Stoichiometry, structure, and transport in the quasi-one-dimensional metal, Li$_{0.9}$Mo$_6$O$_{17}$

J. L. Cohn,$^1$ P. Boynton,$^1$ J. S. Triviño,$^1$ J. Trastoy,$^1$ B. D. White,$^2$ C. A. M. dos Santos,$^3$ and J. J. Neumeier$^2$

$^1$Department of Physics, University of Miami, Coral Gables, FL 33124
$^2$Department of Physics, Montana State University, Bozeman, Montana 59717
$^3$Escola de Engenharia de Lorena - USP, P. O. Box 116, Lorena-SP, 12602-810, Brazil

A correlation between lattice parameters, oxygen composition, and the thermoelectric and Hall coefficients is presented for single-crystal Li$_{0.9}$Mo$_6$O$_{17}$, a quasi-one-dimensional (Q1D) metallic compound. The possibility that this compound is a compensated metal is discussed in light of a substantial variability observed in the literature for these transport coefficients.

Introduction. Li$_{0.9}$Mo$_6$O$_{17}$ known as “lithium purple bronze” (LiPB), is a low-temperature superconductor ($T_c \approx 2$ K) first synthesized and studied in the 1980s.$^1$–$^3$ It has attracted interest more recently for its quasi-one dimensionality and Luttinger-liquid candidacy.$^4$–$^9$ It is distinguished among quasi-one-dimensional (Q1D) compounds by the absence of a conventional density-wave transition either charge or spin$^{10,11}$ (either charge or spin) throughout a broad temperature range, $T \geq T_c$. An upturn in its resistivity below $T_M \approx 30$ K may be associated with localization, dimensional crossover or the development of unconventional (e.g., electronically-driven) charge density-wave order.$^{10,11}$

Values reported for the chain-axis ($b$-axis) electrical resistivity of LiPB$^{10,13,17}$ vary by more than an order of magnitude, from 0.4 m$\Omega$cm to more than 10 m$\Omega$cm at 300 K, and appear to be responsible for similar differences in reported values for the anisotropy ratio, $\rho_c/\rho_b$ ($\rho_c$ is the resistivity along the next most conducting direction). Some of the differences may be associated with inadequate shorting$^{18}$ for current along the chains, of the voltage drops in directions transverse to the current flow, a delicate matter in highly anisotropic conductors. Increases in $\rho_b$ for crystals$^{15}$ annealed in air at 200°C suggest that a variable oxygen stoichiometry also contributes to the reported differences. Recent thermoelectric and Hall measurements$^{19}$ support such a view, indicating small differences in structure and stoichiometry that correlate with transport. This is an important issue given the renewed attention being paid to LiPB and the sensitivity of conduction in such low-dimensional materials to defects or impurities that may alter the low-energy electronic structure. A variable stoichiometry that allows for control of charge-carrier density could prove useful in the study of LiPB which is proposed as a model, bulk system exhibiting Luttinger-liquid physics.

The principal finding reported here is a correlation between oxygen content and the $c$ lattice parameter for a number of as-grown LiPB crystals. Seebeck (thermopower) and Hall coefficient measurements on LiPB crystals from our own work$^{19}$ and those of others$^{15,16,20,21}$ are then presented together. Measured under open circuit conditions, the thermopower is not prone to the same challenges of transverse shorting that may complicate comparison of resistivity measurements. Hall measurements are also less susceptible to such errors given proper averaging with reversed current and magnetic field directions. The low-$T$ chain-axis thermopower varies considerably among the crystals measured$^{19}$ and correlates with their $c$-axis lattice parameters. Results for the Hall coefficient show considerable variability but the role of stoichiometry is less definitive as there are not enough data available on individual crystals for which structure, stoichiometry and transport coefficients have all been measured. The possibility that LiPB is a compensated metal, motivated by the behavior of the thermoelectric coefficients,$^{19}$ is examined in light of the Hall data.

Crystal Structure and Stoichiometry. Single-crystal growth of Li$_{0.9}$Mo$_6$O$_{17}$ using a temperature-gradient flux...
A total of ten crystals were studied and their indicative of separate domains misaligned by small angles to a convolution of two or more resolution-limited peaks, (inset, Fig. 1). For the latter, rocking curves exhibit a modest mosaicity, FWHM (between the a and c lattice planes (Fig. 1), and angles β for specimens discussed in the text. Upper panel: β vs. c for all crystals studied.

Fig. 2 shows the correlation between c and oxygen content for these crystals. Standardless oxygen determinations from EDS typically show small systematic discrepancies due to inadequate accounting for absorption. As a measure of this discrepancy we use the neutron scattering result which indicate full oxygenation (17 O/f.u., corresponding to 32.09 Wt% ignoring Li) for c = 9.4909(2) Å. Comparing our data for the same c values suggests that the EDS oxygen results are ≈ 2.5 Wt% too low. The right (left) ordinates of Fig. 2 correspond to the EDS (corrected: EDS+2.5 Wt%) oxygen contents.

The maximum variation in oxygen content for the crystals examined, ~ 2 Wt%, corresponds to ~ 1 oxygen atom per f.u. The corrected EDS oxygen scaling in Fig. 2 implies that some crystals have excess oxygen, presumably accommodated as interstitials. On the other hand, the fact that four of the crystals have the same measured oxygen content within uncertainties but differing c parameters suggests that other factors may influence c, e.g. variations in the Li concentration or inhomogeneity of the oxygen distribution (on a scale smaller than 1 µm). Though prior work suggests a very narrow range of Li nonstoichiometry (0.87 – 0.93 per f.u.), small Li concentration variations between crystals may exist and might correlate with those observed here for oxygen. The c parameter is thus as a surrogate indicator for stoichiometric variation in oxygen and possibly Li. We note that a crystal with oxygen excess (labeled “A1” in Fig. 2) was remeasured after 18 months stored in a dessicator and found to have larger c (labeled “A2” in Fig. 2), suggesting a tendency of crystals with oxygen excess to slowly lose oxygen or for oxygen to redistribute, via diffusion, over long periods of time. Small increases in the angle β with increasing c parameter are shown in Fig. 2.

Interstitial oxygen in other oxides (e.g. cuprates) may affect the electronic structure through local charge doping, lattice distortion, or magnetic moment formation. The quasi-one-dimensional, conducting Mo-O double chains of LiPB may be especially susceptible to perturba-
FIG. 3. (color online) (a) Fermi surface from Ref. 5 (a), schematic of the conducting Mo-O-Mo zig-zag chains along the crystallographic $b$ axis, and (c) the arrangement of double chains within the $ac$ plane.

These transverse hopping parameters attributable within tight-binding parameterizations is associated with an opposite warping of the FS sheets, $\Gamma P X$ plane. This favors a two-carrier (ambipolar) conduction scenario in which very large hole and electron partial thermopowers, $S_h$ and $S_e$ ($S_c < 0$), nearly cancel due to compensation: $S_o \propto S_h + S_e$, $\nu \propto \mu (S_h - S_e)$ ($\mu$ is the carrier mobility). A departure from the compensation condition in specimens with larger $c$ parameter could explain the appearance of their large low-$T$ values for $S_o$. The mechanism underlying such very large partial thermopowers at low $T$ remains to be established, but phonon-drag appears to be a plausible candidate.

Though all specimens have positive 300 K thermopowers, their $T$ dependencies approach a linear-in-$T$ form with negative slope that results in negative values for $S_o$ above room temperature (specimen D, Fig. 3). This implies a negative (electron-like) carrier diffusion thermopower along the chains that is independent of the low-$T$ behavior.

**Hall Coefficient.** The Hall coefficients of crystals A2 and C having $c = 9.482(4)$ and 9.491(4), respectively (arrows in Fig. 2), were reported elsewhere. Their oxygen contents were not measured; their Hall data are shown in Fig. 5. Also shown are data from three other sources in the literature. All of the data show very similar $T$ dependencies, but magnitudes vary by a factor of 10. Note that $R_H > 0$ throughout the $T$ range for all measurements.

At present it is not possible to draw conclusions about a dependence of $R_H$ on $c$ parameter with complete data sets only for specimens A2 and C ($c$ was not reported...
along with the other data reproduced in Fig. 5. In a more recent work27 studying crystals from the same source as that of Ref. 16, lattice parameters \(a = 12.73\) Å and \(c = 9.51\) Å where reported, both differing significantly from those reported here. Thus in addition to a stoichiometric variability observed for the present crystals, there may well be other differences between specimens prepared by different groups that have yet to be identified.

The Hall data might be reconciled with the compensation scenario motivated by the thermoelectric data. Empirically, that \(R_H\) is always positive (a sign opposite to that of the diffusion thermopower) and varies substantially in magnitude among those crystals measured tends to support such a view. To examine this issue in more detail, first note that for Q1D systems with open Fermi surfaces the relation between the low-field Hall coefficient and carrier density differs from the free-electron expression, and for constant mean-free-path is generalized to:

\[
R_H = \frac{\eta}{(e|n|)} = \frac{\eta}{(e|n|)}(\frac{\sigma_{xy}}{B})_{\rho_b \rho_c},
\]

from the perspective of correlation effects, LiPB is one-quarter filled (approximately half an electron per band crossing \(E_F\)) with a tight-binding dispersion \(\epsilon(k_b) = -t \cos(k_b b/2)\). The Hall coefficient corresponding to \(k_F = \pi/(2b)\) of LiPB would then be:

\[
R_H = \frac{\eta}{(e|n|)} = -1.7 \times 10^{-9} \text{ m}^3/\text{C} \text{ assuming } 1.9e^-/\text{unit cell as dictated by the chemistry and bonding. Though this value is in the middle of the experimental magnitudes near room temperature, the sign is opposite to those observed. The Hall coefficient for coupled Luttinger chains differs from the noninteracting case only by small power-law in } T \text{ corrections.}\]

Theoretical treatments of the thermopower for single Luttinger chains with impurity scattering indicate a linear temperature dependence for the carrier diffusion contribution similar to the noninteracting case.

A positive sign for \(R_H\) can arise from negative curvature in the dispersion \((\eta > 0)\) along one or both of the FS sheets (e.g., the density functional bands suggest this is the case for the band that crosses at higher momentum along the \(P - K\) direction), or from a strong momentum dependence for the mean-free path due to electron-electron or electron-phonon interactions, though such scattering anisotropy tends to be weaker at high \(T\). Two-carrier fits to the \(R_H\) data for crystals A2 and C yield hole and electron partial Hall coefficients that are an order of magnitude or more larger than \(R_H\), implying carrier densities substantially smaller than expected. A reduced mobile carrier density is suggested by observations of localized charge in optical studies as might be anticipated for carriers confined to chain fragments isolated by disorder.

An alternate, intriguing possibility is that strong correlations modify the FS from that predicted within density functional theory [Fig. 5(a)]. The Mott gap \((\Delta)\) in LiPB appears to be quite small, such that \(t_\perp > \Delta\). In such systems having strong on-site and longer-range Coulomb repulsion, calculations reveal as a regime intermediate between 1D insulator and 2D metal where the suppression of the Mott gap via transverse hopping leads to the formation of a FS broken into narrow electron and hole pockets. This physics was recently invoked as a possible explanation for Fermi arcs found in photoemission studies of Y-124 due to the CuO chains. Such a picture is appealing for LiPB as it offers a possible explanation for two-carrier physics apparent in the thermoelectric coefficients, positive values for \(R_H\) (provided there is a higher weighting of hole-like pockets), and carrier densities inferred from a two-carrier analysis of \(R_H\) that are much smaller than expected. Whether this scenario can be consistent with photoemission observations of the FS awaits a more complete and higher-resolution mapping throughout the Brillouin zone.

**Summary.** Variations in the \(c\) lattice parameter of \(\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}\) crystals, attributable to stoichiometric variations in oxygen and possibly Li, correlate with the low-\(T\) thermopower. The implication is that the low-energy electronic structure is sensitive to small variations in stoichiometry in as-grown crystals. Thus the \(c\) parameter is revealed by this work to be an important metric with which to compare specimens. The data suggest formation of interstitial oxygen during growth as a possible source of oxygen variability. The available Hall data are less conclusive as to trends with \(c\), but the observed variations in magnitude may be consistent with a two-carrier picture motivated by thermoelectric data.

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\* Present address: Physics Department, University of California, San Diego, La Jolla, CA 92093-0319.

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