Dimensional Crossover in the Purple Bronze Li$_{0.9}$Mo$_6$O$_{17}$

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Thermal expansion of Li$_{0.9}$Mo$_6$O$_{17}$ is $a$-axis dominated which reduces the separation of the conducting chains at low temperature enhancing the interchain coupling. This destabilizes the Luttinger-liquid fixed point leading to an electronic charge- (or spin-) density wave dominated by Coulomb repulsion, as predicted by theories for Luttinger liquids.

Electrical transport in ordinary metals is usually well described by Fermi liquid theory which states that, in the presence of Coulomb interactions, the elementary excitations (quasiparticles) behave essentially like noninteracting electrons. In particular, the quasiparticle momentum distribution preserves the discontinuity at the Fermi surface. However, theoretical work by Luttinger [1] showed that this model breaks down for one-dimensional (1D) systems where even weak Coulomb interactions can cause strong perturbations. In a Luttinger liquid (LL) there is no discontinuity in the momentum distribution at the Fermi surface. Other key features are spin-charge separation and power-law dependence of the correlation functions [1]. The fundamental nature of these predictions has led to the search for a real example of a system possessing LL behavior [2–4]. Some candidates are carbon nanotubes [4] and inorganic compounds such as NbSe$_3$ and TaS$_3$ [5]. Compared to these, the purple bronze Li$_{0.9}$Mo$_6$O$_{17}$ is unique as a 3D crystal with quasi-1D band structure and highly anisotropic metallic behavior above $\sim 28$ K [2,3,6,7].

An important issue regarding Li$_{0.9}$Mo$_6$O$_{17}$ is the cause of the crossover from metallic to semiconductlike behavior [7–9] near $T_M = 28$ K. Magnetic susceptibility reveals no long-range magnetic order at $T_M$ [7,9], but a charge-density wave (CDW) might occur [8]. Related Mo compounds [10,11] are well-known CDW systems because structural distortions due to Peierls instabilities are observed through diffraction or thermal expansion experiments; herein this is referred to as a phonon-induced CDW. For Li$_{0.9}$Mo$_6$O$_{17}$, high-resolution x-ray diffraction reveals no phonon-induced CDW [12] and a difference of opinion exists in interpreting the photoemission data: in one case they are thought to support LL behavior [2], while in the other Li$_{0.9}$Mo$_6$O$_{17}$ is classified as a 3D metal above $T_M$ and a gap is observed below, consistent with CDW behavior [8]. Localization was invoked as a potential explanation for the upturn in electrical resistivity below $T_M$ based on optical conductivity measurements which reveal a decrease near $T_M$, but no gap [7]. However, the addition of more disorder by doping Li with 30% and 40% K has little affect on the upturn [13]. Clearly, an understanding of the crossover from metallic to semiconductlike behavior does not exist.

This Letter reports the first high-resolution thermal expansion measurements of Li$_{0.9}$Mo$_6$O$_{17}$. A novel [14] fused quartz thermal expansion cell is employed. It can detect 0.1 Å changes in specimen length for a relative resolution of about 10$^{-5}$, nearly 1000 times better than the highest resolution diffraction measurements. The thermal expansion is highly anisotropic, promoting one-dimensional behavior above $T_M = 28$ K. The feature at $T_M$ is very different from that typical for compounds exhibiting phonon-induced CDW transitions, where electron-phonon coupling leads to a sizable jump in the thermal expansion coefficient. These observations indicate that $T_M$ represents a crossover in dimensionality which destabilizes the LL fixed point leading to a CDW dominated by electronic interactions, as suggested by LL theories [15,16].

Single crystals of Li$_{0.9}$Mo$_6$O$_{17}$ were grown using a temperature-gradient flux method [17]. Li$_2$MoO$_4$, MoO$_2$, and Mo$_3$ were weighed in a glove box, sealed in an evacuated 15 cm long quartz tube, held at 575 °C for 4 days and then reacted 10 days in a gradient of 10°C/cm (490 and 640°C at the tube ends). The tube was cooled to room temperature and opened. The mixture was immersed in hydrochloric acid for 3 days to separate the single crystals from the flux. The largest obtained crystal was $3.0 \times 2.5 \times 0.5$ mm$^3$ (mass $\sim 8.5$ mg) with purple and bronze colors depending on the optical orientation. X-ray powder diffractometry carried out with ground single crystals showed only Bragg reflections of monoclinic Li$_{0.9}$Mo$_6$O$_{17}$ with lattice parameters $a = 12.762$, $b = 5.523$, $c = 9.499$ Å, and $\beta = 90.61^\circ$ [17,18]. The single crystals used for thermal expansion had dimensions $2.538 \times 2.078 \times 0.523$ mm$^3$ (crystal $A$) and $2.768 \times 2.167 \times 0.308$ mm$^3$ (crystal $B$). Crystal orientation was determined by Laue diffraction. Four-probe electrical resistance measurements were performed in the range $300 < T < 0.4$ K along the $b$ axis, the highest electrical conductivity axis [6,9].

Figure 1 displays the electrical resistance as a function of temperature $R(T)$ for crystal $A$. As expected [7,9], a
crossover from metallic to semiconductorlike behavior is observed at $T_M = 28$ K. The normal to superconducting phase transition at 1.9 K is highlighted in the upper inset. Similar results were obtained for crystal $B$. These aspects in $R(T)$ are common to high-quality $\text{Li}_0\text{Mo}_6\text{O}_{17}$ single crystals.

Linear thermal expansion normalized to the length at 300 K, $\Delta L/L_{300}$, for the $a$, $b$, and $c$ axes of crystal $A$ is displayed in Fig. 2. These are raw data, corrected [14] only for the thermal expansion of quartz with no further processing. In spite of possible small variations in composition, the same behaviors are observed for crystal $B$ indicating good reproducibility. The results reveal strong anisotropic behavior. The in-plane linear thermal expansions ($b$ and $c$ axes) display small linear thermal expansions, which are about 1 order of magnitude smaller than that of the $a$ axis, revealing the layered character. Along the $c$ axis the crystal contracts from room temperature to 220 K followed by an expansion with further cooling [see inset of Fig. 2(a)]. This behavior may be related to the curvature in $R(T)$ above 200 K (see Fig. 1). Figure 2(b) highlights the $b$ axis $\Delta L/L_{300}$ for crystals $A$ and $B$ (inset) below 100 K. A maximum is evident at $\sim 20$ K and a minimum occurs at $\sim 60$ K; such behavior is not unusual for layered systems where negative thermal expansions (i.e., contraction upon warming) are generally associated with strongly anharmonic planar lattice vibrations [19]. This anomalous phonon behavior could be further investigated with spectroscopic methods. The bar in Fig. 2(b) provides an absolute scale for our measurements. For instance, the size of the peak below 28 K corresponds to a 20 Å length change of the 2.708 mm long sample, requiring relative resolution better than $10^{-6}$; in fact, our resolution is 100 times higher.

Figure 3(a) displays the linear thermal expansion coefficients, $\mu_i = d(\Delta L/L_{300})/dT$ for the $i = a$, $b$, and $c$ directions of crystal $A$, obtained following the procedure reported previously [14]. The volumetric thermal expansion coefficient [Fig. 3(a)] was calculated via $\Omega = \mu_a + \mu_b + \mu_c$; the region near 28 K is highlighted in the inset revealing a distinct minimum near $T_M$. We note that this anomaly must be of the same origin as the small, broad peak observed in our (not shown) and reported heat capacity measurements [7,20]. Changes in the slope of $\mu_i$ are evident in all three crystallographic directions near 28 K, as illustrated in Fig. 3(b). This is the first time that distinct features have been reported in a physical property of $\text{Li}_0\text{Mo}_6\text{O}_{17}$ near $T_M$, a tribute to the high resolution of our measurements.

The character of the features near $T_M$ in Fig. 3 is an important aspect of our observations. For continuous phase transitions, either a peak, jump, or cusp in susceptibilities such as $\mu_i$ and $\Omega$ will appear. The soft transformation of slopes in the data of Fig. 3 underscores the subtle changes in $\mu_i$ and $\Omega$ near $T_M$; this leads us to identify it as a crossover of purely electronic nature. Furthermore, the features in Fig. 3 near $T_M$ differ markedly from those observed in well-known phonon-induced CDW systems.
such as $K_0.3MoO_3$ [10,11], where sizable jumps in $\mu_i$, $\Omega$, and heat capacity occur. The absence of such characteristic behavior leads us to conclude that the upturn in the electrical resistivity at $T_M$ is not the result of a phonon-induced CDW transition. However, the possibility remains that the dimensional crossover is governed by two-fermion hopping (for larger $\alpha$) or two-fermion hopping (for larger $\alpha$). The former leads to a Fermi liquid [15,21,22], while the latter leads to a semiconductor CDW or SDW (hereafter referred to as CDW/SDW) behavior provided that the electron-electron interaction is repulsive and singlet or triplet superconducting states if it is attractive [15].

For the purple bronze analyzed in the context of LL theory, $\alpha$ lies in the range $0.5 < \alpha < 0.9$ [26]. Thus, it is likely that the dimensional crossover is governed by two-

![FIG. 3. Linear thermal expansion coefficient $\mu_i$ and the volumetric thermal expansion coefficient $\Omega$. Inset highlights $\Omega$ near $T_M$. (b) Absolute value of $\mu_i$, near $T_M$, $\mu_b$ and $\mu_c$ are negative in this region. Solid lines guide the eye.](image)

![FIG. 4. Behavior of the linear thermal coefficients for $b$ axis and the $[\overline{1}02]$ direction. Inset highlights region near 28 K.](image)
fermion hopping leading to insulator or semiconductorlike behavior due to CDW/SDW formation; unlike typical phonon-induced CDW/SDWs, this one is dominated by electronic interactions \[15,16\]. Furthermore, the small, broad features in the heat capacity \[7,20\] and \(\Omega\) indicate a small entropy change, one that is likely electronic in origin. Analysis of photoemission data \[8\] suggests a small, phonon-induced CDW/SDW, this one is dominated by electrons; this causes the CDW. No appreciable lattice distortion is expected since phonons, although present, play a minor role.

In summary, changes in interchain spacing of \(\text{Li}_{0.9}\)Mo\(_6\)O\(_{17}\) that could facilitate the crossover in dimensionality have been revealed. This and the subtle nature of the feature in the thermal expansion coefficients near \(T_M\) lead us to identify this temperature as the dimensionality crossover temperature \(T_{1D}\) predicted in LL theories when \(T > T_M\). Nonetheless, based on our results, if at \(T > T_M\) the system indeed follows LL behavior, then it most likely will crossover near \(T_M\) to a CDW/SDW \[15\]. Not only is this consistent with the observed upturn in the electrical resistivity at \(T < T_M\), the dimensionality crossover may also set the stage for superconductivity occurring at 1.9 K, a 3D phenomenon.

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[16] A phonon-induced CDW originates from electron-phonon coupling; the electron’s kinetic energy is lowered at the expense of elastic energy. A purely electronic CDW is specific to quasi-1D systems. It originates from Coulomb repulsion which can lead to backscattering and mixing of electrons; this causes the CDW. No apprecicable lattice distortion is expected since phonons, although present, play a minor role.
[22] Summing the leading-logarithmic divergence to all orders, \(\alpha\) scales to zero below the crossover temperature; see E. Arrorgoni, Phys. Rev. Lett. 83, 128 (1999).
[23] Electrical resistivity below 28 K (\(\log(R(T))\) vs \(1/T\)) is nonlinear. A crude linear fit in the narrow range \(6 < T < 17\) K gives an estimate of 1.3 meV for the gap.