



This is the accepted manuscript made available via CHORUS. The article has been published as:

Superconductivity at carrier density 10^{17} cm⁻³ in quasi-one-dimensional $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$

J. L. Cohn, C. A. M. dos Santos, and J. J. Neumeier

Phys. Rev. B **108**, L100512 — Published 29 September 2023

DOI: [10.1103/PhysRevB.108.L100512](https://doi.org/10.1103/PhysRevB.108.L100512)

Superconductivity at carrier density 10^{17} cm^{-3} in quasi-one-dimensional $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$

J. L. Cohn,^{1,*} C. A. M. dos Santos,² and J. J. Neumeier³

¹*Department of Physics, University of Miami, Coral Gables, FL 33124*

²*Escola de Engenharia de Lorena—USP, Lorena-SP, 12602-810, Brazil*

³*Department of Physics, Montana State University, Bozeman, MT 59717*

Quasi-one-dimensional systems, having tendencies toward density-wave order in competition with superconductive pairing in their ground states, may give rise to unconventional superconductivity, a central theme in condensed matter physics. Partial density-wave gapping of electronic bands at the Fermi surface in such systems can yield superconductivity at very low carrier density that challenges Bardeen-Cooper-Schrieffer (BCS) theory since the pairing energy scale may approach or exceed the Fermi energy and render screening of the Coulomb interaction ineffective. Here we present low- T magnetotransport measurements on the quasi-one-dimensional conductor $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ showing the metallic state from which superconductivity emerges ($T_c \simeq 2$ K) to possess among the lowest known carrier densities, $\sim 10^{17} \text{ cm}^{-3}$, and a ratio of T_c to Fermi temperature within the BCS-Bose Einstein condensate (BEC) crossover regime. A semimetallic state caused by a density-wave-induced Fermi surface reconstruction with highly anisotropic electron and hole pockets is implied. The degree of interpocket nesting appears to determine whether the extreme low-density ground state is superconducting or undergoes additional Fermi surface gapping.

Electron pairing in the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity, arising from weak attractive interactions in a degenerate fermionic system, results in a superconducting transition temperature that is typically orders of magnitude smaller than the Fermi temperature, $T_c/T_F \sim 10^{-4}$. In the opposite limit of a Bose-Einstein condensate (BEC), strongly-coupled fermions (composite bosons) condense into a coherent quantum state and typically $T_c/T_F \gtrsim 0.1$ [1]. A small number of materials having $T_c/T_F \sim 0.04 - 0.1$ within the BCS-BEC crossover regime include high- T_c cuprates, heavy-fermion and Fe-based compounds, superconductors believed to involve spin-mediated pairing [2–4].

Quasi-one-dimensional (q1D) electron systems may harbor unconventional superconductivity within the BCS-BEC crossover regime when partial density-wave gapping of electronic bands at the Fermi surface, induced by competing density wave order, yields a metallic state with very small Fermi energy. $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ (lithium purple bronze, LiPB) is a transition metal oxide with q1D electronic properties. Its resistivity is metallic at high T , exhibits a minimum at $15 \text{ K} \lesssim T_{min} \lesssim 30 \text{ K}$ and rises below T_{min} to the superconducting transition at $T_c \simeq 2 \text{ K}$ [5–7]. The metallic phase at $T \geq T_{min}$ exhibits features [8, 9] of a Tomonaga-Luttinger liquid (TLL) [10] with spin-charge separation [11–13]. The mechanisms for the upturn in the resistivity at $T < T_{min}$ and superconductivity remain a mystery in spite of substantial experimental efforts over decades. The superconducting state is three dimensional with highly anisotropic upper-critical fields (H_{c2}) consistent with its normal-state electrical anisotropy [7]. For field applied along the q1D chains, H_{c2} substantially exceeds the Pauli paramagnetic limit, motivating the proposal [7] that LiPB is a triplet superconductor [14–18].

The LiPB band structure, studied extensively via photoemission [19] and computation [11, 19–22], consistently re-

veals two q1D, nearly degenerate electron bands crossing the Fermi energy, derived from d_{xy} orbital overlap along the zig-zag Mo-O chains (crystallographic b axis). Superconductivity requires a dimensionality increase for which the resistivity minimum is presumed to be the signature. Potential explanations include charge- or spin-density wave (CDW or SDW) formation, a structural change [23, 24], and a recent proposal involving the ordering of long-lived excitons [25, 26]. Experiments rule out CDW [23, 27, 28] and SDW [29] order (though the latter less convincingly), and good agreement between the local-density approximation band structure and photoemission [19] for the bands near E_F is compelling evidence against the occurrence of a TLL fluctuation-induced suppression of dimensional crossover [30].

Here we report comprehensive magnetotransport measurements within the most conducting bc -plane (field along a) at $T \gtrsim 0.4 \text{ K}$ for both superconducting (SC) and non-superconducting (non-SC) LiPB crystals, revealing extremely low carrier densities ($n \sim 10^{17} \text{ cm}^{-3}$) throughout the range $T \leq 100 \text{ K}$ and a rich multi-carrier physics. The mobile carrier densities are among the lowest known for any superconductor [31, 32], placing superconductivity of LiPB in a regime at the border between BCS and BEC. A density-wave-induced semimetallic reconstruction of the Fermi surface comprised of highly anisotropic electron and hole pockets is implicated at $T \gg T_{min}$ for both sets of samples. Competition for the ground state appears to be controlled by the degree of interpocket nesting, leading to further density wave gapping (non-SC samples) or superconductivity. This nesting is manifested in the strong scattering and localization of in-chain hole and interchain electron states on the reconstructed FS at $T \gtrsim T_{min}$. A sharp suppression of this scattering in SC samples at $T \lesssim T_{min}$ signals delocalization of these states and emergence of quasi-two-dimensional transport within each of the pockets as a precursor to superconductive pairing.

Figure 1 (a)-(d) show the field-dependent Hall and longitudinal resistivities for two orientations of the electric current

* Corresponding Author: jjohn@miami.edu

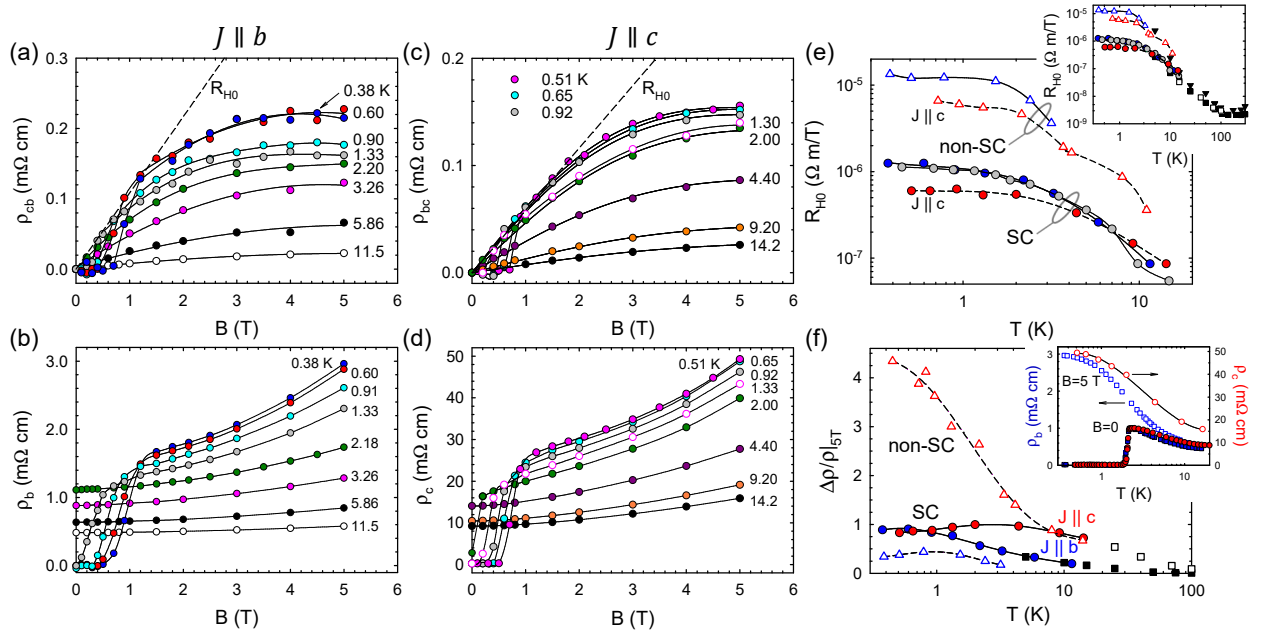


Fig. 1. (a)-(d) Hall and longitudinal resistivities for two orientations of the current flow (\mathbf{J}) in superconducting crystals. Dashed lines in (a) and (c) are the initial slopes, $R_{H0} \equiv d\rho_{xy}/dB|_{B \rightarrow 0}$, at low T . (e) R_{H0} vs. T for all crystals (SC–filled symbols, non-SC–open symbols). The inset compares data from the main panel to that at higher T for crystals from Refs. 35 and 36 with current $\parallel b$ (filled squares and inverted triangles) and $\parallel c$ (open squares). (f) longitudinal magnetoresistance at $B = 5$ T vs. T for all crystals. The inset shows $\rho_b(T)$ (squares, left ordinate) and $\rho_c(T)$ (circles, right ordinate) at $B = 0, 5$ T. Solid and dashed curves are guides.

flow ($\mathbf{J} \parallel \mathbf{b}$ and $\mathbf{J} \parallel \mathbf{c}$) in SC crystals at various T . Similar data for the non-SC crystals are presented in the Supplementary Material [33] (Fig. S1). Superconducting transitions are evident at low fields for temperatures $T < T_c$ [see also inset, Fig. 1 (e)]; the inferred upper critical fields and range of values for T_{min} [~ 18 K (30 K) for the SC (non-SC) specimens] agree with those of prior studies [5–7] (Fig. S2 [33]).

Substantial nonlinearities of the Hall resistivities with field (especially at the lowest T) suggest the presence of charge carriers with opposing signs. The initial slopes, $R_{H0} \equiv d\rho_{xy}/dB|_{B \rightarrow 0}$ [Fig. 1 (e)] yield $T \rightarrow 0$ values $R_{H0} \approx 10^{-6}$ (10^{-5}) Ω m/T for SC (non-SC) samples, corresponding to approximate carrier densities, $n = 1/(R_{H0}e) \approx 6 \times 10^{18}$ (6×10^{17}) cm^{-3} . But the data are more aptly described by an anisotropic, two-carrier model, for which $R_{H0} = (n_h \mu_h^2 - n_e \mu_e^2)e/[\sigma_b(0)\sigma_c(0)]$ [$\sigma_b(0)$ and $\sigma_c(0)$ are the zero-field conductivities] as discussed further below.

The thermoelectric coefficients tell a similar story of extremely low carrier density. The field dependencies of the Nernst signal, $N_{yx} = E_y/|\nabla T_x|$ and thermopower, $S_x = E_x/\nabla T_x$ ($x, y = b, c$) for the SC crystals are shown in Fig. 2 (a)-(d). Note the different vertical scales (mV versus μV) for N_{cb} (heat current $\mathbf{J}_q \parallel \mathbf{b}$) and N_{bc} ($\mathbf{J}_q \parallel \mathbf{c}$): extreme anisotropy, $N_{cb} \approx 300N_{bc}$, is observed. Sharp maxima in the low-field Nernst signals for $T < T_c$ (especially for N_{cb}) near the midpoints of the SC transitions are attributed to a flux-flow Nernst effect [34]. Very similar results for N_{cb} were found for a second SC crystal (Fig. S3 [33]). Possible contaminating signals associated with the Righi-Leduc (thermal Hall) effect are negligible for both orientations (Fig. S4

[33]). In comparison to the Nernst signal, the thermopower is more isotropic, with a stronger field dependence evident for S_c . Though the in-chain thermopower (S_b) is positive, it is decidedly electron-like at $T \gtrsim 30$ K – linear-in- T with negative slope, resulting in negative values at $T \gtrsim 300$ K [35–37].

Like the Hall resistivity, significant nonlinearity of the Nernst signals (particularly at low T) suggest competing electron and hole contributions. For comparison to the estimates from R_{H0} , we compute carrier densities from the $B = 5$ T, $T \rightarrow 0$ limiting values for ν/T ($\nu = N/B$) and S/T indicated by the dashed lines in Fig. 2 (e) and (f). For a broad spectrum of correlated and low-dimensional metals it has been shown [38] that these quantities scale well with carrier mobility (μ) and Fermi temperature (T_F) as prescribed by the free-electron, Boltzmann theory expressions for carrier diffusion, $\nu/T = (\pi^2/3)(k_B/e)(\mu/T_F)$ and $S/T = (\pi^2/3)(k_B/e)(1/T_F)$. Using $\mu = 0.2 \text{ T}^{-1}$ (determined from analysis below) and averaging values for the two experimental orientations, $\nu/T \approx 15 \mu\text{V}/\text{TK}^2$ ($S/T \approx 12 \mu\text{V}/\text{K}^2$), we find $T_F \approx 19$ K (23 K). The free-electron relation, $E_F = k_B T_F = (\hbar^2/2m)(3\pi^2 n)^{2/3}$ thus implies $n \approx 3.5 \times 10^{17} \text{ cm}^{-3}$.

To refine understanding of the magnetotransport, consider a two-carrier model for the bc -plane, with holes and electrons (densities n_h and n_e , respectively) for each direction having different mobilities, μ_{ib}, μ_{ic} , ($i = h, e$) [39]. The model has four carrier densities (holes and electrons for each direction), but is simplified because for each pair of crystals (two orientations each, SC and non-SC), we observe $\rho_{cb} \approx \rho_{bc}$ [Fig. 1 (a), (c), (e) and Fig. S1 [33]].

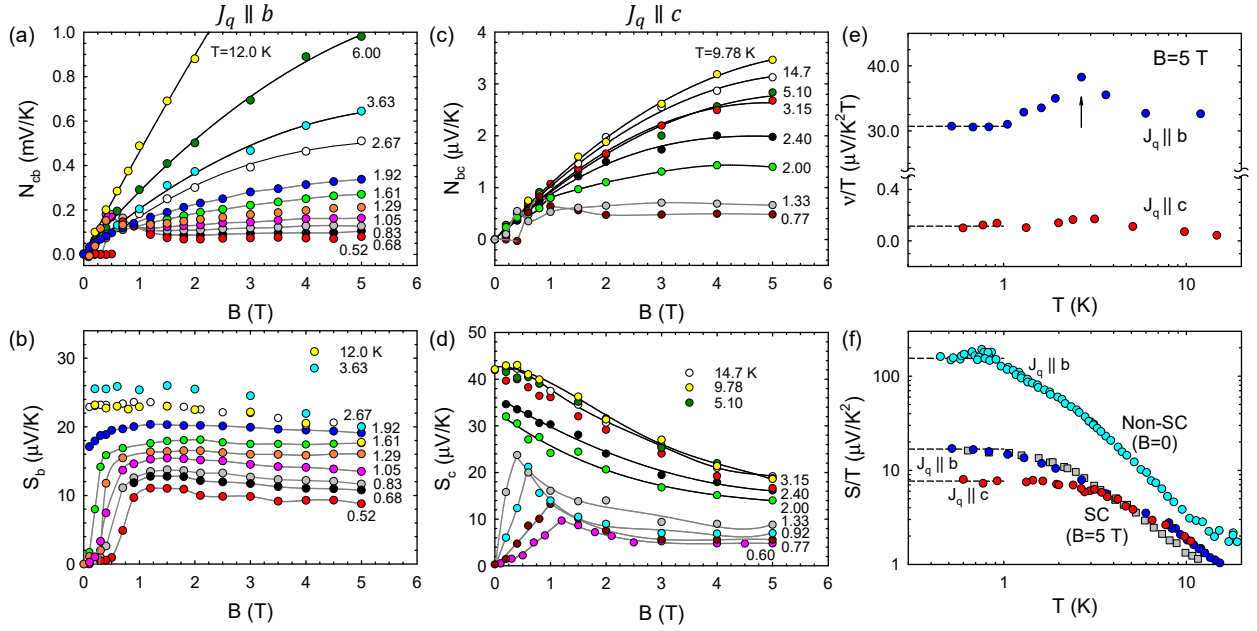


Fig. 2. (a)-(d) Nernst signal and thermopower for two orientations of the heat current (J_q) in superconducting crystals. Solid curves are guides. (e) T dependence of ν/T and (f) S/T . The vertical arrow in (e) marks a “kink” in ν/T near $T \simeq 3$ K (see text and Supplementary Information). Squares in (f) are from a second superconducting b -axis specimen.

This isotropy of the transverse magnetoresistivities contrasts with the anisotropy of the longitudinal magnetoresistivities, $\Delta\rho(B)/\rho(0)$ [Fig. 1 (f)]. In such a case, the model dictates isotropy of hole and electron densities [39]. Switching to the equivalent and simpler conductivity expressions, the field dependencies of the coefficients are then given by,

$$\begin{aligned}\sigma_b &= \sigma_{hbb} + \sigma_{ebb} = \frac{n_h e \mu_{hb}}{(1 + \mu_h^2 B^2)} + \frac{n_e e \mu_{eb}}{(1 + \mu_e^2 B^2)} \\ \sigma_c &= \sigma_{hcc} + \sigma_{ecc} = \frac{n_h e \mu_{hc}}{(1 + \mu_h^2 B^2)} + \frac{n_e e \mu_{ec}}{(1 + \mu_e^2 B^2)} \\ \sigma_{bc} &= \sigma_{cb} = \sigma_{hbc} + \sigma_{ebc} = \frac{n_h e \mu_h^2 B}{(1 + \mu_h^2 B^2)} - \frac{n_e e \mu_e^2 B}{(1 + \mu_e^2 B^2)},\end{aligned}$$

where $\mu_h = \sqrt{\mu_{hb}\mu_{hc}}$ and $\mu_e = \sqrt{\mu_{eb}\mu_{ec}}$ are effective mobilities governing the field dependencies. Examples of the simultaneous fitting to these equations at various temperatures and the computed partial conductivities are presented in Figs. S5-S7 [33]. The fitted values of the carrier densities and mobilities as functions of T are shown in Fig. 3. The analysis was extended to higher T for SC crystals using data from prior work [35, 36] in the range $25\text{K} \leq T \leq 100$ K [open and filled squares in Fig. 1 (e), inset, and Fig. 1 (f)], where the magnetoresistance and Hall resistivity are quadratic and linear, respectively, in applied fields $B \leq 5$ T, consistent with prior studies [6, 7, 40, 41]. The same model parameters were employed to fit the field-dependent thermoelectric coefficients (Eqs. S1-S3, Figs. S8, S9 [33]) to extract partial coefficients for holes and electrons. The “kink” in the ν/T curve [arrow in Fig. 2 (e)] is found to arise from competi-

tion between Nernst terms (carrier diffusion and the product of Hall conductivity and thermopower) with opposite sign (Eq. S2 and Fig. S9 [33]).

A central outcome of the analysis is that, consistent with the measured $R_{H0}(T)$ for multiple specimens and orientations [inset, Fig. 1 (e)], the carrier densities for both SC and non-SC crystals [Fig. 3 (a)] are comparable at $T \gtrsim 10$ K, with $n_e \sim 3.5n_h \simeq 10^{17}$ cm^{-3} in the former. Thus LiPB is partially compensated, with extremely low carrier densities throughout the entire T range. This result is not in conflict with established TLL physics at higher T for LiPB since TLL characteristics are independent of carrier density [42]. The single-band expression $n = 1/R_{H0}e$ at 100 K yields $n \sim 3 \times 10^{21}$ cm^{-3} , a substantial overestimate of the actual value, and coincidentally comparable to, though opposite in sign, that expected from the band structure and chemical valence, 1.9 e /unit cell [13, 35]. The rise in R_{H0} by more than two orders of magnitude from $T \sim 100$ K to 10 K [35, 40, 41, 43] is almost entirely attributable to an increase in the effective carrier mobilities [dashed curves, Fig. 3 (b)] [44].

The small density (or T_F) is incompatible with the large Fermi wavenumber $k_F \simeq \pi/(2b)$ determined by photoemission and density functional theory, but is entirely consistent, as is compensation, with LiPB’s giant Nernst coefficient over a broad range of T ($\sim 45\mu\text{V}/\text{K}^2\text{T}$ at 100 K) [36]. A reconstruction of the FS (at $T > 100$ K) into small electron and hole pockets with highly anisotropic q1D character is implied. The prospect of spin-density wave gapping of the FS for commensurate nesting vector $q_{SDW} = 2k_F$ along k_b was considered in Ref. 19. The nesting is imperfect due to small warping of the two d_{xy} FS sheets, associated with interchain (k_c)

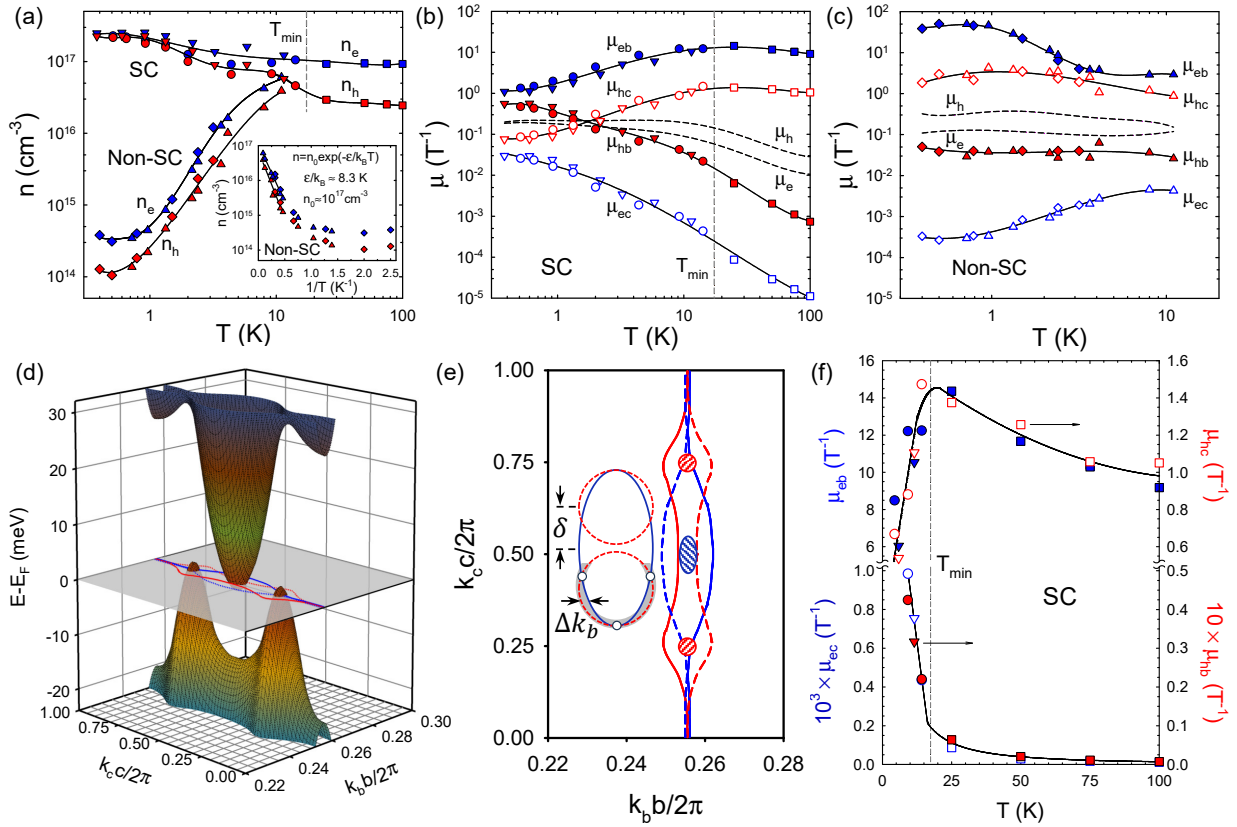


Fig. 3. Carrier densities (a) and mobilities for (b) SC and (c) non-SC specimens determined by simultaneous fitting to the anisotropic two-band model (see text and Supplementary Information). Different symbols represent the two crystals for which $\mathbf{J} \parallel \mathbf{b}$ and $\mathbf{J} \parallel \mathbf{c}$. Solid and dashed curves are guides. (d) Energy band scheme and Fermi plane (adapted from Ref. 19) assuming a SDW gap-induced reconstruction to a semimetal with $E_F = 1.5$ meV for both hole and electron bands (see text). Shown in the $E = E_F$ plane of (d) and in (e) is the incomplete nesting of the unreconstructed FS (solid curves: upper sheet – red, lower sheet – blue) and their translations by the nesting vector $q_{SDW} = 2k_f \simeq \pi/b$ along k_b (dashed curves), defining hole (red) and electron (blue) pockets between their respective boundaries. Note the greatly expanded scale for the k_b axis in both (d) and (e). The inset in (e) shows a magnified view of potential nesting for the electron and hole pockets (hatched regions in main panel) – the best nesting is shown by the dashed hole pockets translated along k_c by $q = \pm(\pi/2c \pm \delta)$, with $\delta \sim 0.1(\pi/2c)$. The shaded region for the lower translation represents the approximate phase space at $T \approx T_{min}$ for its nesting instability, the width of which normal to the FS is $\sim k_B T$ and at $T = 0$ is confined to the hot spots (small open circles). (f) mobilities for SC samples with linear scaling (curves are guides).

dispersions, and caused by hybridization with the gapped xz and yz valence and conduction bands via long-range indirect hopping. Gapping throughout the Brillouin zone occurs for $\Delta_{SDW} \approx 65$ meV, though the interaction strength was estimated to be 2-3 times too small for such an instability [19]. Assuming a slightly smaller value for Δ_{SDW} , Fig. 3 (d) depicts a semimetallic reconstruction of the bands [45] and FS using the gapped (unreconstructed) k_b (k_c) dispersions from Ref. 19 (Fig. S10 [33]). Consistent with estimates above from the thermoelectric coefficients, a small overlap was assumed with electron and hole Fermi energies the same, $E_{F,e} = E_{F,h} = 1.5$ meV. The occupied FS areas for electrons and holes within this picture are each $\sim 3 \times 10^{-4} A_{BZ}$ ($A_{BZ} = (2\pi)^2/bc$ is the unreconstructed Brillouin zone area), consistent with the observed carrier densities [Fig. 3 (e)]. Note the greatly expanded scale for the k_b axes in Fig. 3 (d) and (e) – the reconstructed pockets are highly anisotropic with a width along k_b of only $\sim 0.01(\pi/b)$. Within mean-

field theory, the SDW transition temperature would be estimated as $T_{SDW} \simeq 2\Delta_{SDW}/(3.5k_B) \approx 420$ K, though incomplete nesting [46] can suppress T_{SDW} . Alternatively, it is possible that rather than gapping large portions of the FS, strong scattering associated with density-wave fluctuations localizes states in extended, nearly-nested regions of the FS sheets so that the photoemission and transport observations could be reconciled.

The overlapping electron and hole bands of the semimetallic FS reconstruction have very similar parabolic b -axis dispersions (Fig. S10 [33]) and thus comparable values for μ_{eb} and μ_{hb} are anticipated. Indeed, for SC crystals at the lowest T (~ 0.4 K) this condition holds true [Fig. 3 (b)]. Given that the unreconstructed band structure does not provide for in-chain hole conduction, this observation, along with the low density, provide compelling support for a semimetallic reconstruction like that depicted in Fig. 3 (d) and (e). However, this low- T electronic structure evolves gradually with the

turning on of strong T dependent mobilities at $T \lesssim T_{min}$, as more clearly seen on the linear scaling of Fig. 3 (f): μ_{hb} and μ_{ec} (in-chain holes and interchain electrons, lower panel) increase sharply below T_{min} , while μ_{eb} and μ_{hc} (in-chain electrons and interchain holes, upper panel) decrease sharply. This opposing scattering behavior for the two groups of carriers is also reflected in opposing signs for their partial Seebeck coefficients (Fig. S8 [33]), as dictated by the scattering term in the Mott expression for diffusion thermopower, $S \sim d \ln \sigma(E)/dE|_{E_F} \sim d \ln \mu(E)/dE|_{E_F}$.

The values for μ_{hb} and μ_{ec} at $T \gtrsim 10 - 20$ K imply incoherence, with mean-free paths comparable to or smaller than the interatomic spacing (Fig. S11 [33]) and two orders of magnitude smaller than those for in-chain electrons and interchain holes. Such highly anisotropic scattering on the FS pockets is likely associated with density-wave fluctuations and interpocket nesting for wave vectors along k_c [inset, Fig. 3 (e)]. The substantial increase in the SC mobile carrier densities from T_{min} to $T \lesssim 1$ K (where they become constant), suggests that portions of the FS harbor large densities of localized states for in-chain holes and interchain electrons, the delocalization of which occurs gradually with decreasing T . This behavior may arise because the phase space for nesting [shaded region for the dashed hole FS, inset Fig. 3 (e)] declines with the thermal energy and at $T = 0$ is confined to hot spots at the intersections of the pockets (small open circles).

Supporting this picture, the in-chain hole and interchain electron states with greatest velocities lie within the shaded (nested) portions of their FSs [inset, Fig. 3 (e)], while the most dispersive in-chain electron and interchain hole states remain unaffected or only partially so. Thus the decrease of the latter mobilities at $T < T_{min}$ is a consequence of FS averaging and an increased weighting, with decreasing T , of delocalized portions of the FS having lower-mobilities. Then $k_B T_{min}$ should correspond to the maximum energy mismatch of pseudo-nesting, expressed approximately as $(\partial E/\partial k_b)\Delta k_b = \hbar v_{F,b}\Delta k_b$, where $v_{F,b}$ is the in-chain Fermi velocity and Δk_b is depicted in the inset of Fig. 3 (e). We find $\hbar v_{F,b}\Delta k_b \simeq 0.9$ meV [$v_{F,b} = 1.8 \times 10^5$ m/s (Table S1 [33]), $E_{F,e} = E_{F,h} = 1.5$ meV as in Fig. 3 (e)] and $\simeq 1.8$ meV ($v_{F,b} = 2.3 \times 10^5$ m/s, $E_{F,e} = 2.0$ meV, $E_{F,h} = 2.5$ meV), in reasonable accord with $k_B T_{min}$ (1.5 meV).

A competition between further density-wave gapping of the FS and the occurrence of superconductivity will undoubtedly be sensitive to the Fermi energies of the electron and hole pockets which presumably differ in SC and non-SC crystals. Indeed further density-wave gapping for most of the FS is implicated in non-SC specimens by the exponential decline in carrier densities at $T \lesssim 10$ K [Fig. 3 (a) and inset], with $n = n_0 \exp(-\varepsilon/k_B T)$ at $T \gtrsim 2$ K and averaged values $\varepsilon/k_B \simeq 8.3$ K (0.7 meV), $n_0 \simeq 10^{17}$ cm $^{-3}$. In spite of this carrier freeze-out, a residual density of carriers survives ($\simeq 1 - 3 \times 10^{14}$ cm $^{-3}$) and the in-chain conductivity

extrapolates to a finite value as $T \rightarrow 0$ (Fig. S12 [33]) – metallicity is maintained by a concomitant increase in the electron mobility μ_{eb} [Fig. 3 (c)]. The high values for μ_{eb} are a consequence of a small band effective mass for the reconstructed k_b dispersions ($\sim 0.016m_e$, Table S1 [33]) and the fact that defects in LiPB (e.g., Li vacancies or O interstitials [35]) are far from the q1D chains confining electrons and expected to interact with weak Coulomb character [22]. Further confirming this extreme low-density metallic state is the thermopower, with $\lim_{T \rightarrow 0} S_b/T \simeq 150 \mu\text{V/K}$ [top dashed line, Fig. 2 (f)]. This value is among the largest reported for any metal [47], exceeding those for strongly-correlated compounds known to have substantial fractions of their FSs gapped by novel ordering [48, 49]. The non-SC interchain conductivity extrapolates to zero at finite T (Supplementary Fig. S12) – this absence of metallicity is consistent with expectations that superconductivity is not possible in lower than two dimensions.

Comparing the non-SC mobilities with those of SC samples at the lowest T , it is notable that the values of both μ_{eb} and μ_{hc} for the former exceed those of the latter by more than an order of magnitude while the opposite is true for μ_{hb} and μ_{ec} . This is consistent with better interpocket nesting for the non-SC samples and a full gapping of these portions of the FS. The absence of this gapping in SC specimens evidently sets the stage for superconductive pairing. T_{min} effectively behaves as a dimensional crossover scale, below which the q1D electron and hole transport along mutually perpendicular directions gradually evolves to the quasi-two-dimensional character of the low- T semimetal characterized by mobile states extending in both crystallographic directions on each FS pocket.

LiPB's low carrier density is comparable to those of SrTiO $_3$ ($T_c \simeq 0.86$ K at $n = 5.5 \times 10^{17}$ cm $^{-3}$) [31] and pure Bi ($T_c = 0.53$ mK at $n = 3 \times 10^{17}$ cm $^{-3}$) [32], and thus its much higher T_c is remarkable. The interelectron distance at T_c , $d_{ee} \simeq 1/n^{1/3} \approx 22$ nm, is comparable to the relevant superconducting coherence lengths [7], $\xi_b = 30$ nm and $\xi_c = 10$ nm, i.e. Cooper pairs do not substantially overlap. This and the ratio of critical temperature to effective Fermi temperature, $T_c/T_F \gtrsim 0.1$, place LiPB's parameters near the border between BCS superconductivity and BEC [50, 51]. The characteristics of LiPB revealed in the present work have similarities to those of Fe-based superconductors [4], and elevate the prospect that unconventional physics is at play, e.g. spin-fluctuation-induced interpocket pairing or pairing without phase coherence at $T > T_c$ [52]. Regarding the latter, the coexistence of pairs with single-particle excitations is evidenced in LiPB [53] for specimens with partial superconducting transitions intermediate between the SC and non-SC crystals reported here.

This material is based on work supported by the U.S. DOE, Off. of BES, Div. of Mater. Sci. and Eng., under grant No. DE-SC0008607 (Univ. Miami) and No. DE-SC0016156 (Montana St. Univ.). J. L. C. acknowledges helpful comments from J. W. Allen and O. K. Andersen.

- [1] M. Randeria and E. Taylor, Crossover from Bardeen-Cooper-Schrieffer to Bose-Einstein condensation and the unitary Fermi gas, *Annu. Rev. Condens. Matter Phys.* **5**, 209 (2014).
- [2] Tôru Moriya and Kazuo Ueda, Antiferromagnetic spin fluctuation and superconductivity, *Rep. Prog. Phys.* **66**, 1299 (2003).
- [3] J. L. Sarrao and J. D. Thompson, Superconductivity in Cerium- and Plutonium-Based ‘115’ Materials, *J. Phys. Soc. Jpn.* **76**, 051013 (2007).
- [4] See, Rafael M. Fernandes, Amalia I. Coldea, Hong Ding, Ian R. Fisher, P. J. Hirschfeld, and Gabriel Kotliar, Iron pnictides and chalcogenides: a new paradigm for superconductivity, *Nature* **601**, 35 (2022), and references therein.
- [5] M. Greenblatt, W. H. McCarrroll, R. Neifeld, M. Croft, J. V. Waszczak, Quasi two-dimensional electronic properties of the lithium molybdenum bronze, $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Solid State Commun.* **51**, 671 (1984).
- [6] Xiaofeng Xu, A. F. Bangura, J. G. Analytis, J. D. Fletcher, M. M. J. French, N. Shannon, J. He, S. Zhang, D. Mandrus, R. Jin, and N. E. Hussey, Directional field-induced metallization of quasi-one-dimensional $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Phys. Rev. Lett.* **102**, 206602 (2009).
- [7] J.-F. Mercure, A. F. Bangura, Xiaofeng Xu, N. Wakeham, A. Carrington, P. Walmsley, M. Greenblatt, and N. E. Hussey, Upper critical magnetic field far above the paramagnetic pair-breaking limit of superconducting one-dimensional $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ single crystals, *Phys. Rev. Lett.* **108**, 187003 (2012).
- [8] J. Hager, R. Matzdorf, J. He, R. Jin, D. Mandrus, M. A. Cazalilla, E. W. Plummer, Non-Fermi liquid behavior in quasi-one-dimensional $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Phys. Rev. Lett.* **95**, 186402 (2005).
- [9] F. Wang, J. V. Alvarez, S.-K. Mo, J. W. Allen, G.-H. Gweon, J. He, R. Jin, D. Mandrus, H. Höchst, New Luttinger-liquid physics from photoemission on $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$. *Phys. Rev. Lett.* **96**, 196403 (2006).
- [10] T. Giamarchi, *Quantum physics in one dimension* (Oxford University Press, 2004).
- [11] Z. S. Popović and S. Satpathy, Density-functional study of the Luttinger liquid behavior of the lithium molybdenum purple bronze $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Phys. Rev. B* **74**, 045117 (2006).
- [12] P. Chudzinski, T. Jarlborg, and T. Giamarchi, Luttinger-liquid theory of purple bronze $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ in the charge regime, *Phys. Rev. B* **86**, 075147 (2012).
- [13] J. Merino and R. H. McKenzie, Effective Hamiltonian for the electronic properties of the quasi-one-dimensional material $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Phys. Rev. B* **85**, 235128 (2012).
- [14] A. G. Lebed and O. Sepper, Possible triplet superconductivity in the quasi-one-dimensional conductor $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Phys. Rev. B* **87**, 100511 (2013).
- [15] O. Sepper and A. G. Lebed, Nodeless versus nodal scenarios of possible triplet superconductivity in the quasi-one-dimensional layered conductor $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Phys. Rev. B* **88**, 094520 (2013).
- [16] W. Cho, C. Platt, R. H. McKenzie, and S. Raghu, Spin-triplet superconductivity in a weak-coupling Hubbard model for the quasi-one-dimensional compound $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Phys. Rev. B* **92**, 134514 (2015).
- [17] N. Lera and J. V. Alvarez, Triplet superconductivity in a model of $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Phys. Rev. B* **92**, 174523 (2015).
- [18] C. Platt, W. Cho, R. H. McKenzie, R. Thomale, and S. Raghu, Spin-orbit coupling and odd-parity superconductivity in the quasi-one-dimensional compound $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Phys. Rev. B* **93**, 214515 (2016).
- [19] L. Dudy, J. W. Allen, J. D. Denlinger, J. He, M. Greenblatt, M. W. Haverkort, Y. Nohara, O. K. Andersen, ARPES and NMTO Wannier Orbital Theory of $\text{LiMo}_6\text{O}_{17}$ - Implications for Unusually Robust Quasi-One Dimensional Behavior, arXiv:1812.03388 [cond-mat.str-el].
- [20] M. H. Whangbo and E. Canadell, Band electronic structure of the lithium molybdenum purple bronze $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *J. Am. Chem. Soc.* **110**, 358-363 (1988).
- [21] M. Nuss and M. Aichhorn, Effective model for the electronic properties of quasi-one-dimensional purple bronze $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ based on ab initio calculations. *Phys. Rev. B* **89**, 045125 (2014).
- [22] T. Jarlborg, P. Chudzinski, and T. Giamarchi, Effects of thermal and spin fluctuations on the band structure of purple bronze $\text{Li}_2\text{Mo}_{12}\text{O}_{34}$, *Phys. Rev. B* **85**, 235108 (2012).
- [23] C. A. M. dos Santos, B. D. White, Yi-Kuo Yu, J. J. Neumeier, and J. A. Souza, Dimensional Crossover in the Purple Bronze $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Phys. Rev. Lett.* **98**, 266405 (2007).
- [24] M. S. da Luz, J. J. Neumeier, C. A. M. dos Santos, B. D. White, H. J. Izario Filho, J. B. Leao, and Q. Huang, Neutron diffraction study of quasi-one-dimensional lithium purple bronze: Possible mechanism for dimensional crossover, *Phys. Rev. B* **84**, 014108 (2011).
- [25] P. Chudzinski, Multi-orbital physics in lithium-molybdenum purple-bronze: Going beyond paradigm, *Eur. Phys. J. B* **90** 148 (2017).
- [26] Jianming Lu, Xiaofeng Xu, M. Greenblatt, R. Jin, P. Tinnemans, S. Licciardello, M. R. van Delft, J. Buhot, P. Chudzinski, N. E. Hussey, Emergence of a real-space symmetry axis in the magnetoresistance of the one-dimensional conductor $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Sci. Adv.* **5**, eaar8027 (2019).
- [27] J. Choi, J. L. Musfeldt, J. He, R. Jin, J. R. Thompson, D. Mandrus, X. N. Lin, V. A. Bondarenko, J. W. Brill, Probing localization effects in $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ purple bronze: An optical-properties investigation, *Phys. Rev. B* **69**, 085120 (2004).
- [28] Guoqing Wu, Xiao-shan Ye, Xianghua Zeng, Bing Wu, and W. G. Clark, Direct observation of charge state in the quasi-one-dimensional conductor $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Sci. Rep.* **6**, 20721 (2016).
- [29] J. Chakhalian, Z. Salman, J. Brewer, A. Froese, J. He, D. Mandrus, and R. Jin, Magnetism in purple bronze $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Physica B: Condensed Matter* **359-361**, 1333 (2005).
- [30] D. Boies, C. Bourbonnais, and A.-M. S. Tremblay, One-Particle and Two-Particle Instability of Coupled Luttinger Liquids, *Phys. Rev. Lett.* **74**, 968 (1995).
- [31] Xiao Lin, Zengwei Zhu, Benoît Fauqué, and Kamran Behnia, Fermi Surface of the Most Dilute Superconductor, *Phys. Rev. X* **3**, 021002 (2013).
- [32] Om Prakash, Anil Kumar, A. Thamizhavel, and S. Ramakrishnan, Evidence for bulk superconductivity in pure bismuth single crystals at ambient pressure, *Science* **355**, 52 (2017).
- [33] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.93.214515> for additional experimental details, data, analysis, and including Ref. [54].
- [34] K. Behnia, Nernst response, viscosity and mobile entropy in vortex liquids, *J. Phys.: Condens. Matter* **35**, 074003 (2023).
- [35] J. L. Cohn, P. Boynton, J. S. Triviño, J. Trastoy, B. D. White,

- C. A. M. dos Santos, and J. J. Neumeier, Stoichiometry, structure, and transport in the quasi-one-dimensional metal $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Phys. Rev. B* **86**, 195143 (2012).
- [36] J. L. Cohn, B. D. White, C. A. M. dos Santos, and J. J. Neumeier, Giant Nernst effect and bipolarity in the quasi-one-dimensional metal $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Phys. Rev. Lett.* **108**, 056604 (2012).
- [37] J. L. Cohn, S. Moshfeghyeganeh, C. A. M. dos Santos, and J. J. Neumeier, Extreme Thermopower Anisotropy and Interchain Transport in the Quasi-One-Dimensional Metal $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, *Phys. Rev. Lett.* **112**, 186602 (2014).
- [38] K. Behnia, The Nernst effect and the boundaries of the Fermi liquid picture, *J. Phys.: Condens. Matter* **21**, 113101 (2009).
- [39] Qiang Deng, Jie Xing, Jianzhong Liu, Huan Yang, and Hai-Hu Wen, Anisotropic electronic mobilities in the nematic state of the parent phase NaFeAs , *Phys. Rev. B* **92**, 014510 (2015).
- [40] H. Chen, J. J. Ying, Y. L. Xie, G. Wu, T. Wu, and X. H. Chen, Magnetotransport properties in purple bronze $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ single crystal, *EPL Europhys. Lett.* **89**, 67010 (2010).
- [41] N. Wakeham, A. F. Bangura, X. Xu, J.-F. Mercure, M. Greenblatt, and N. E. Hussey, Gross violation of the Wiedemann–Franz law in a quasi-one-dimensional conductor, *Nat. Commun.* **2**, 396 (2011).
- [42] Sheng Wang, Fanqi Wu, Sihan Zhao, Kenji Watanabe, Takashi Taniguchi Chongwu Zhou, and Feng Wang, Logarithm Diameter Scaling and Carrier Density Independence of One-Dimensional Luttinger Liquid Plasmon, *Nano Lett.* **19**, 2360 (2019).
- [43] J. Dumas and C. Schlenker, Charge Denisty Wave Properties of Molybdenum Bronzes, *Int. J. Mod. Phys. B* **7**, 4045 (1993).
- [44] Contrary to the case for a single band, the mobilities do not cancel in the Hall expression even when momentum independent, $R_{H0} \simeq \frac{1}{B} \frac{\sigma_{bc}}{\sigma_b \sigma_c} \simeq \frac{1}{n_e e} \frac{\mu_{hb}}{\mu_{eb}} - \frac{1}{n_h e} \frac{\mu_{ec}}{\mu_{hc}}$, valid for most of the T range where $\mu_{eb} \gg \mu_{hb}$ and $\mu_{hc} \gg \mu_{ec}$.
- [45] The approximate energy band scheme depicted in Fig. 3 (d) employs the k_c dispersions at a single value $k_b(b/2\pi) = 0.25$ from Fig. 12 of Ref. 19 – it does not incorporate changes in the dispersions with energy. For the very small Fermi energies depicted, this should have little effect on the shape of the electron and hole pockets of the reconstructed FS. See Supplemental Information for additional details.
- [46] Xiaozhou Huang and Kazumi Maki, Imperfect nesting in spin-density waves, *Phys. Rev. B* **46**, 162 (1992).
- [47] Kamran Behnia, Didier Jaccard, and Jacques Flouquet, On the thermoelectricity of correlated electrons in the zero-temperature limit, *J. Phys.: Condens. Matter* **16**, 5187 (2004).
- [48] A. Hiess, C. Geibel, G. Sparn, C.D. Bredl, F. Steglich, T. Takabatake, and H. Fujii, Transport properties of CeNiSn at low temperatures and in high magnetic fields, *Physica B* **199–200**, 437 (1994).
- [49] A. Pourret, K. Behnia, D. Kikuchi, Y. Aoki, H. Sugawara, and H. Sato, A. Pourret, K. Behnia, D. Kikuchi, Y. Aoki, H. Sugawara, and H. Sato, Drastic Change in Transport of Entropy with Quadrupolar Ordering in $\text{PrFe}_4\text{P}_{12}$, *Phys. Rev. Lett.* **96**, 176402 (2006).
- [50] Y. J. Uemura, Classifying superconductors in a plot of T_c versus Fermi temperature T_F , *Physica C: Superconductivity* **185–189**, 733 (1991).
- [51] Alexandre Pourret, Liam Malone, Arlei B. Antunes, C. S. Yadav, P. L. Paulose, Benoît Fauqué, and Kamran Behnia, Strong correlation and low carrier density in $\text{Fe}_{1+y}\text{Te}_{0.6}\text{Se}_{0.4}$ as seen from its thermoelectric response, *Phys. Rev. B* **83**, 020504(R) (2011).
- [52] Andrey V. Chubukov, Ilya Eremin, and Dmitri V. Efremov, Superconductivity versus bound-state formation in a two-band superconductor with small Fermi energy: Applications to Fe pnictides/chalcogenides and doped SrTiO_3 , *Phys. Rev. B* **93**, 174516 (2016).
- [53] C. A. M. dos Santos, M. S. da Luz, Yi-Kuo Yu, J. J. Neumeier, J. Moreno, and B. D. White, Electrical transport in single-crystalline $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$: A two-band Luttinger liquid exhibiting Bose metal behavior, *Phys. Rev. B* **77**, 193106 (2008).
- [54] W. H. McCarroll and M. Greenblatt, Preparation of lithium molybdenum oxide bronzes by a temperature gradient flux growth technique, *J. Solid State Chem.* **54**, 282 (1984).