Quantum Critical Scaling in the Single-Particle Spectrum of a Novel Anisotropic Metal

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We report an angle resolved photoemission spectroscopy study of quantum critical scaling in the single-particle spectral function of a novel anisotropic metal $Li_{0.9}Mo_6O_{17}$. We find a temperature (T) scaling exponent value and also low-T angle resolved photoemission spectroscopy line shapes that are very challenging for current one-dimensional theory frameworks. These results add a new spectroscopic component to a growing collection of puzzling low-T transport behaviors of this material.

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Interacting metallic electrons in a single one-dimensional (1D) chain manifest very novel quantum behavior [1], as displayed by the paradigm one band model due to Tomonaga [2] and Luttinger [3] (TL). The TL model's lack of quasiparticle excitations and electron fractionalization into independently propagating density fluctuations (spinons and holons) is by now a well known aspect of its energy (ω) and momentum (k) dependent single-particle spectral function $A(k, \omega)$, which can be measured by angle resolved photoemission spectroscopy (ARPES). Of at least equal conceptual importance, but perhaps less generally well known and not previously studied by ARPES, are the model's quantum critical (QC) scaling properties, manifest [4] in the temperature (T) dependence of $A(k, \omega, T)$. An example of the importance of QC scaling is provided by its central role in general arguments for the one band TL model [5–8] that below some definite crossover temperature the quantum motion of electrons perpendicular to the many chains of a solid—interchain "hopping" characterized by a parameter known as $t_\perp$—destroys the 1D behavior and restores some well known 3D state of matter based on the usual Landau Fermi liquid. In the language of the renormalization group $t_\perp$ is always a "relevant perturbation" on the 1D physics.

QC systems display scale invariance; i.e., in the long-distance and long-time asymptotics for temperature $T = 0$, the correlation functions lack a characteristic scale and take the simplest possible scale-free, functional form, a power law. Departures from temperature $T = 0$ satisfy simple scaling laws [9,10] with T the only scale. For the one band TL model with a spin rotationally invariant interaction $A(k, \omega, T) = T^\eta \bar{A}(vk/T, \omega/T)$ where $\bar{A}$ is a universal scaling function, k is measured from the Fermi momentum k_F, ω is measured from the Fermi energy E_F, and v is a constant with units of velocity [4]. The k-integrated spectrum does not show a Fermi edge, but approaches E_F as a power law from which a frequency scaling exponent known as α can be determined [11]. Within the one band TL model the T scaling exponent η is then also determined by a scaling relation $\eta = (\alpha - 1)$, which provides an initial framework for presenting our data. We report here QC scaling observed by T-dependent ARPES in a quasi-1D solid $Li_{0.9}Mo_6O_{17}$ having generic TL properties at high-T and at low-T novel transport properties that continue [12] to provide surprises. In ARPES we find a surprising value of η and low-T line shapes that are very puzzling for theory, as we discuss. We have previously published only a brief sketch [13] of our T-dependent ARPES data, and to our knowledge this is the first ARPES study of QC scaling in any quasi-1D solid.

The compound $Li_{0.9}Mo_6O_{17}$, known as the "lithium purple bronze" (LiPB), is a quasi-1D metal with highly anisotropic transport [14,15]. The Li ions contribute electrons to two zigzag Mo-O chains per unit cell lying in separated layers of the crystal. Band structure calculations [16,17] show four bands, two of which (denoted A, B) are always below the Fermi energy E_F and the other two (denoted C, D) disperse with wave vector k across E_F to define the Fermi surface (FS). The FS is predicted [17] to have observable splitting and warping due to perpendicular hopping $t_\perp$ of the order of 30 meV both within and between unit cells. The dispersing peaks found in ARPES studies [18–20] confirm these essentials except that the $t_\perp$ FS effects are so far not observed, i.e., the FS is both unsplit and straight [21], and the C-D spectra show signatures generic to TL behavior. The k-integrated ARPES spectrum [20] approaches E_F as a power law and is very well described by TL model spectral theory to yield a value for α. Spectra from scanning tunneling microscopy (STM) [22] down to 5 K also find a power law and α values

consistent with the ARPES result. The C-D ARPES line shapes in the T range 250 K to 300 K are well described by TL spectral theory, showing electron fractionalization signaled by holon peak and spinon edge components that disperse with different velocities [18,23]. Also generic to the TL model, we find that the T dependences of the electrical resistivity [14,15,24] parallel and perpendicular to the chains show power-law behaviors. An exponent sign crossover producing a resistivity upturn below 26 K could indicate the presence of weak disorder [25]. In any case it does not signal any conventional 3D charge or spin density wave ordering because no single-particle gap appropriately sized to the upturn temperature [in mean field $\approx(26/11.6)(3.52) \approx 8$ meV] is found in the T-dependent magnetic susceptibility [14,15,24], optical conductivity [26], or STM spectra [22], and repeated x-ray diffraction studies [27] have failed to find such ordering. Thus there is no direct evidence for cooperative 3D ordering until superconductivity sets in below 1.9 K [14,28], although indirect arguments for various dimensional crossover scenarios at a higher T have been made based on transport studies [12,29,30]. It is safe to say that no settled understanding of the low-T properties that evolve from the TL behavior at high T has yet been achieved.

Temperature-dependent ARPES experiments were performed at the U1-NIM undulator beam line of the Synchrotron Radiation Center of the University of Wisconsin, using photon energy $h\nu = 30$ eV. Single crystal $Li_{0.9}Mo_6O_{17}$ samples grown using the temperature gradient flux method were cleaved *in situ* to expose a fresh surface. A Scienta SES2002 spectrometer was used to collect and analyze the photoelectrons. The sample was prealigned using Laue diffraction so that the analyzer slit was parallel to the Γ-Y direction of the reciprocal lattice. The vacuum was always better than 1×10^{-10} torr during the entire experiment. Freshly evaporated gold was measured before and after the experiment at $T \approx 15$ K for a careful calibration of the Fermi energy as well as the combined instrumental energy resolution, $\Delta E \approx 18$ meV FWHM. The angular resolution of the experiment is estimated to be 0.3°, corresponding to $\Delta k = 0.013$ Å^{-1}. The sample temperature was controlled by using an embedded resistive heater and a closed-cycle He cryostat. For each cleaved sample, data were collected for ten values of T over a range from 30 to 300 K, both increasing and decreasing. The very important observation presented below of decreased E_F intensity with decreasing T cannot be the result of sample deterioration with time after cleave because T is initially increasing in the experiment.

Figure 1(a) shows the 300 K spectra of our T-dependent ARPES study for wave vector k varying along the Γ-Y direction of the Brillouin zone. Bands A and B approach E_F no closer than 0.12 eV. Bands C and D merge and disperse to cross E_F together. For the particular k path shown, the D band is too weak to observe, and so its

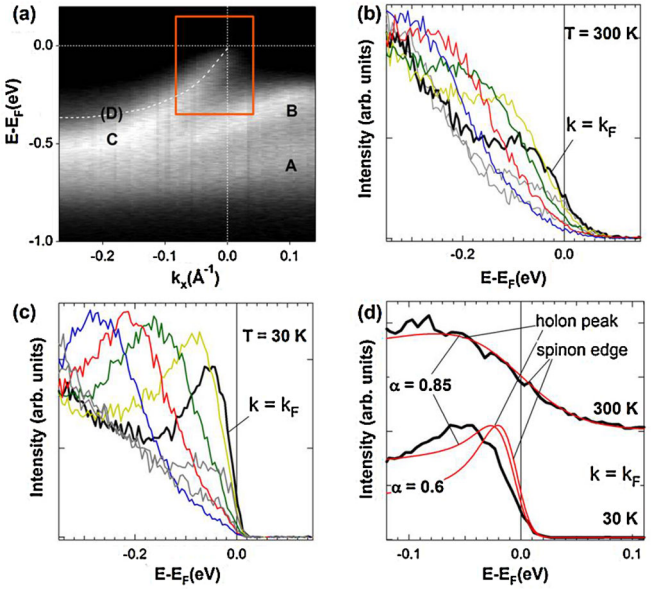

FIG. 1 (color online). ARPES spectra of $Li_{0.9}Mo_6O_{17}$. (a) Intensity map of 300 K spectra of T-dependent data set analyzed quantitatively in this Letter. Band D is shown as a dashed line because [12–14] it is too weak to observe in this particular experimental geometry. (b) Overplot of spectra in range of box in (a). (c) 30 K spectra show sharpening. Different colors in (b,c) represent different k values with increments 3.6% of Γ-Y. (d) Comparison of k_F spectra of (b,c) to TL model spectra [16], showing lack of full sharpening predicted for decreasing T.

dispersion based on data [18–20] from other k paths is sketched as a dashed line. Figure 1(b) overplots the spectra in the range of the box of Fig. 1(a) to show the dispersing holon peak and spinon edge approaching E_F. The general features of the spectra are like those of spectra analyzed previously [20,23], although the need to measure for multiple T values within the lifetime of the sample necessitated poorer statistics for the new spectra. When integrated over the k range of Fig. 1(a), the new spectra exhibit a T-dependent variation of α similar to that found previously [20], in this case from 0.85 at 300 K to 0.60 at 200 K and below. Figure 1(c) shows spectra for $T = 30$ K, taken separately with better statistics to show clearly the change that occurs with lowering T. Figure 1(d) shows for 300 K and 30 K the ARPES data for $k = k_F$ and TL theory curves, including the effect of the experimental energy and momentum resolutions. The broadened theoretical holon peak and spinon edge features are labeled. The data sharpen considerably at low T, but not in a way that matches the TL theory for any relevant α value. Nonetheless the T dependence shows QC behavior as described next.

Figures 2 and 3 show the T dependence of the spectra and test for QC scaling. If the general scaling form of the spectral function holds, then $T^{-\eta}A(k, \omega, T)$ is independent of T if k is chosen for each T so that k/T does not change,

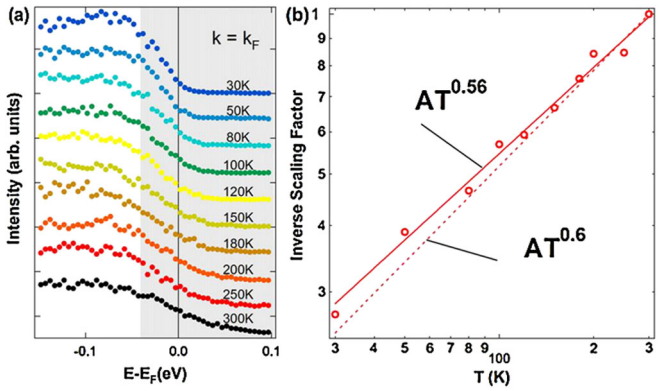

FIG. 2 (color online). T scaling of ARPES spectra. (a) Spectra for $k = k_F$ normalized as described in text. (b) Log-log plot of T dependence of inverse of scaling factors obtained from data of (a) and used to obtain Figs. 3(b) and 3(d). Lines show that power-law fitting data are essentially T^{α}.

i.e., $k = 0$ (the k_F spectra) or $k = cT$ where c is a constant, chosen here as 1.67×10^{-4} Å^{-1}/K to maximize the range of k for the available range of T. Since the A-, B-band parts of the spectra are far from E_F and have no apparent change with T, we can use band B as a reference for the low-energy T-dependent behavior of interest. The k_F spectra were first normalized to match the leading edges of their B-band peaks over the binding range 0.25 to 0.4 eV with the result shown in Fig. 2(a). The spectral intensities were then matched at E_F by a multiplicative factor whose inverse does indeed have a power law T dependence [Fig. 2(b)] from which η can then be deduced. Figures 3(a) and 3(b) plot the unscaled spectra vs $(E - E_F)$ and the T-scaled spectra vs $(E - E_F)/k_B T$, respectively. The unscaled k-dependent spectra of Fig. 3(c) were normalized and T scaled using exactly the same numerical factors as determined for the k_F spectra, resulting in the plot of Fig. 3(d). As seen in Figs. 3(b) and 3(d), the leading (spinon) edges of the spectra generally scale very well as highlighted in gray [Figs. 2(a), 3(a) and 3(c)], but the peaks vary with T, i.e., do not scale. The lack of scaling of the holon peaks is another deviation from TL spectral theory. As shown in the insets of Figs. 3(b) and 3(d), for $T = 50$ K and $T = 30$ K we observe above E_F small but increasingly detectable deviations to the nearly perfect scaling of the edges. These small deviations can be ascribed to the effects of the experimental resolutions. The thin solid lines through the data in the insets result from fitting the scaled edge, as shown in the main figure panels, and then broadening to account for the experimental resolutions.

These experimental results present for theory an intriguing puzzle which challenges interpretation within known 1D frameworks. The value of the exponent $\eta = 0.56$ [Fig. 2(a)], determined directly and independently for the first time with ARPES, violates the one band TL model scaling relation $\eta = (\alpha - 1)$, which would imply a small negative value for η. Within a quasi-1D framework the

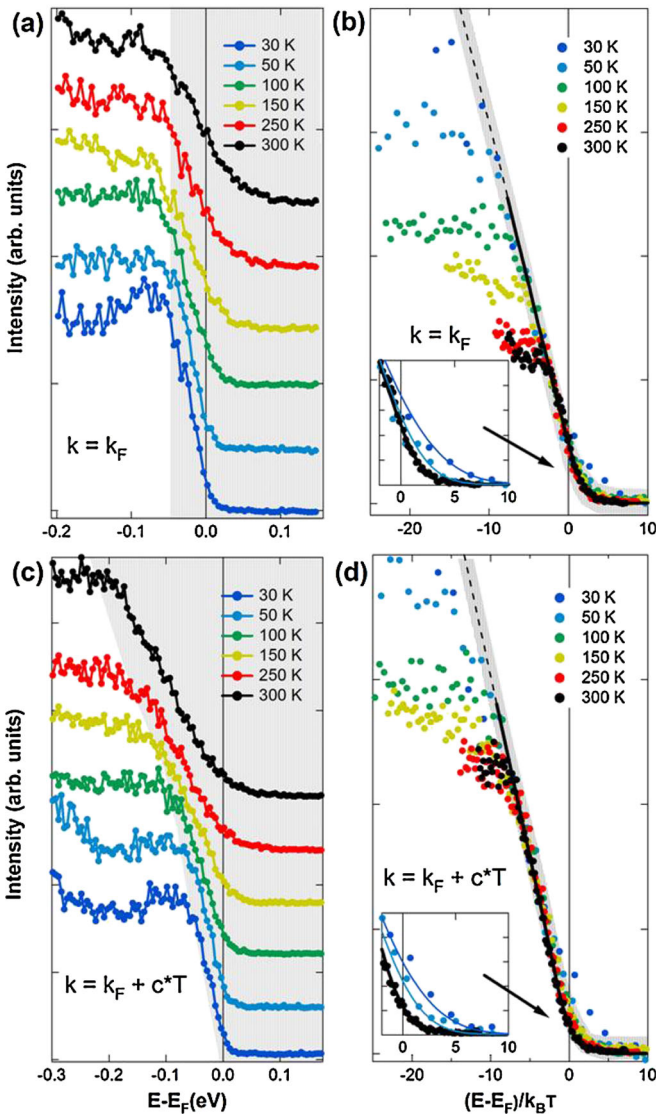

FIG. 3 (color online). ω/T scaling of the spectra. (a) $k = k_F$ spectra; (b) $k = k_F$ spectra after T scaling, and plotted vs $(E - E_F)/k_B T$. The edges fall together onto a T-independent line shape (solid line). (c,d) Same as (a,d) but for $k = cT$. Low-temperature deviations from scaling above E_F in (b) and (d) can be accounted for by the experimental resolutions, as shown in the insets and described in the text.

measured value of η implies that the Green's function decays faster than expected in a TL system. This fact suggests that short-ranged correlations prevent the experimental ARPES spectra from sharpening enough to develop the $T = 0$ power-law singularities that a gapless TL system shows. One possible starting point to understand the anomalous scaling is the fact that there are two bands crossing E_F. In the absence of chirality-breaking interactions, the low-energy fluctuations of the densities can be decoupled in four independent modes consisting of the addition and difference of the charge and spin densities in each band. However, if the four modes would remain

gapless the TL scaling relation is preserved. One then could consider that additional in-chain interactions can open a gap in one or more of these modes [31]. In such a case, the flat FS found to date and the failure to detect quasiparticles in ARPES or in STM even down to 5 K could be seen as a consequence of the 1D TL behavior and the irrelevance of the single-particle hopping $t_\perp$ that is inherent [8] to models with a gap. But to explain the range of temperatures over which the violation of the scaling takes place, such a gap should be larger than any temperature studied, and this seems inconsistent with the STM [22] and k-integrated photoemission [20] data. On the other hand, short-ranged correlations can be induced in 1D also by disorder in a non-half-filled system, as mentioned above already in connection with the upturn of the parallel resistivity. On the experimental side, without a specifically relevant theory we cannot assess and absolutely exclude some role of instrumental momentum resolution in our finding of the anomalous scaling relation.

In conclusion we have presented the results of the first ARPES study of QC scaling in the single-particle spectral function of a quasi-1D material, $Li_{0.9}Mo_6O_{17}$. We find a T-scaling exponent and low-T ARPES line shapes that pose a difficult puzzle for current 1D theory frameworks, but which are qualitatively compatible with each other and with STM spectra down to 5 K. These results add a spectroscopic component to a growing set of novel low-T transport properties of this material that are equally difficult to explain within usual 1D frameworks. On the experimental side much remains to be done. ARPES measurements could probe in detail along the FS, and transport measurements could study the SC for some possible unconventional character. What is more, it is not likely that these unusual phenomena are entirely unique to LiPB. The results that we present show a new spectroscopic way to search for this physics.

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[1] F. D. M. Haldane, J. Phys. C **14**, 2585 (1981).
[2] S. Tomonaga, Prog. Theor. Phys. **5**, 544 (1950).
[3] J. M. Luttinger, J. Math. Phys. (N.Y.) **4**, 1154 (1963).
[4] D. Orgad, Philos. Mag. B **81**, 377 (2001).
[5] C. Bourbonnais and L. G. Caron, Int. J. Mod. Phys. B **5**, 1033 (1991).
[6] M. Fabrizio and A. Parola, Phys. Rev. Lett. **70**, 226 (1993).
[7] D. Boies, C. Bourbonnais, and A.-M. S. Tremblay, Phys. Rev. Lett. **74**, 968 (1995).
[8] T. Giamarchi, *Quantum Physics in One Dimension* (Oxford University Press, Oxford, 2004), Chap. 8.
[9] J. A. Hertz, Phys. Rev. B **14**, 1165 (1976).
[10] S. Sachdev, *Quantum Phase Transitions* (Cambridge University Press, Cambridge, 1999).
[11] B. Dardel *et al.*, Phys. Rev. Lett. **67**, 3144 (1991).
[12] X. Xu *et al.*, Phys. Rev. Lett. **102**, 206602 (2009).
[13] F. Wang *et al.*, Physica (Amsterdam) **403B**, 1490 (2008).
[14] M. Greenblatt *et al.*, Solid State Commun. **51**, 671 (1984).
[15] J. Choi *et al.*, Phys. Rev. B **69**, 085120 (2004).
[16] M.-H. Whangbo and E. Canadell, J. Am. Chem. Soc. **110**, 358 (1988).
[17] Z. S. Popovic and S. Satpathy, Phys. Rev. B **74**, 045117 (2006); S. Satpathy (private communication).
[18] J. D. Denlinger *et al.*, Phys. Rev. Lett. **82**, 2540 (1999).
[19] G.-H. Gweon *et al.*, J. Electron Spectrosc. Relat. Phenom. **117–118**, 481 (2001).
[20] F. Wang *et al.*, Phys. Rev. Lett. **96**, 196403 (2006).
[21] Our earlier result in [18] is unchanged with the improved resolution of the current work and at the lower temperature of 60 K.
[22] J. Hager *et al.*, Phys. Rev. Lett. **95**, 186402 (2005).
[23] G.-H Gweon, J. W. Allen, and J. D. Denlinger, Phys. Rev. B **68**, 195117 (2003).
[24] Y. Matsuda, M. Sato, M. Onoda, and K. J. Nakao, J. Phys. C **19**, 6039 (1986).
[25] T. Giamarchi and H. J. Schulz, Phys. Rev. B **37**, 325 (1988).
[26] L. Degiorgi *et al.*, Phys. Rev. B **38**, 5821 (1988).
[27] J. P. Pouget (private communication).
[28] C. Schlenker, H. Schwenk, C. Escribe-Filippini, and J. Marcus, Physica (Amsterdam) B **135**, 511 (1985).
[29] C. A. M. dos Santos, B. D. White, Y.-K. Yu, J. J. Neumeier, and J. A. Souza, Phys. Rev. Lett. **98**, 266405 (2007).
[30] C. A. M. dos Santos, M. S. da Luz, Y.-K. Yu, J. J. Neumeier, J. Moreno, and B. D. White, Phys. Rev. B **77**, 193106 (2008).
[31] C. Wu, W. V. Liu, and E. Fradkin, Phys. Rev. B **68**, 115104 (2003), and references therein.