# Electrical transport in single-crystalline $Li_{0.9}Mo_6O_{17}$: A two-band Luttinger liquid exhibiting Bose metal behavior

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Temperature-dependent electrical resistance in quasi-one-dimensional $Li_{0.9}Mo_6O_{17}$ is described by two Luttinger liquid anomalous exponents $\alpha$, each associated with a distinct one dimensional band. The band with $\alpha<1$ is argued to crossover to a higher dimension below the temperature $T_{M'}$, leading to superconductivity. Disorder and magnetic fields are shown to induce the Bose metal behavior in this bulk compound.

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One dimensional (1D) electrical conductors are attractive because of their inherent simplicity. However, theory shows that weak Coulomb interactions lead to strong perturbations that destroy the discontinuity in the electron occupation at the Fermi surface, which is preserved for three-dimensional (3D) conductors. Other predictions for 1D systems, generally referred to as Luttinger liquids (LL), are spin-charge separation[1] and electrical resistivity obeying a simple power law of temperature.[2] Examples of LLs offer the opportunity to test these predictions.[3] Furthermore, the interplay of disorder, Coulomb interactions, and superconductivity in low-dimensional systems is of general importance.

The purple bronze $Li_{0.9}Mo_6O_{17}$ possesses quasi-1D electrical conductivity[4] and some experiments suggest LL behavior.[3,5] Two important issues regarding LL physics for $Li_{0.9}Mo_6O_{17}$ are the change from metallic-like to semiconducting-like behavior [hereafter referred to as *metallic* with $dR/dT>0$ and *insulating* with $dR/dT<0$, $R(T)$ is the electrical resistance as a function of temperature $T$] near 28 K and superconductivity[4] below $T_c\sim1.9$ K. Attempts to explain the change in $dR/dT$ at 28 K have[3,5,6] reached no consensus. Furthermore, superconductivity should not occur in a truly 1D system. These issues were investigated through thermal expansion experiments,[7] which suggest the possibility of a dimensional crossover at 28 K, where $dR/dT$ changes sign. The dimensional crossover phenomenon is an important element in theories for LL systems.[8]

Experiments and band structure calculations[3,9] reveal two quasi-1D bands crossing the Fermi level in $Li_{0.9}Mo_6O_{17}$. In this paper, each 1D band is shown to have its own distinct value of $\alpha$, the anomalous exponent characterizing the LL. As a natural consequence, the change from *metallic* to *insulating* behavior is explained. Disorder or magnetic field leads to a metallic region below $T_c$, commonly referred to as a Bose metal. Such behavior has not previously been observed in a bulk superconducting compound. This underscores the unusual nature of superconductivity developing from a LL that has undergone dimensional crossover.

Single crystals of $Li_{0.9}Mo_6O_{17}$ were prepared as previously described.[7] Gold contacts were deposited on the samples and four-probe dc electrical resistance was measured in the $b$-$c$ plane.[10] In this work, 22 single crystals were measured with either superconducting (18 crystals with an average $T_c=1.92\pm0.15$ K) or *insulating* behaviors [no drops in $R(T)$ to 0.4 K].

The $R(T)$ for a typical crystal is shown in Fig. 1. The superconducting transition (magnetic field $H=0$) is shown only in Fig. 1(b) for clarity. The *metallic* state and change to *insulating* behavior at $T_M\approx28$ K are features common to all the crystals. The $R(T)$ is fitted by using two power laws, $R(T)=AT^{a}+BT^{-b}$, where $A$ and $B$ are constants. The fit qual-

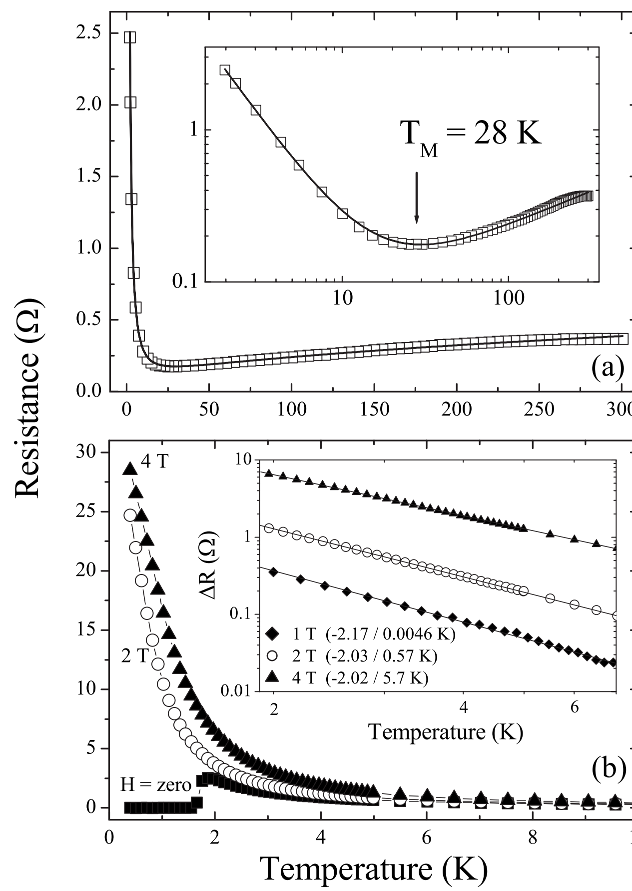


FIG. 1. (a) Electrical resistance for a typical $Li_{0.9}Mo_6O_{17}$ crystal. The inset shows a log-log scale. Lines are fits [Eq. (2) with $T_0=0$]. $T_M=28$ K separates *metallic* and *insulating* behaviors. (b) Data for $H\leq4$ T. The inset compares to 1D hopping mechanism [Eq. (3)]. Numbers in parentheses are $n$ and $T_0$.

    

ity is excellent [solid lines in Fig. 1(a)]. Fits for 18 superconducting crystals provide $a=0.43\pm0.04$ and $b=1.6\pm0.3$.

We find a natural explanation for the fit by using a two-band scenario[3,9] under the assumption that the purple bronze is composed of segregations of two 1D LL bands. Ogata and Anderson[2] showed that the dc resistance of a one-band LL has a temperature dependence of $R(T)\sim T^{1-\alpha}$, where a larger $\alpha$ generally indicates stronger Coulomb interactions. This equation and the values for $a$ and $b$, reveal[11] $\alpha_a=0.57\pm0.04$ and $\alpha_b=2.6\pm0.3$. This allows easy interpretation of $R(T)$ provided an interaction exists, allowing phase-randomizing hopping between the $\alpha_a$ and $\alpha_b$ bands. That is, the Hamiltonian[8] may have the generic form

$$\mathcal{H}=\sum_i [H_{i,a}+H_{i,b}+B_{i,a\leftrightarrow b}]+\sum_{ij} T_{i,j}, \quad (1)$$

where $i$ and $j$ are chain indices, $a$ and $b$ are band indices, $H_{i,a}$ and $H_{i,b}$ are the 1D LL Hamiltonians for the respective bands, $B_{i,a\leftrightarrow b}$ describes interband hopping, and $T_{i,j}=T_{i_a\leftrightarrow j_a}+T_{i_b\leftrightarrow j_b}$ is an interchain hopping term. In this picture, the charge carriers experience scattering in both bands and the net scattering rate becomes a weighted linear sum of the scattering rates for each band. Consequently, the net resistance becomes a weighted linear sum of the contributions from the two 1D LL bands. Band structure calculations[9] lend support to this assumption since they show two 1D bands crossing the Fermi surface. Thus, our analysis reveals the minimum at $T_M$ to be a consequence of the two-band nature.

It is known that a LL with $\alpha<1$ is unstable, and $\alpha>1$ is stable, against dimensional crossover.[8] Thus, only the $\alpha_a$ band is susceptible to crossover. The dimensional crossover induced by two-fermion hopping in $\alpha_a$ may lead to superconductivity or a Coulomb-repulsion induced[7] charge or spin density wave (CDW/SDW).[8] The excellent fitting of $R(T)$ suggests that the 1D LL behavior of both bands persists in temperatures below 28 K. Thus, the *true* crossover temperature $T_{M'}$ of $\alpha_a$ is lower than previously suggested.[7]

Whether superconductivity at 1.9 K is a direct consequence of the dimensional crossover, or a CDW/SDW is an intermediate state for $T_c<T<T_{M'}$, requires further study. In the former case, the fit suggests that the $\alpha_a$ contribution to $R(T)$ does not appreciably change at $T_{M'}$ as a result of precursor behavior that eventually leads to superconductivity. In the latter, if a CDW/SDW occurs below $T_{M'}$, the $\alpha_a$ channel might form a poorly conducting 3D background that will be short circuited by the 1D $\alpha_b$ channels.[12] That is, in both cases, we expect the $\alpha_b$ band to constitute the dominant term in our $R(T)$ fit below $T_{M'}$. However, the absence of any feature in $R(T)$ in the region $T_c<T<T_M$ implies that the CDW/SDW scenario is not reflected in the data. Superconductivity, being a 3D effect, must occur in $\alpha_a$. Once it does, $R\rightarrow0$ and the electrical resistance associated with $\alpha_b$ would no longer be visible.

This discussion provides insight into the effect of pressure,[13] which reduces $R$, decreases $T_M$, and increases $T_c$. In many conventional superconductors, pressure suppresses phonons, which weakens the electron-phonon interaction,[14] thereby decreasing $T_c$. In the purple bronze, pressure will bring the charged particles of the 1D conducting chains closer together. The resultant enhancement of the Coulomb interaction in the $\alpha_b$ band will increase its chemical potential, causing charge carriers to flow from $\alpha_b$ to $\alpha_a$. These carriers will increase occupancy of the $\alpha_a$ band (with lower electrical resistance relative to $\alpha_b$), thereby increasing the weight of $\alpha_a$'s contribution to $R(T)$ and decreasing $T_M$. Decreasing $T$ below $T_{M'}$ then leads to more interchain two-fermion hopping within the $\alpha_a$ band and more fermion pairs in $\alpha_a$. This will increase the effective number of bosons, triggering superconductivity at higher temperature than at ambient pressure.[13]

We now turn to the influence of magnetic field. For the $\alpha_a$ band at $T<T_c$, the two fermions making up an effective boson will most likely have their spins pointing to the opposite direction (to form a singlet state), thereby minimizing their mutual Coulomb interaction. Magnetic field will break up the boson, destroying superconductivity. This mechanism, known as Pauli pair breaking, is rare for isotropic superconductors but may occur for anisotropic or filamentary superconductors. In fact, measurements[15] reveal a critical magnetic field $H_{c2}$ near the Chandrasekhar–Clogston limit, as well as the anisotropic nature of the superconducting state, which implies anisotropy after the dimensional crossover. For $T_c<T<T_{M'}$ (at ambient pressure), destruction of the effective bosons by magnetic field will have a relatively weak influence on $R(T)$, since the contribution of $\alpha_a$ is minimal. For the $\alpha_b$ band, magnetic field will localize charges, impeding the flow of current resulting in larger resistance. With the presence of weak disorder (i.e., impurities or localized charges) and magnetic field, it is possible that each linear chain becomes segmented. Within each segment, the $\alpha_b$ LL exists while the $\alpha_a$ LL exists *only* if the CDW/SDW is not formed. When segmented, charge transport requires hopping along the chain from one segment to the next. Note that when $\alpha>1$ (or when $T>T_{M'}$ for $\alpha<1$), one may ignore interchain hopping.[8] 1D intrachain hopping will contribute an additional factor of $e^{(T_0/T)^{1/2}}$ to the electrical resistance,[16] where $T_0$ characterizes the magnetic field dependent hopping energy. Thus, one anticipates the resistance to behave as

$$R(T,H)=AT^{1-\alpha_a}e^{(T_0/T)^{1/2}}+BT^{1-\alpha_b}e^{(T_0/T)^{1/2}}. \quad (2)$$

The difference of $\Delta R=R(T,H)-R(T,0)$, at $T>T_c$ is, with $n_a=1/2-\alpha_a$ and $n_b=1/2-\alpha_b$,

$$\Delta R(T,H)\approx AT_0^{1/2}T^{n_a}+BT_0^{1/2}T^{n_b}\approx BT_0^{1/2}T^{n_b}, \quad (3)$$

for small $T_0$ and $T$. This behavior is evident in the inset of Fig. 1(b).

Crystals from several batches and different regions in the closed reaction vessel, which was under a temperature gradient,[7] exhibit superconducting, *metallic*, or *insulating* behavior at the lowest measured temperature. The metallic state below $T_c^{\text{onset}}$ is defined as $[dR/dT]_{T\rightarrow0}\approx0$ in our measurement range, $T_c^{\text{onset}}$ is the transition temperature onset in zero magnetic field with no disorder. Treatment of superconducting crystals in air at 200 °C for 10 h destroys superconductivity, suggesting that the disorder is induced by oxygen defects. Examples of these behaviors are shown in Figs. 2 and

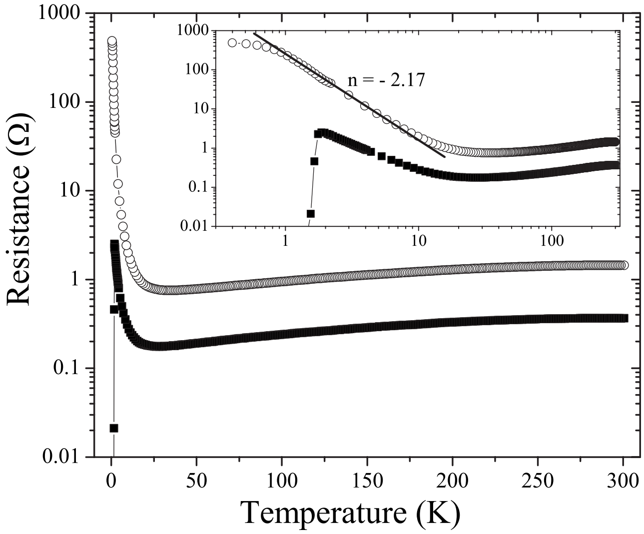


FIG. 2. Electrical resistance for superconducting and nonsuperconducting crystals. *Insulating* behavior was induced through 10 h anneal of a superconducting crystal in air at 200 °C. The metallic regimes above $T_M$ have similar $\alpha_a$ values. The inset shows a log-log scale and fit to Eq. (3).

3. For nonsuperconducting crystals, the low temperature region can be fitted (inset of Fig. 2) with Eq. (3). The fitting suggests that disorder and magnetic field have a *similar* effect on $R(T)$. Another important issue involves $R$ associated with $\alpha_a$ above $T_M$. The samples of Fig. 2 exhibit $\alpha_a$ values of 0.55 and 0.57 for the superconducting and nonsuperconducting crystals, respectively, indicating the minor role that disorder has on $\alpha_a$. Fits to four nonsuperconducting crystals provide $\alpha_a = 0.61 \pm 0.04$, which are comparable to the superconducting crystals (see above), within the uncertainty. These observations may be important in advancing current understanding of disorder's influence on LL systems.[2]

It is evident that a superconductor-insulator transition occurs in $Li_{0.9}Mo_6O_{17}$ (see Figs. 1–3); this phase boundary includes a distinct metallic state below $T_c^{onset}$. In particular, Fig. 3 (main panel) shows $R(T)$ below 4 K for four crystals with different degrees of disorder. The insensitivity of $T_c^{onset}$ to disorder (see arrow in Fig. 3) is similar to superconductivity in granular superconductors,[17] where a lack of phase coherence results in nonzero resistance with no change in $T_c^{onset}$. The inset of Fig. 3 illustrates that magnetic field has an effect *similar* to disorder, creating a metallic region at the lowest temperatures followed by an insulating state at higher fields [see Fig. 1(b)]. However, an important distinction from the simple case of disorder is that magnetic field decreases $T_c^{onset}$. The appearance of a metallic state below $T_c^{onset}$ (induced by field or disorder) in thin films is often referred to as a Bose metal;[18] the purple bronze is an example of such behavior in a bulk superconductor.

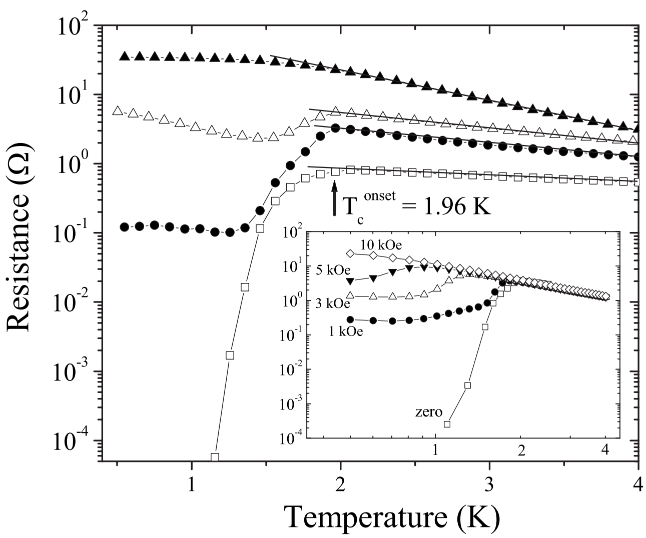


FIG. 3. $R(T)$ for four as-grown (i.e., no annealing) crystals showing disorder-induced metallic state below $T_c^{onset}$. The inset shows sample of main panel (open squares) in magnetic field.

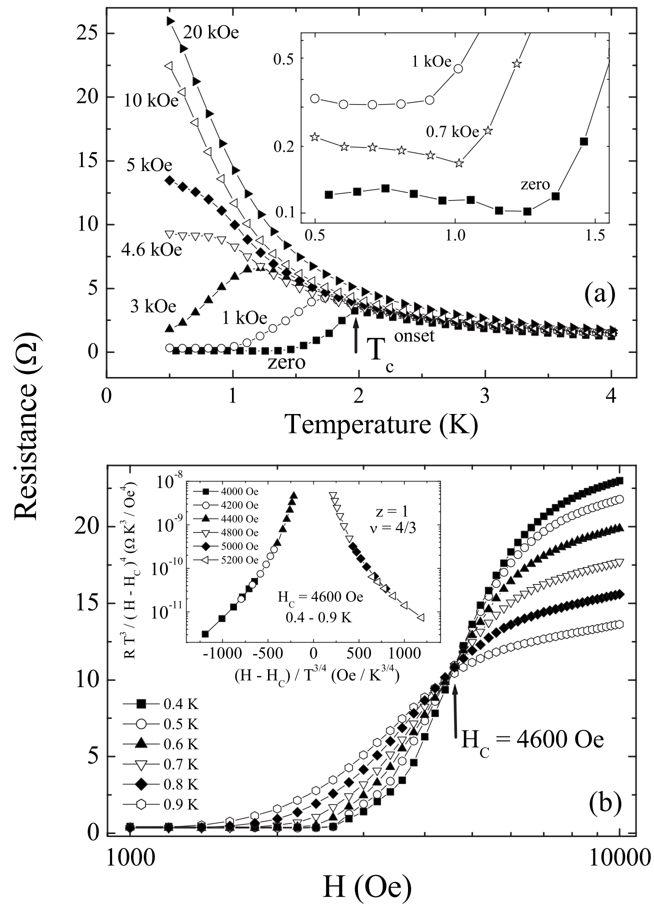


FIG. 4. (a) $R(T)$ in magnetic field for sample displaying metallic behavior below $T_c^{onset}$. The inset highlights metallic behavior at low $H$. (b) Isotherms showing $H_C$=4600 Oe. The inset shows data collapse near $H_C$ by using two-parameter scaling (Ref. 21).

To further characterize the Bose metal behavior, the metallic regime below $T_c^{onset}$ for the sample with the solid circles in the main panel of Fig. 3 is focused on next. Figure 4(a) reveals the magnetic-field induced metal-insulator transition (MIT) at $H_C \sim 4600$ Oe separating the metallic and insulating regimes. Metallic states below $T_c^{onset}$ and a MIT have been reported for disordered, superconducting MoGe and Ta films.[18–21] Nonsuperconducting bulk graphite and Bi also reveal a MIT.[22] The insulating behavior in such systems has been experimentally tied to Cooper pairing.[23] In the inset, the temperature-independent metallic resistance is clearly visible for $H=0$, 0.7, and 1 kOe. Figure 4(b) shows magnetoresistance measurements at fixed temperatures from 0.4 to 0.9 K, in which the data intersect at $H\sim 4600$ Oe. In the absence of a proper fundamental theory to describe the MIT and Bose metal behavior, we apply the two-parameter scaling argument proposed by Das and Doniach.[21] By using the scaling parameters $z=1$ and $\nu=4/3$, reported for MoGe films,[21] and $H_C=4600$ Oe, a remarkable scaling collapse above and below the transition is observed [inset of Fig. 4(b)].

Conventional superconductivity, with boson formation and condensation at the same temperature, differs from superconductivity in a LL that has undergone dimensional crossover. In the latter, bosons (from two-fermion hopping) may form above $T_c$ but the condensation temperature is essentially limited by the interchain hopping energy.[24] The bosons remain largely confined to 1D until the temperature drops below the interchain hopping energy, where superconductivity can occur. If the disorder is too strong, it is possible that the system does not Bose condense, becoming either a 3D Bose metal or even an insulator;[18] such behavior is confirmed in Figs. 2–4.

In summary, the temperature dependence of the electrical resistance of $Li_{0.9}Mo_6O_{17}$, including its minimum at $T_M$, lends itself to a simple description as a two-band LL. The $\alpha_a$ band, responsible for the metallic regime above 28 K, undergoes an increase in dimensionality below $T_{M'}$ that eventually leads to superconductivity at 1.92 K. The unusual nature of superconductivity in $Li_{0.9}Mo_6O_{17}$ is confirmed by the observation of Bose metal behavior.

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[1] J. Voit, Rep. Prog. Phys. **58**, 977 (1995).
[2] M. Ogata and P. W. Anderson, Phys. Rev. Lett. **70**, 3087 (1993).
[3] F. Wang, J. V. Alvarez, S.-K. Mo, J. W. Allen, G.-H. Gweon, J. He, R. Jin, D. Mandrus, and H. Höchst, Phys. Rev. Lett. **96**, 196403 (2006).
[4] M. Greenblatt, Chem. Rev. (Washington, D.C.) **88**, 31 (1988).
[5] J. Hager, R. Matzdorf, J. He, R. Jin, D. Mandrus, M. A. Cazalilla, and E. W. Plummer, Phys. Rev. Lett. **95**, 186402 (2005).
[6] 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).
[7] C. A. M. dos Santos, B. D. White, Yi-Kuo Yu, J. J. Neumeier, and J. A. Souza, Phys. Rev. Lett. **98**, 266405 (2007).
[8] D. Boies, C. Bourbonnais, and A.-M. S. Tremblay, Phys. Rev. Lett. **74**, 968 (1995).
[9] Z. S. Popović and S. Satpathy, Phys. Rev. B **74**, 045117 (2006).
[10] The *a*, *b*, and *c* axes are defined as in Ref. 7.
[11] The value of $\alpha$ used here and in Refs. 5 and 8 is twice that defined in Ref. 2, a point missed in Ref. 1. This is confirmed through the two-point Green's function $G(x\gg 1, t=0)\approx |x|^{-1-\alpha}$.
[12] A SDW or CDW need not imply an insulating state. See E. Fawcett, Rev. Mod. Phys. **60**, 209 (1988).
[13] C. Escribe-Filippini, J. Beille, M. Boujida, and C. Schlenker, Physica C **162-164**, 427 (1989).
[14] J. S. Schilling and S. Klotz, in *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1992), Vol. III, p. 59.
[15] C. Schlenker, H. Schwenk, C. Escribe-Filippini, and J. Marcus, Physica **135B**, 511 (1985).
[16] B. I. Shklovskii and A. L. Efros, in *Electronic Properties of Doped Semiconductors*, edited by M. Cardona (Springer-Verlag, Berlin, 1984), p. 202.
[17] A. M. Finkel'stein, Physica B (Amsterdam) **197**, 636 (1994).
[18] P. Phillips and D. Dalidovich, Science **302**, 243 (2003).
[19] Y. Qin, C. L. Vicente, and J. Yoon, Phys. Rev. B **73**, 100505(R) (2006).
[20] N. Mason and A. Kapitulnik, Phys. Rev. Lett. **82**, 5341 (1999), and references therein.
[21] D. Das and S. Doniach, Phys. Rev. B **64**, 134511 (2001); S. Doniach and D. Das, Braz. J. Phys. **33**, 740 (2003).
[22] Y. Kopelevich, J. C. Medina Pantoja, R. R. da Silva, and S. Moehlecke, Phys. Rev. B **73**, 165128 (2006); Y. Kopelevich, Braz. J. Phys. **33**, 737 (2003).
[23] M. D. Stewart, Jr., A. Yin, J. M. Xu, and J. M. Valles, Jr., Science **318**, 1273 (2007).
[24] V. J. Emery, in *Highly Conducting One-Dimensional Solids*, edited by J. T. Devreese, V. E. van Doren, and S. J. Cambell (Plenum, New York, 1979), p. 247.