Non-Fermi-Liquid Behavior in Quasi-One-Dimensional $Li_{0.9}Mo_6O_{17}$

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We present temperature dependent scanning tunneling spectroscopy data of the quasi-one-dimensional conductor $Li_{0.9}Mo_6O_{17}$. The differential tunneling current in our low-temperature spectra shows a power-law behavior around the Fermi energy, which is expected for a clean Luttinger liquid. The power-law exponent is found to be 0.6. Spectra for a temperature range of 5 to 55 K can be fitted fairly well with a model for tunneling into a Luttinger liquid at the appropriate temperature. A fit with a model based on a zero bias anomaly is significantly worse compared to the Luttinger liquid model. No signature of a phase transition at $T = 24$ K is observed in our temperature dependent data.

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The so-called purple bronze $Li_{0.9}Mo_6O_{17}$ is known to show a highly anisotropic conductivity of 250:10:1 along the crystallographic b, a, and c axes, respectively [1]. Optical measurements show an even greater in-plane anisotropy (100:1) [2], further confirming the quasi-one-dimensional (Q1D) behavior of the system.

This Q1D characteristic is in contrast to that of the sister materials $Na_{0.9}Mo_6O_{17}$, $K_{0.9}Mo_6O_{17}$, and $TlMo_6O_{17}$, which are quasi-two-dimensional. In general, reducing the dimensionality of an electronic system increases the electron correlations. This may result in a Luttinger liquid as predicted for a 1D electron gas [3–6]. To date, only a few experimental observations of Luttinger liquid properties have been reported, including carbon nanotubes [7], semiconductor quantum wires [8], $SrCuO_2$ [9], and organic $(TMTSF)_2X$ salts [10]. However, in Q1D systems there are many instabilities that prevent the observation of Luttinger liquid behavior, for example, a charge density wave (CDW) due to the coupling of the electronic system to the lattice. Such a CDW is observed in $K_{0.3}MoO_3$, another quasi-one-dimensional molybdenum oxide. Detailed information on various properties of above mentioned materials can be found elsewhere [11,12].

In $Li_{0.9}Mo_6O_{17}$, a resistivity upturn is observed near 24 K, which has received conflicting interpretations in the literature. Three different models have been proposed as explanations: CDW, spin-density wave, and localization (Ref. [13], and references therein). In addition, Luttinger liquid behavior has been discussed for $T > 24$ K (Refs. [14,15], and references therein). A CDW scenario is, however, unlikely since there is no noticeable change in the lattice through the 24 K metal-insulator transition [2] and no optical gap is observed [16]. In addition, recent muon spin relaxation measurements showed no sign of spin-density wave formation below 24 K [17]. In this Letter, we present scanning tunneling spectroscopy data of the density of states (DOS) around the Fermi energy (ϵ_F), taken in a temperature range of T = 5 to 55 K. While a CDW is accompanied by an energy gap, a power-law behavior in energy is predicted for the DOS around ϵ_F in the case of a Luttinger liquid. Even though the cleaved surface shows inhomogenities, our averaged spectra are well described by a model that describes tunneling into a Luttinger liquid at low and ambient temperature. Localization of the electrons due to disorder in low-dimensional systems also can result in a depression of DOS around the Fermi energy, a so-called zero bias anomaly (ZBA) [18]. However, the predicted energy dependence of the DOS for a ZBA does not fit our data with the same quality as the Luttinger liquid model.

Single crystals of $Li_{0.9}Mo_6O_{17}$ were grown using the temperature gradient flux method (see [2] for details). The single phase nature of the samples was confirmed by x-ray powder diffraction. To prepare a clean surface for STM study, the samples were cleaved in ultrahigh vacuum at a pressure of 2×10^{-10} mbar. During cleaving, the sample was held at $T = 100$ K and then directly transported into the precooled STM ($T = 4.9$ K). We used a commercial Omicron LT-STM with Pt/Ir tips. For temperatures different than $T = 4.9$ K, a counter heating controller was used, which allowed us to vary the temperature between 4.9 and 60 K. dI/dV spectra were calculated from averaged $I(V)$ spectra, which were taken at different places on a typical scan area of (10×10) nm^2.

In low-temperature dI/dV spectra ($T = 4.9$ K), a dip-like feature is observed at ϵ_F (Fig. 1). Assuming a structureless DOS in the tip and a constant tunneling transmission probability, the dI/dV signal is proportional to the DOS in the sample. Test spectra taken on noble metal surfaces show a constant dI/dV signal in the relevant energy range between ± 50 meV around the Fermi level, justifying the assumption of a structureless DOS in the tip. The energy dependence of the tunneling transmission probability can be neglected in the energy range of interest,

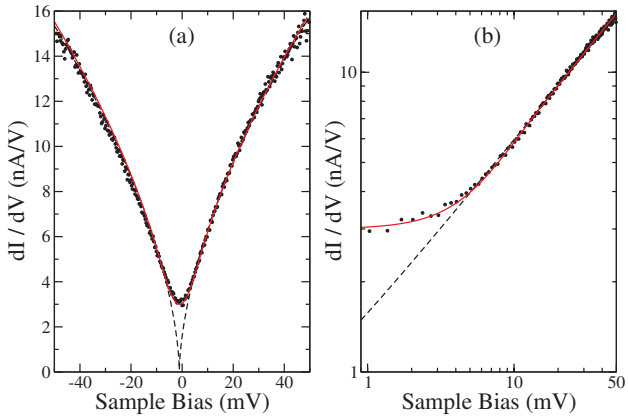

FIG. 1 (color online). The dI/dV (4.9 K) spectrum near the Fermi energy ($\epsilon_F = 0$) (dots) plotted in both (a) linear and (b) double logarithmic scale (positive bias energy only). The dashed lines represent the power-law function [Eq. (2)] with (a) $\alpha = 0.6$ and (b) 0.61, respectively. The solid lines (red) are the fit of Eq. (2), convoluted with a Gaussian (FWHM = 9 mV), to the data.

since 50 meV is small compared to the tunneling barrier height. For a clean Luttinger liquid at zero temperature, the DOS $\rho(\epsilon)$ is expected to converge to zero at ϵ_F with a power law [5] when approaching from either side in energy:

$$\rho(\epsilon) \propto |\epsilon - \epsilon_F|^{\alpha}, \tag{1}$$

where α is an interaction dependent exponent. The same power-law behavior is expected for the differential tunneling current [7]:

$$\frac{dI}{dV} \propto |V|^{\alpha}, \tag{2}$$

where V is the sample bias voltage. Equation (2) fits the experimental data very well as shown in Fig. 1(a). The energy scale had to be shifted by less than 1 mV to compensate for electrical artifacts such as thermocouple voltages, for example. The exponent used in Fig. 1(a) is $\alpha = 0.6$. As shown in Fig. 1(b), the data fall into a straight line in a wide energy range when plotted in double logarithmic scales, thus allowing a more reliable fit of Eq. (2) to the data. Because of finite experimental energy resolution, the slope of the data in the energy range below 10 meV is modified. This can be seen in Fig. 1(a) as a roundoff in experimental data at ϵ_F, while theory predicts an infinitely sharp dip. Using a convolution of Eq. (2) with an energy resolution function approximated by a Gaussian with a full width of half maximum FWHM = 9 meV, a good fit to the data over the whole energy range of Fig. 1 is found. For the extraction of α from the data an energy range from 10 to 50 meV has been used. Using different samples, different cleavings, and different tip conditions, a total of 56 dI/dV spectra, each averaging over >1000 single spectra, have been used for statistical analysis. The resulting exponent is

$$\alpha = 0.62 \pm 0.17. \tag{3}$$

The data discussed above were taken at the lowest temperature we can achieve in the experiment ($T = 4.9$ K) and compared to theory for $T = 0$. For $T > 0$ a power-law variation of the DOS is also expected in temperature [Eq. (4)] but only for very small energies $\epsilon \ll kT$ (k is the Boltzmann constant):

$$\rho(\epsilon = 0, T) \propto T^{\alpha}. \tag{4}$$

The Fermi energy is set to zero. α is the same exponent as in Eqs. (1) and (2). In the energy range relevant to our experiment, however, the temperature dependence cannot be approximated by Eq. (4). The temperature and energy dependence of the DOS, at the crossover between $\epsilon \gg kT$ and $\epsilon \ll kT$, is generally given by [7]

$$\rho(\epsilon, T) \propto T^{\alpha} \cosh\left(\frac{\epsilon}{2kT}\right) \left| \Gamma\left(\frac{\alpha+1}{2} + \frac{i\epsilon}{2\pi kT}\right) \right|^2, \tag{5}$$

where Γ is the gamma function. The differential tunneling current can be assumed to be proportional to the DOS given in Eq. (5) only if the tip is at zero temperature. At higher temperatures, the Fermi-distribution function in the tip has to be considered. The differential tunneling current from the tip at temperature T into the Luttinger liquid at the same temperature is given by the convolution of Eq. (5) with the derivative of the Fermi-distribution function $df/dV = 1/4kT \,\mathrm{sech}^2((\epsilon - eV)/2kT)$ [7]:

$$\frac{dI}{dV}(V, T) = \int_{-\infty}^{\infty} \rho(\epsilon, T) \frac{df(\epsilon - eV, T)}{dV} d\epsilon. \tag{6}$$

Figure 2 shows a typical dI/dV series for various temperatures and a fit according to Eq. (6). Each spectrum of the series and both polarities of the sample bias have been fitted with separate parameters for scaling and α, but no offset has been used. The variation in α as shown in Fig. 2 is not significant within our statistical error and is not reproducible. A possible weak temperature dependence may be buried in the statistical spread of α.

In Fig. 3 the temperature dependence of the tunneling current at zero bias voltage is plotted. A power law (dashed line) is plotted as expected from Eq. (4) for the DOS. The broadening of the Fermi-distribution function in the tip as considered in Eq. (6) for zero energy results in a power law of $dI/dV(T)$ as well. The instrumental broadening, however, changes the observed temperature dependence at zero temperature significantly. It has been modeled using a convolution with the instrumental energy resolution function and results in a function plotted as a solid line in Fig. 3. It fits the experimental data well.

Thus far, we have demonstrated that the energy and temperature dependence of the differential tunneling current in our experiment is well described by a Luttinger model.

Alternatively, localization of electrons in low-dimensional disordered systems can result in a suppression

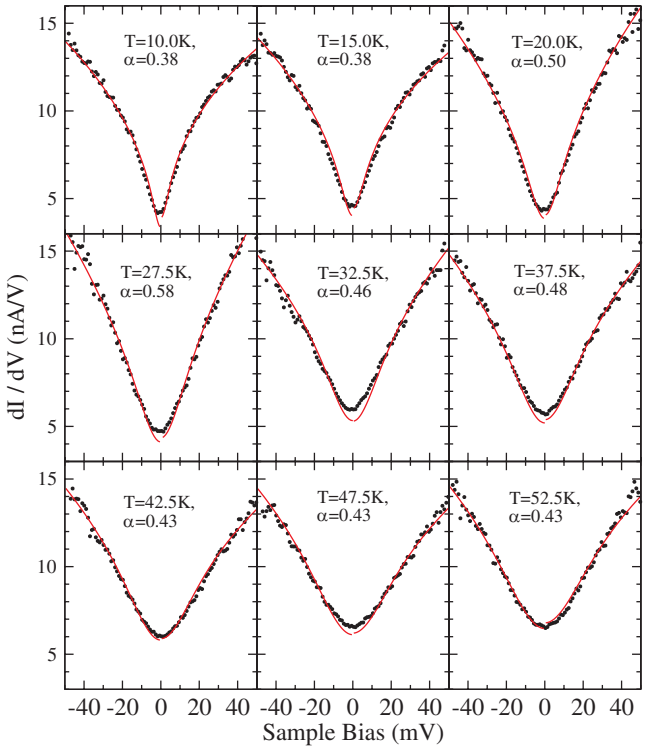

FIG. 2 (color online). Dots: Temperature dependent dI/dV spectra fitted by a Luttinger liquid model including thermal broadening (solid red line). α values averaged over both polarities used for the fit are given in each panel. A scaling factor was used for each spectrum and polarity separately.

of the DOS at the Fermi energy [18–20]. This suppression, called ''zero bias anomaly'' induced by disorder, will be abbreviated in the following by ZBA. To test whether the ZBA model may be appropriate to explain our data as well, we have fitted all data with this model.

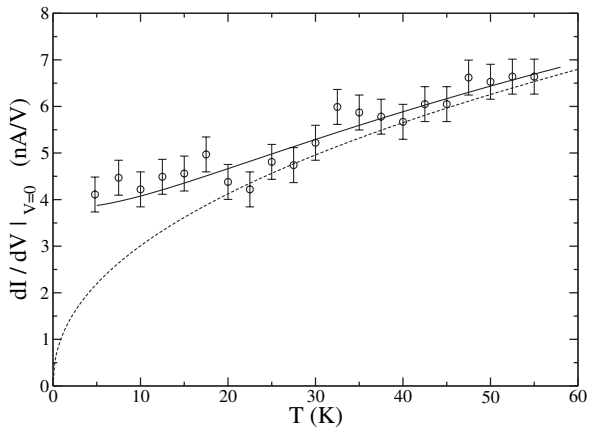

FIG. 3. Data points with error bars taken from a temperature series partly plotted in Fig. 2. Dashed line: power law according to Eq. (4) using $\alpha = 0.46$. Solid line: fit as described in the text using $\alpha = 0.46$ and a Gaussian (FWHM = 8 mV). Both calculated functions include a scaling factor fitted to the data.

The energy dependence of the DOS at zero temperature for a disordered Q1D system of interacting electrons is given by Eq. (7) [18]:

$$\rho(\epsilon, T=0) = \frac{\rho_0}{\pi}\,\mathrm{Re}\int_0^\infty \frac{\sin x^2}{x}\exp\left(-2x\sqrt{\frac{i\Omega_1}{|\epsilon|}}\right)dx. \quad (7)$$

Ω_1 is a parameter depending on the effective electron-electron interaction and the strength of the disorder. ρ_0 is the DOS of the noninteracting system. A fit of our experimental data with Eq. (7) is shown in Fig. 4. In the linear plot Fig. 4(a) and much better in the double logarithmic plot Fig. 4(b), it is visible that this model does not fit the data with the same quality as the Luttinger liquid model shown in Fig. 1.

For $T > 0$ the DOS of a disordered Q1D system of interacting electrons as a function of energy and temperature is given by Eq. (8) [18]:

$$\rho(\epsilon, T) \approx \rho_0 \coth\left(\frac{\epsilon}{2T}\right) 2T \int_0^\infty dt \frac{\sin(\epsilon t)\cos(\sqrt{2\Omega_1 t})}{\sinh(\pi t T)} \times \exp\left[-\sqrt{\frac{\Omega_1}{\pi}}\int_0^\infty d\epsilon' \frac{1-\cos(\epsilon' t)}{(\epsilon')^{3/2}\tanh(\epsilon'/2T)}\right]. \quad (8)$$

The effect of the Fermi-distribution function in the tip has to be considered in the same way as described above, by a convolution with the derivative of the Fermi-distribution function. The best fit to our temperature dependent data is shown in Fig. 5.

In particular, the temperature dependent data can be used to argue that the Luttinger liquid model fits our data significantly better than the one-dimensional ZBA model.

In conclusion, our data show strong evidence for Luttinger liquid behavior in $Li_{0.9}Mo_6O_{17}$ for temperatures between 4.9 and 55 K. The energy dependent dI/dV spectra can be well described using clean Luttinger liquid theory and including the influence of thermal broadening due to the tunneling process. Recent ZBA theories due to

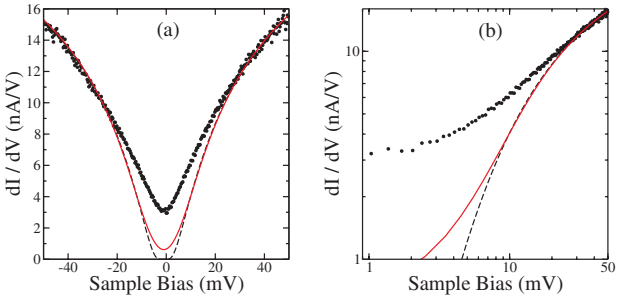

FIG. 4 (color online). Data (dots) from Fig. 1 fitted by the ZBA model. Dashed line: fit according to Eq. (7). Solid red line: fit according to Eq. (7) convoluted with a Gaussian (FWHM = 9 mV). (a) Linear plot. (b) Double logarithmic plot for positive sample bias polarity of plot (a).

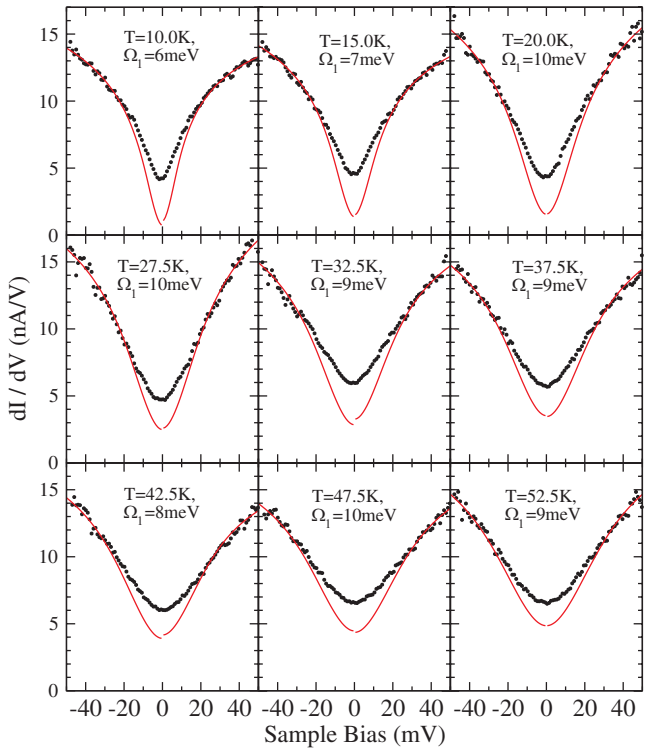

FIG. 5 (color online). Dots: Temperature dependent dI/dV spectra fitted by a ZBA model including thermal broadening (solid red line). Ω_1 values used for the fit are noted in each panel. They are average values for positive and negative polarity of the sample bias. A scaling factor was used for each spectrum separately.

disorder in Q1D Fermi liquids can be excluded as a description, since they predict a suppression of the DOS at the Fermi level which is too strong compared to our data. The extracted $\alpha = 0.62 \pm 0.17$ for this system is definitely below 1 and slightly above 0.5, which is consistent with photoemission data from Allen [15]. However, there is still some discussion regarding photoemission data in the literature [21,22]. With respect to the upturn of resistivity at 24 K discussed in the literature, we do not observe any signature in our temperature dependent data at this temperature.

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[1] M. Greenblatt, W. H. McCarroll, R. Neifeld, M. Croft, and J. V. Waszczak, Solid State Commun. **51**, 671 (1984).
[2] J. Choi, J. L. Musfeldt, J. He, R. Jin, J. R. Thompson, D. Mandrus, X. N. Lin, V. A. Bondarenko, and J. W. Brill, Phys. Rev. B **69**, 085120 (2004).
[3] J. M. Luttinger, J. Math. Phys. (N.Y.) **4**, 1154 (1963).
[4] F. D. M. Haldane, J. Phys. C **14**, 2585 (1981).
[5] J. Voit, Rep. Prog. Phys. **58**, 977 (1995).
[6] T. Giamarchi, *Quantum Physics in One Dimension* (Clarendon, Oxford, 2004).
[7] M. Bockrath, D. H. Cobden, J. Lu, A. G. Rinzler, R. E. Smalley, L. Balents, and P. L. McEuen, Nature (London) **397**, 598 (1999).
[8] Y. Tserkovnyak, B. I. Halperin, O. M. Auslaender, and A. Yacoby, Phys. Rev. B **68**, 125312 (2003).
[9] C. Kim, A. Y. Matsuura, Z.-X. Shen, N. Motoyama, H. Eisaki, S. Uchida, T. Tohyama, and S. Maekawa, Phys. Rev. Lett. **77**, 4054 (1996).
[10] A. Schwartz, M. Dressel, G. Grüner, V. Vescoli, L. Degiorgi, and T. Giamarchi, Phys. Rev. B **58**, 1261 (1998).
[11] *Physics and Chemistry of Low-Dimensional Inorganic Conductors*, edited by C. Schlenker, J. Dumas, M. Greenblatt, and S. van Smaalen, NATO ASI Series B: Physics Vol. 354 (Plenum, New York, 1996).
[12] M. Greenblatt, Int. J. Mod. Phys. B **7**, 3937 (1993).
[13] M. Greenblatt, Chem. Rev. **88**, 31 (1988).
[14] J. D. Denlinger, G.-H. Gweon, J. W. Allen, C. G. Olson, J. Marcus, C. Schlenker, and L.-S. Hsu, Phys. Rev. Lett. **82**, 2540 (1999).
[15] J. W. Allen, Solid State Commun. **123**, 469 (2002).
[16] L. Degiorgi, P. Wachter, M. Greenblatt, W. H. McCarroll, K. V. Ramanujachary, J. Marcus, and C. Schlenker, Phys. Rev. B **38**, 5821 (1988).
[17] J. Chakhalian, Z. Salman, J. Brewer, A. Froese, J. He, D. Mandrus, and R. Jin, Physica (Amsterdam) **359B**, 1333 (2005).
[18] L. Bartosch and P. Kopietz, Eur. Phys. J. B **28**, 29 (2002).
[19] J. Rollbühler and H. Grabert, Phys. Rev. Lett. **87**, 126804 (2001).
[20] E. G. Mishchenko, A. V. Andreev, and L. I. Glazman, Phys. Rev. Lett. **87**, 246801 (2001).
[21] K. E. Smith, Solid State Sci. **4**, 359 (2002).
[22] G.-H. Gweon, S.-K. Mo, J. W. Allen, J. He, R. Jin, D. Mandrus, and H. Höchst, Phys. Rev. B **70**, 153103 (2004).