice with respect to T gives the decrease in F below T_c as $\delta F = -\frac{1}{2}V\delta\gamma\,(T_c - T)^2$. For an isotropic solid, differentiating twice with respect to volume gives the change in bulk modulus. Hence the fractional change in frequency at, or just below, T_c for a uniform dilation mode in which the crystal does not change its shape is given by

$$\frac{\delta f}{f} = \frac{1}{2}\frac{\delta\kappa_T}{\kappa_T} = -\frac{1}{2}\frac{\delta\gamma\;T_c^2}{\kappa_T}\left(\frac{d(\ln T_c)}{d(\ln V)}\right)^2. \qquad (1)$$

We note that similar arguments hold for continuous phase transitions described by non-mean-field critical exponents, since $(\partial^2 F/\partial V^2)_T$ will usually be dominated by a term of the form $(\partial^2 F/\partial T_c^2)_T(dT_c/dV)^2$. For an isotropic classical superconductor with $T_c = 1.14\theta_D \exp(-1/\lambda)$, where θ_D is the Debye temperature and λ the dimensionless electron-phonon coupling constant, Eq. (1) leads to the formula $\delta f/f \sim (T_c/T_F)^2$, where T_F is the Fermi temperature, given in the SM of Ref. [15] but with a prefactor $[d\ln\theta_D/d\ln V + (1/\lambda)d\ln\lambda/d\ln V]^2$. This will be of order 4 for a strong-coupling superconductor such as lead but much larger for a weak-coupling one such as aluminum where λ is small.

In the anisotropic case, for a uniform strain e_{xx} along the x direction and all other strain components set to zero, Eq. (1) becomes

$$\frac{\delta f}{f} = \frac{1}{2}\frac{\delta c_{11}}{c_{11}} = -\frac{1}{2}\frac{\delta\gamma T_c^2}{c_{11}}\left(\frac{d(\ln T_c)}{de_{xx}}\right)^2. \qquad (2)$$

In general, c_{11} and e_{xx} in Eq. (2) should be replaced by the appropriate linear combinations of elastic constants and strains that can be obtained by finding the normal vibrational modes of the crystal subject to appropriate boundary conditions [20]. Note that Eqs. (1) and (2) always give a negative frequency shift in the lower T phase because (i) the linear combination of elastic constants mentioned above must always be positive so that the restoring force opposes the deformation and (ii) $\delta\gamma$ will invariably be positive because the lower T phase will have lower entropy.

We have used c_{11} as an example in Eq. (2) but experimentally for well-oxygenated YBCO, $dT_c/de_{aa} = 230 \pm 23$ K and $c_{aa} = 2310$ kbar, while the corresponding values for the crystallographic b axis are -220 ± 22 K and 2680 kbar [21], assuming that the fractional errors are the same as those quoted for $dT_c/dP_{a,b}$. Simply substituting the a-axis values into Eq. (2) and taking $\delta\gamma(T_c) = 56$ mJ/mol/K² [1] or 0.54 mJ/cm³/K² only gives $\delta f/f = 0.6 \times 10^{-4}$, over a factor of 10 smaller than the experimental value of 7×10^{-4} shown in Fig. 1(c) of Ref. [15]. Although the vibrational modes are not specified, it is reasonable to suppose that the authors of Ref. [15] showed their clearest SC anomaly for which the positive a and negative b axis $dT_c/de_{aa,bb}$ terms reinforce each other. Detailed calculations of the kind described in Ref. [20] are clearly desirable. However, the elastic constants given in Ref. [21] are reasonably isotropic. For isotropic cubic crystals, a standard textbook calculation of acoustic phonon modes [22] gives a transverse wave propagating in the (1,1,0) direction with a velocity equal to $\sqrt{(c_{11} - c_{12})/(2\rho)}$, where

ρ is the density, for which the atomic displacements are along (1,−1,0). Generalizing Eq. (2) to this case with $c_{11} = c_{aa}$ and $c_{12} = c_{ab} = 1320$ kbar [21], and replacing dT_c/de_{xx} by $(dT_c/de_{aa} - dT_c/de_{bb})/\sqrt{2}$, gives $\delta f/f = -5.5 \pm 1.5 \times 10^{-4}$, in good agreement with the measured value for the authors' well-oxygenated YBCO crystal.

For their underdoped crystal the elastic constants are not known as precisely. Uniaxial pressure along the a axis has a factor of 2 smaller effect on a crystal with $T_c = 60$ K while the b-axis value is similar to that of the overdoped crystal [23]. From Fig. 1(b) of Ref. [15] we see that $\delta f/f$ at T_c is a factor of 10 or so smaller for the underdoped crystal. This is consistent with the fact that $\delta\gamma(T_c)$ is a factor of 7 smaller [2], combined with the somewhat reduced value of dT_c/de_{aa}.

We conclude that the reported anomalies in RUS at the SC transitions for both the overdoped and underdoped samples are consistent with the specific heat, pressure derivatives of T_c, and the known values of the elastic constants. In contrast to Ref. [15], we attribute the lower value of $\delta\gamma(T_c)$ for the underdoped crystal to the effect of the pseudogap rather than to possible oxygen disorder. (Note that quantum oscillations, which are extremely sensitive to disorder, have been observed in similar underdoped YBCO crystals [24,25].)

Turning to the RUS anomalies at the putative T^* values, we find a very different picture. For both overdoped and underdoped samples, relatively abrupt changes in the slope of $\delta f/f$ are observed at T^*, in contrast with the discontinuities seen at the SC transitions. Interpreted in terms of a phase transition, this may perhaps be attributed to non-mean-field critical exponents as in the current loop model proposed by Varma [19] [see comment after Eq. (1)]. Although Eq. (1) does not strictly apply in this situation, estimates given later suggest that the observed changes in $\delta f/f$ are incompatible with the absence of corresponding anomalies in the specific heat.

We reproduce in Fig. 1 the T dependence of $\delta f/f$ for the overdoped sample from Fig. 2(b) of Shekhter *et al.* [15]. Note that the right-hand scale has been corrected to units of 10^{-2}, as must be the case for consistency with their Fig. 1. This correction in scale has been confirmed by the authors [17]. We superimpose on Fig. 1 the experimentally determined electronic specific heat coefficient $\gamma(T)$ for fully oxygenated YBCO [2] where, for comparison, the scale is chosen such that the anomaly in $\gamma(T)$ at T_c is 90× the anomaly in $\delta f/f$ at T_c. The figure shows an abrupt increase of slope in $\delta f/f$ below $T^* \approx 68$ K. It is more convenient to discuss this increase and its relation with the thermal expansion coefficient $\alpha(T)$ [26] in terms of the standard Ehrenfest equations derived via the Gibbs free energy [27]. Taking $dL = (\partial L/\partial T)_P dT + (\partial L/\partial P_x)_T dP_x$ and $dS = (\partial S/\partial T)_P dT + (\partial S/\partial P_x)_T dP_x$, for uniaxial pressure along the x direction and requiring that there are no length (L) or entropy (S) changes at T_c, i.e., $dL_1 = dL_2$ and $dS_1 = dS_2$ for phases 1 and 2, leads to [27]

$$\frac{dT_c}{dP_x} = \frac{\delta\alpha_x}{\delta\gamma} = \frac{\delta\mathbf{S}_{xx}}{\delta\alpha_x}. \tag{3}$$

These relate the uniaxial pressure dependence of T_c to the changes in γ and α at constant pressure and the elastic constants. Here the compliance tensor $\mathbf{S}_{ij}$ is the inverse of the full elasticity tensor c_{ij} defined earlier. Equation (3) applies to abrupt changes, $\delta\alpha_x$ etc., at a second-order phase transition and to positive or negative changes in slope $\delta(d\alpha_x/dT)$, etc., at a third-order transition. We can only invert c_{ij} approximately (see Ref. [28]). Using $dT_c/dP_a = -0.2 \pm 0.02$ K/kbar [21], and the same value of $\delta\gamma$, Eq. (3) then gives $\delta c_{aa}/c_{aa} = -2.1 \pm 0.4 \times 10^{-4}$ at the SC T_c of the overdoped crystal rather than-1.2×10^{-4} obtained from Eq. (2). Importantly, using Eq. (3) and $\delta\alpha_a = -2.3 \times 10^{-6}$/K, half of the measured jump in $\delta\alpha_{b-a}$ for a fully oxygenated crystal [29], to obtain $\delta\mathbf{S}_{aa}$, gives $\delta c_{aa}/c_{aa} = -2.2 \times 10^{-4}$, in good agreement with the value from $\delta\gamma$.

On the basis of the RUS data and Eqs. (1), (2), or (3), then assuming that dT^*/dP and dT_c/dP have similar values, the changes in $d\gamma(T)/dT$ and $d\alpha_a(T)/dT$ at T^* should be ≈100 times larger than the measured slopes of $\gamma(T)$ and $\alpha_a(T)$ near 68 K, and should be easily detectable. As Fig. 1 shows, there is no discernible anomaly in γ at T^* and similarly there is no clear anomaly in α_{b-a} near 68 K for $\delta = 1.0$ [29].

Since these estimates of $\delta\gamma$ and $\delta\alpha_a$ from the mode frequency changes are based on thermodynamic arguments, they do not depend on the detailed mechanism, but only assume thermal equilibrium. The absence of associated anomalies in $\gamma(T)$ and $\alpha(T)$ could, however, be explained if the anomalies in $\delta f/f$ result instead from irreversible changes, such as those associated with anelastic relaxation, as we will see.

Evidence against a phase transition at 68 K for the overdoped crystal also emerges when considering the proposed critical slowing down near T^*. The authors interpret the peak temperatures of the resonance widths at different frequencies in terms of coupling to fluctuations of the pseudogap order parameter. They ascribe this frequency dependence to critical slowing down of these fluctuations as $T \to T^*$. The modern theory of phase transitions tends to focus on the value of the dynamical exponents rather than the magnitudes of physical parameters. However, for electronic or magnetic phase transitions where quantum effects are important, the time scale τ of these fluctuations is often given by $\tau^{-1} \approx (k_B/h)|T - T^*|$ with a slope of 2.1×10^{10} Hz/K. Examples of this include the

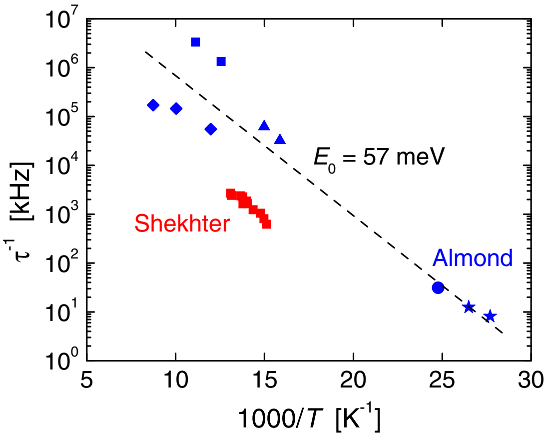

FIG. 2. (Color online) An Arrhenius plot of the data in Fig. 4(b) of Ref. [15] for the $YBa_2Cu_3O_{6.98}$ crystal, where $\tau^{-1} = 2\pi f$, f is the RUS frequency, and T is the temperature of the peak in RUS width Γ. Also included are the data reported by Almond *et al.* from ultrasonic anelastic relaxation studies. Both show an activation energy of about 60 meV.

time-dependent Ginzburg-Landau theory of superconductors [30] and the critical slowing down of fluctuations in the antiferromagnet $RbMnF_4$ where the slope of τ^{-1} vs T, near the Néel temperature of 83 K, is $\sim 1.2 \times 10^{10}$ Hz/K (see Fig. 9 of Ref. [31] based on neutron scattering data from Ref. [32]). For YBCO with $T_c = 88$ K, Shekhter *et al.* observe (over a wide temperature range) a much smaller slope of $\sim 2 \times 10^5$ Hz/K, which we feel is unlikely to be caused by critical fluctuations.

This low slope, combined with the absence of a relationship between $\delta f/f$ and both $\delta\gamma$ and $\delta\alpha_{b-a}$ at T^*, reinforces our view that the features reported in Ref. [15] are more consistent with the effects of anelastic relaxation. Indeed, these features are reminiscent of those obtained in earlier ultrasonic studies reviewed by Almond *et al.* [33] where a small activation energy $\sim$60 meV was found for one set of relaxation times. Figure 2 shows the data from Fig. 4(b) in Ref. [15] interpreted as an inverse relaxation time, plotted on an Arrhenius plot. The data are parallel to those summarized by Almond *et al.*: They have a similar activation energy ($\sim$60 meV) but the attempt frequency is a factor of 10 lower. Such a low activation energy could, for example, be associated with hopping of copper and/or oxygen atoms between bistable sites [34].

We now turn to the anomalies near 245 K for the underdoped crystal shown in Fig. 2(a) of Ref. [15]. In our own work we have found no anomalies or features in the specific heat in this temperature region that could not be explained by magnetic anomalies from a low concentration of CuO impurities. Early evidence for the sporadic appearance of anomalies in the 200–250 K range was provisionally ascribed to “a sluggish and hysteretic transition which may involve oxygen ordering” [11]. This may still be a possibility in that 245 K is relatively close to the temperature of 280 K where the measured magnetic susceptibility starts to depend on the cooling and warming rates [35]. This hysteresis is typical of a kinetic transition involving oxygen disorder in the CuO chains, whose effects have also been observed in heat capacity and thermal expansion for oxygen deficient crystals above 280 K [36,37].

Alternatively, the abrupt slope changes, $d(\delta f/f)/dT = -1$ to -2×10^{-4}/K below $T_0 = 245$ K in Fig. 2(a) of Ref. [15], can be ascribed to a second-order phase transition smeared out over $\sim$30 K below 245 K or to a third-order transition with $\delta F = a(T - T_0)^3$ and $a > 0$. In either case the slopes $d(\delta f/f)/dT$ and $d(\delta\gamma)/dT$ are related in the same way as $\delta f/f$ and $\delta\gamma$ in Eqs. (1), (2), and, less directly, Eq. (3). If we assume that T_0 has the same moderate strain dependence as T_c of the overdoped SC crystal, then Eq. (2) predicts an increase of 0.5–1.1 mJ/mol/K^3 in the slope of $\gamma(T)$ below 245 K. These changes in slope are equivalent to a change in $\gamma(T)$ over 30 K, which is 0.6–1.2× the electronic term of fully oxygenated YBCO and should have been readily visible in differential heat capacity measurements. They are actually a severe lower limit because the reinforcement of the a- and b-axis contributions in the strain dependence of the SC T_c described earlier is unlikely to apply to the strain dependence of T_0 for all three RUS frequencies reported. But if T_0 were $\sim$10× more strain dependent than the SC T_c, then, for the same change in df/dT, Eq. (2) gives a very small change in $d\gamma/dT$, as observed. So to summarize, we cannot exclude the possibility of a highly strain-dependent phase transition at 245 K, but the absence of a detectable specific heat anomaly there clearly demonstrates (on entropy grounds) that the RUS anomaly at 245 K cannot reflect the onset of the pseudogap.

As implied above, it is important to consider possible instabilities in the 100–300 K temperature region that could have a much larger effect on RUS data than on the specific heat. The hard x-ray diffraction experiments for a YBCO crystal with $T_c = 67$ K [14] reveal the T dependence of the CDW amplitude below the CDW onset at 150 K, where any oxygen-ordering effects are probably insignificant. Application of high magnetic fields shows that the CDW and SC instabilities are in competition [14,38,39] and therefore must have similar energy gaps. Based on this, a model calculation [40] suggests that if a CDW with such a T-dependent gap developed out of a metallic state with no pseudogap, then it would give a large anomaly in the heat capacity. However, if the CDW onset occurs when the DOS at the Fermi energy is already heavily depleted by the pseudogap, then its effect on the heat capacity would be much less obvious. This is further evidence that CDW or similar magnetic transitions between 100 and 300 K are *not* causing the pseudogap. RUS could be very sensitive to these transitions since the mean-field formula for the CDW transition temperature of a quasi-one-dimensional solid is similar to that for a weakly coupled superconductor, but with the Θ_D prefactor replaced by T_F, and can be very volume dependent. However, the volume dependence of the pseudogap energy might also play a part and could help clarify whether the CDW is caused by electron-lattice or electron-electron interactions. Therefore, RUS experiments on an YBCO crystal with a T_c of 67 K, where the T dependence of the CDW gap is known [14], could give interesting results.

Irrespective of these questions, it not clear that the RUS data represent conclusive evidence for countercirculating current loops [18]. Some anomalous changes in resonant frequency have been observed but their origin is undetermined and, at least for the overdoped crystal, perhaps more consistent with thermally activated relaxation. Only one doping state (underdoped $T_c = 61.6$ K) has a nominal T^* which coincides with the neutron data. The overdoped sample ($T_c = 88$ K) sits well beyond the doping range of the neutron data.

In summary, we maintain that the pseudogap T^* line represents a crossover over a broad temperature interval, as shown by the scaling behavior of the entropy, susceptibility, resistivity, thermopower, and Hall effect, over a wide range of T/T^*. It reflects an underlying energy scale which falls to zero within the SC dome and is definitely zero for well-oxygenated YBCO. There may be phase transitions near the experimentally defined T^* line, but they are not having large effects on the entropy of the charge carriers because they have not been seen in the heat capacity. It seems that they are not causing the pseudogap, but instead they involve charge or spin order developing in the pseudogap state.

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