

## Extreme Thermopower Anisotropy and Interchain Transport in the Quasi-One-Dimensional Metal $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$

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Thermopower and electrical resistivity measurements transverse to the conducting chains of the quasi-one-dimensional metal  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$  are reported in the temperature range  $5 \leq T \leq 500$  K. For  $T \geq 400$  K the interchain transport is determined by thermal excitation of charge carriers from a valence band  $\sim 0.14$  eV below the Fermi level, giving rise to a large,  $p$ -type thermopower that coincides with a small,  $n$ -type thermopower along the chains. This dichotomy—semiconductorlike in one direction and metallic in a mutually perpendicular direction—gives rise to substantial transverse thermoelectric effects and a transverse thermoelectric figure of merit among the largest known for a single compound.

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Conducting materials with highly anisotropic Seebeck coefficients (thermoelectric powers [TEPs]) are potentially useful in transverse thermoelectric applications for energy detection and cooling [1–3]. Bulk conductors for which the TEPs in different crystallographic directions have opposite signs and yield a large magnitude for their difference ( $\Delta S \geq 200 \mu\text{V}/\text{K}$ ) are quite rare [3,4]; thus, recent developments have focused on artificial synthesis of stacked bulk materials [1,2] or semiconductor heterostructures [3] to achieve large Seebeck anisotropy. Here we present transport measurements on the quasi-one-dimensional (q1D) metal,  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ , known as “lithium purple bronze” (LiPB), that reveal a surprisingly simple mechanism for extreme Seebeck anisotropy in a bulk conductor. Direct electron transfer between the q1D metallic chains of this material is sufficiently weak that interchain transport above 400 K is predominated by thermal activation of valence band states ( $\sim 0.14$  eV below  $E_F$ ), yielding a large,  $p$ -type interchain Seebeck coefficient that coexists with  $n$ -type metallic behavior confined along the q1D chains. A substantial transverse Peltier effect is demonstrated. These ingredients may exist in other materials or might possibly be engineered to develop transverse thermoelectrics based on a single compound.

A resistivity that is metallic at low temperature and decreases anomalously at high temperatures is a ubiquitous characteristic of transport transverse to the planes or chains of many q2D [5–8] and q1D metals [9–11], respectively. It is generally accepted that this behavior is due to the onset of an additional conduction mechanism in parallel with band transport, possibly related to interplane or interchain defects (e.g., resonant tunneling) [12].

Much less is known about the TEP transverse to the planes or chains of such materials, partly because TEP measurements are difficult to perform in small single

crystals for which the transverse transport directions have very small dimensions (e.g., thin platelet or needlelike habits). In the few compounds where transverse TEP measurements have been reported [13–18], high anisotropy has not been observed.

$\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ , known as “lithium purple bronze” (LiPB), is a low-temperature superconductor ( $T_c \approx 2$  K) first synthesized and studied in the 1980s [19–21]. It has attracted interest more recently for its quasi-one-dimensionality and Luttinger-liquid candidacy [22–28]. Crystal growth [20,25] and transport properties along the chains (crystallographic  $b$  axis) for crystals similar to those discussed here have been presented elsewhere [29,30]. The resistivity anisotropy of LiPB is approximately [31]  $\rho_b:\rho_c:\rho_a = 1:80:1600$ . Single-crystal specimens were oriented by x-ray diffraction and cut or polished into thin rectangular plates with the thinnest dimension (along the  $a$  axis) typically 40–80  $\mu\text{m}$ . The  $bc$ -plane dimensions were typically  $0.4 \times 1.0$  mm with the longest dimension coinciding with the transport axis ( $b$  or  $c$  direction). Electrical contacts were made with Au leads attached with silver epoxy. Current contacts covered the specimen ends and voltage contacts encircled the crystals across both large faces and the sides. For thermopower measurements, specimens were suspended from a Cu heat sink with silver epoxy and affixed with a heater and 25- $\mu\text{m}$ -diameter differential chromel-constantan thermocouple, both attached with stycast epoxy. Separate radiation-shielded vacuum probes were employed for the cryogenic and high- $T$  ( $T > 320$  K) measurements.

Figure 1(a) shows for two crystals the interchain resistivity and TEP,  $\rho_c(T)$  and  $S_c(T)$ , along with the intrachain TEP,  $S_b(T)$ , for two different crystals [29]. Additional  $c$ -axis data for two more crystals can be found in the Supplemental Material [32]. The increase in all three

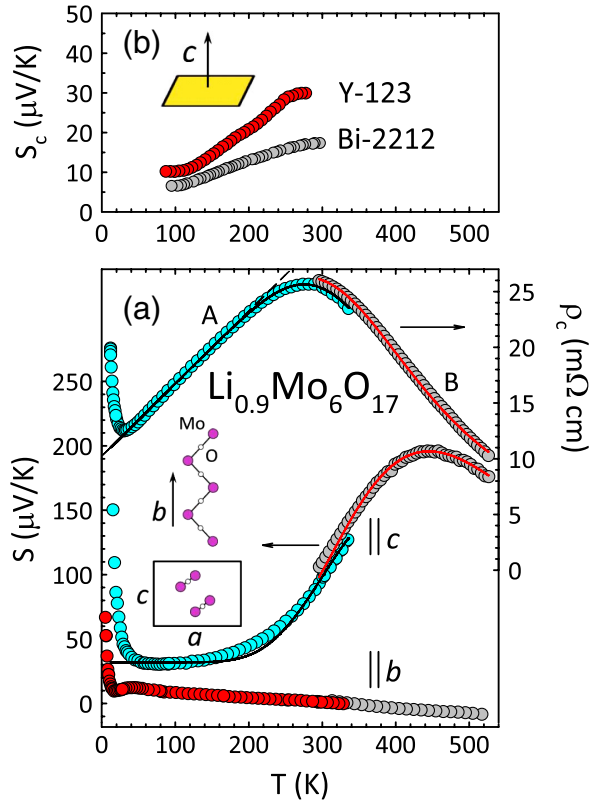


FIG. 1 (color online). (a) LiPB interchain ( $c$ -axis) thermopowers (left ordinate) and resistivities (right ordinate) for two crystals (labeled A and B), and intrachain ( $b$ -axis) thermopowers for two different crystals. Solid curves through the  $c$ -axis data are fits to the parallel conduction model discussed in the text; parameters for the semiconducting component are listed in Table I. Dashed line is a linear-least-squares fit to the low- $T$   $\rho_c(T)$  (see text). Inset: orientation of the crystallographic axes with respect to the q1D Mo-O chains (two per unit cell). (b) interplane ( $c$ -axis) thermopowers for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (Y-123, Ref. [16]) and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  (Bi-2212, Ref. [17]).

coefficients below 30 K has been discussed extensively elsewhere [29] and may be associated with localization, dimensional crossover or the development of unconventional (e.g., electronically-driven) charge density-wave order [24,25]. The focus of the present work is the interchain TEP in the region  $T > 40$  K where it rises sharply with increasing  $T$ , coincident with a deviation of  $\rho_c(T)$  from its low- $T$ , linear- $T$  behavior (dashed line, Fig. 1). The intrachain TEP is linear-in- $T$ , modest in magnitude, and becomes negative above 300 K, consistent with electronlike carrier diffusion as noted previously [29], and extended here to 520 K.

Several features of  $S_c(T)$  are noteworthy. It remains positive throughout the temperature range. In the linear- $T$  regime of  $\rho_c$  ( $40 \text{ K} < T < 140 \text{ K}$ ),  $S_c$  is nearly  $T$  independent at  $\sim 32 \mu\text{V/K}$  and essentially the same for all crystals measured. Near the maximum in  $S_c$  at  $T \approx 440 \text{ K}$ ,  $\Delta S = S_c - S_b \geq 200 \mu\text{V/K}$ . The interchain transport in

LiPB is incoherent, the metallic character of  $\rho_c$  in the lower- $T$  regime likely reflecting the intrachain scattering rate [33], consistent with very weak and indirect interchain hopping [28]. The nearly constant TEP at low- $T$  is a characteristic of narrow-band hopping [34]. As for the increase in  $S_c$  to very large values at higher  $T$ , it is instructive to compare with the behavior found for the interplane ( $c$ -axis) TEPs of the q2D metals [16,17],  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  [Fig. 1(b)]. The TEPs of the latter materials, truncated by the onset of superconductivity at low- $T$ , also rise for  $T \gtrsim 120 \text{ K}$ , but their overall increases ( $\lesssim 20 \mu\text{V/K}$ ) are substantially smaller than for LiPB and a tendency toward saturation is evident at the highest  $T$ . Their upturns are plausibly attributed to the onset of interplane tunneling, though theoretical work [35] has not yet treated the TEP within a model that incorporates resonant tunneling through defects [12]. The upturn in the interchain TEP for LiPB is qualitatively and quantitatively different.

We propose that this difference has its origin in the LiPB band structure which is distinguished from these other compounds by the presence of valence and conduction bands in close energy proximity to  $E_F$  and with sufficient dispersion for interchain momentum so as to become increasingly important for interchain transport with increasing  $T$ . Figure 2 shows the calculated band structure [21,23,27,28] within the  $b^*$ - $c^*$  plane (dispersion along

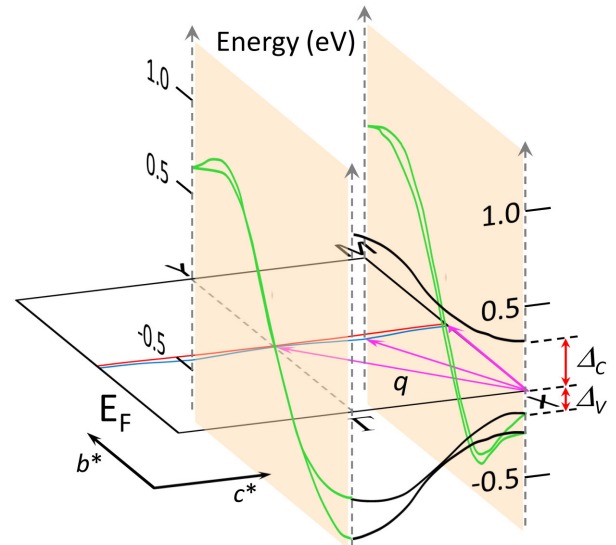


FIG. 2 (color online). Bands along main symmetry directions (curves within the vertical shaded planes along  $b^*$ , dark curves along  $c^*$ ) and projected Fermi surface (curves within the plane labeled “ $E_F$ ”) in the  $b^*$ - $c^*$  plane for LiPB (adapted from Ref. [28]).  $\Delta_V$  and  $\Delta_C$  are excitation energies for valence- and conduction-band states, respectively, dispersing along  $c^*$  near the X point of the Brillouin zone. Indirect transitions between these states and the Fermi surface are possible through thermal excitation and absorption of a phonon with sufficient momentum along  $b^*$  (wave vectors for excitation of valence-band states are represented by arrows from the X point within the  $E_F$  plane).

$a^*$  is negligible). The projected Fermi surface (curves within the plane labeled “ $E_F$ ”) is also shown. Electrons in valence bands dispersing along  $c^*$  (dark curves) can make indirect, interband transitions to states at  $E_F$  through thermal excitation ( $\Delta_V$ , Fig. 2) and absorption of phonons with sufficient momenta ( $q$ ) along the  $b^*$  direction (arrows from the  $X$  point within the  $E_F$  plane, Fig. 2). Similarly, electrons at  $E_F$  in states dispersing along  $b^*$  can be thermally excited ( $\Delta_C$ ) to the lowest-lying interchain conduction band above  $E_F$  near the  $X$  point by absorbing phonons with opposite momenta. These phonons, with momenta  $q \lesssim \sqrt{2\pi}/2b$  and energies  $\hbar qv \lesssim 6$  meV (assuming a dispersionless, acoustic phonon with velocity  $v = 3$  km/s), will be excited in large numbers at room temperature and above. The activation energies, from averaging the various band structure calculations, are  $\Delta_V = 0.16$  and  $\Delta_C = 0.20$  eV. With  $\Delta_V < \Delta_C$  a  $p$ -type thermopower should result.

These observations motivate an interpretation of the interchain transport in LiPB that reflects parallel conduction through bandlike states ( $lo$ ), predominant at  $T \lesssim 140$  K, and a thermally activated, semiconductor contribution ( $hi$ ), predominant at  $T > 300$  K,

$$\begin{aligned}\sigma &= \sigma^{lo} + \sigma^{hi} \\ S &= (\sigma^{lo}/\sigma)S^{lo} + (\sigma^{hi}/\sigma)S^{hi}.\end{aligned}\quad (1)$$

The low- $T$  TEP is taken as  $S^{lo} = 32 \mu\text{V}/\text{K}$ , independent of  $T$  as motivated by the  $S_c(T)$  data, and  $\sigma^{lo} = 1/(A + BT)$  from linear-least-squares fits (dashed lines, Fig. 1) to the  $\rho_c(T)$  data in the range  $40 \text{ K} \leq T \leq 140 \text{ K}$ . For the high- $T$  contribution we first tried a single semiconductor component to minimize the number of free parameters:  $\sigma^{hi} = C \exp(-E_\sigma/k_B T)$  and  $S^{hi} = (k_B/e|)(E_S/k_B T + D)$ , where  $C$  and  $D$  are constants and  $E_\sigma$  and  $E_S$  are activation energies. The solid curves through the  $\rho_c(T)$  and  $S_c(T)$  data (Fig. 1) demonstrate the agreement achieved with Eq. (1) throughout the range  $T \geq 40$  K using these simple forms for  $\sigma^{hi}$  and  $S^{hi}$  (parameter values are listed in Table I). The discrepancy between the computed and measured TEPs in the transition region (near 200 K) may reflect our neglect of a tunneling contribution, like that observed for the cuprates [Fig. 1(b)], but has negligible impact on the fitting at high  $T$  if, as in the latter materials,

TABLE I. Fitting parameters for the semiconductor, high- $T$  component ( $hi$ ) of the parallel conduction model discussed in the text.

Specimen	$C(\Omega^{-1} \text{ cm}^{-1})$	$E_\sigma$ (eV)	$D$	$E_S$ (eV)
A	$2.40 \times 10^3$	0.155	-3.00	0.220
B	$2.41 \times 10^3$	0.159	-2.90	0.250
C	$1.60 \times 10^3$	0.146	-2.68	0.241
D	$1.85 \times 10^3$	0.146	-2.15	0.241

this contribution adds a small constant. The average activation energies found for the four crystals (with s.d. uncertainties) are  $E_\sigma = 0.15 \pm 0.01$  and  $E_S = 0.24 \pm 0.01$  eV.

The observation  $E_S > E_\sigma$  is incompatible with single-band ( $E_S = E_\sigma$ ) and intrinsic two-band ( $E_S \leq E_\sigma$ ) semiconductor conduction for the high- $T$  component, but is naturally explained [32], consistent with the band structure, if both valence and conduction band states are excited with differing activation energies,  $\Delta_V$  and  $\Delta_C$ . Analyzing the data with a three-component model, low- $T$  metallic and two high- $T$  semiconducting contributions [32], yields average energies  $\Delta_V \approx 0.14$  and  $\Delta_C \approx 0.23$  eV, i.e., nearly the same as  $E_\sigma$  and  $E_S$  in the two-component model. The interband transitions evidently serve as the predominant mechanism for interchain ( $c$ -axis) transport above 400 K where the semiconducting components represent more than 50% of the total conductivity [32]. In this regime LiPB thus behaves simultaneously as a  $p$ -type semiconductor and  $n$ -type metal along mutually perpendicular directions, leading to its high Seebeck anisotropy.

To test for the transverse Peltier effect, a rectangular specimen ( $x \times y \times z = 1.9 \times 0.9 \times 0.2 \text{ mm}^3$ ) with its long axis at an angle  $\alpha = 32^\circ$  to the  $b$  axis (Fig. 3, inset), was mounted with one edge thermally anchored to a copper heat sink in vacuum; current was applied along the  $x$  direction. Cooling or warming at the free edge of the crystal, monitored by a differential thermocouple with junctions along the  $y$  direction (separation  $d \approx 0.4$  mm), was induced by forward or reverse current, respectively, and was linear in the current (Fig. 3). The averaged temperature gradient,  $dT/dy = [\Delta T(I+) - \Delta T(I-)]/2d$ , is shown as

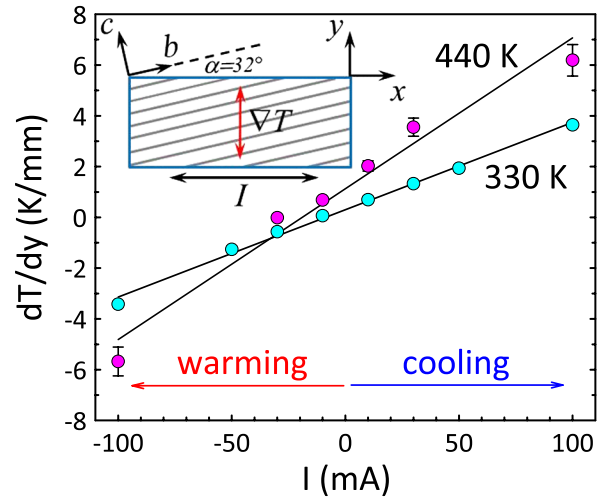


FIG. 3 (color online). Current dependence of the transverse Peltier-induced temperature gradient for a LiPB crystal at  $T = 330$  and  $440$  K. Error bars reflect uncertainty due to slow oscillations in the Cu block temperature ( $\leq 0.1$  K), particularly at the highest  $T$ . The inset shows the orientation of current and heat flow relative to the specimen ( $x$ - $y$ ) and crystallographic ( $b$ - $c$ ) axes.



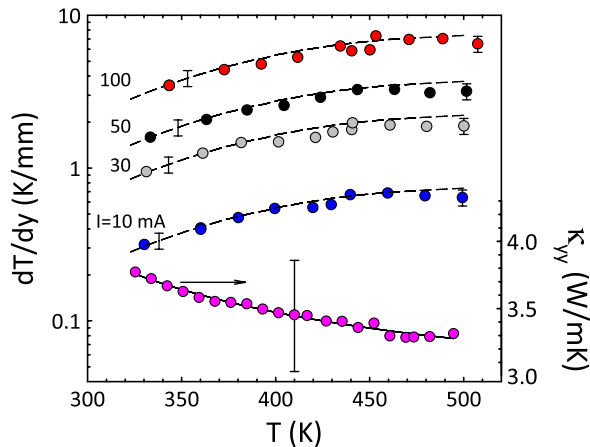


FIG. 4 (color online).  $dT/dy$  (averaged for  $+$ ,  $-$  current) vs the average specimen temperature at fixed applied currents (left ordinate), and  $\kappa_{yy}(T)$  (right ordinate). The dashed curves are computed (see text) using  $\kappa_{yy}$  and  $\Delta S$  interpolated from Fig. 1(a). Error bars for the data and computed curves (12%) are determined by uncertainty in the thermocouple junction separation. The  $\kappa_{yy}$  data were corrected for radiation losses and conduction through the leads estimated from direct measurements on similar specimens suspended from their leads. These corrections amounted to 6% at 300 K and 30% at 500 K. The solid curve is a guide to the eye.

a function of the average specimen temperature in Fig. 4 for fixed values of the current. The dashed curves in Fig. 4 were computed using  $\Delta S$  [interpolated from data for crystal B, Fig. 1(a)], the transverse thermal conductivity ( $\kappa_{yy}$ ) measured in a separate experiment with a heater attached to the free end of the specimen (Fig. 4, right ordinate), and the heat flux equation [2],  $dT/dy = (TS_{xy}/\kappa_{yy})j$ , where  $S_{xy} = (1/2)\Delta S \sin(2\alpha)$  and  $j$  is the current density. This expression ignores a joule heating term (varying as  $j^2$ ), justified by the linearity of  $dT/dy$  with current noted above. Because LiPB has a rather low thermal conductivity along the  $c$  axis [30], the transverse thermoelectric figure of merit is among the largest known for a single-phase material [36],  $Z_{xy}T = TS_{xy}^2/(\rho_{xx}\kappa_{yy}) \approx 0.024 \pm 0.007$  at 450 K [37].

LiPB may itself prove useful in converting waste heat to electrical power or in energy detection. Given that the features underlying its extreme Seebeck anisotropy appear fairly generic – low-dimensional, metallic electronic structure and dispersing bands for the transverse direction in close proximity to  $E_F$ —the larger implication from this study is that other materials with such properties may yet to be revealed.

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- [1] H. J. Goldsmid, *J. Electron. Mater.* **40**, 1254 (2011).
- [2] C. Reitmaier, F. Walther, and H. Lengfellner, *Appl. Phys. A* **99**, 717 (2010).
- [3] C. Zhou, S. Birner, Y. Tang, K. Heinselman, and M. Grayson, *Phys. Rev. Lett.* **110**, 227701 (2013).
- [4] K. P. Ong, D. J. Singh, and P. Wu, *Phys. Rev. Lett.* **104**, 176601 (2010); K. P. Ong, J. Zhang, John S. Tse, and Ping Wu, *Phys. Rev. B* **81**, 115120 (2010).
- [5] C. Uher, R. L. Hockey, and E. Ben-Jacob, *Phys. Rev. B* **35**, 4483 (1987).
- [6] N. Hussey, A. Mackenzie, J. Cooper, Y. Maeno, S. Nishizaki, and T. Fujita, *Phys. Rev. B* **57**, 5505 (1998).
- [7] I. Terasaki, Y. Sasago, and K. Uchinokura, *Phys. Rev. B* **56**, R12685 (1997).
- [8] J. G. Analytis, A. Ardavan, S. J. Blundell, R. L. Owen, E. F. Garman, C. Jeynes, and B. J. Powell, *Phys. Rev. Lett.* **96**, 177002 (2006).
- [9] N. E. Hussey, M. N. McBrien, L. Balicas, J. S. Brooks, S. Horii, and H. Ikuta, *Phys. Rev. Lett.* **89**, 086601 (2002).
- [10] Z. Mao, T. He, M. Rosario, K. Nelson, D. Okuno, B. Ueland, I. Deac, P. Schiffer, Y. Liu, and R. Cava, *Phys. Rev. Lett.* **90**, 186601 (2003).
- [11] W. Kobayashi, *Phys. Rev. B* **79**, 155116 (2009).
- [12] D. B. Gutman and D. L. Maslov, *Phys. Rev. B* **77**, 035115 (2008); *Phys. Rev. Lett.* **99**, 196602 (2007).
- [13] M. Stordeur and W. Heiliger, *Phys. Status Solidi (b)* **78**, K103 (1976).
- [14] C. Uher, *Phys. Rev. B* **25**, 4167 (1982).
- [15] E. S. Choi, H. Y. Kang, Y. J. Jo, J. Yeom, and W. Kang, *Synth. Met.* **120**, 1069 (2001).
- [16] J. W. Cochrane, A. Hartmann, and G. J. Russell, *Physica (Amsterdam)* **265C**, 135 (1996).
- [17] T. Fujii, I. Terasaki and A. Matsuda, *Physica (Amsterdam)* **408C–410C**, 674 (2004).
- [18] G. D. Tang, H. H. Guo, T. Yang, D. W. Zhang, X. N. Xu, L. Y. Wang, Z. H. Wang, H. H. Wen, Z. D. Zhang, and Y. W. Du, *Appl. Phys. Lett.* **98**, 202109 (2011).
- [19] M. Greenblatt, *Chem. Rev.* **88**, 31 (1988).
- [20] W. H. McCarroll and M. J. Greenblatt, *J. Solid State Chem.* **54**, 282 (1984).
- [21] M. H. Whangbo and E. Canadell, *J. Am. Chem. Soc.* **110**, 358 (1988).
- [22] L. Dudy, J. D. Denlinger, J. W. Allen, F. Wang, J. He, D. Hitchcock, A. Sekiyama, and S. Suga, *J. Phys. Condens. Matter* **25**, 014007 (2013) and references therein.
- [23] Z. S. Popović and S. Satpathy, *Phys. Rev. B* **74**, 045117 (2006).
- [24] J. Choi, J. Musfeldt, J. He, R. Jin, J. Thompson, D. Mandrus, X. Lin, V. Bondarenko, and J. Brill, *Phys. Rev. B* **69**, 085120 (2004).
- [25] C. A. M. dos Santos, B. D. White, Y. K. Yu, J. J. Neumeier, and J. A. Souza, *Phys. Rev. Lett.* **98**, 266405 (2007).
- [26] J. Merino and R. H. McKenzie, *Phys. Rev. B* **85**, 235128 (2012).
- [27] T. Jarlborg, P. Chudzinski, and T. Giamarchi, *Phys. Rev. B* **85**, 235108 (2012); P. Chudzinski, T. Jarlborg, and T. Giamarchi, *ibid.* **86**, 075147 (2012).
- [28] M. Nuss and M. Aichhorn, *Phys. Rev. B* **89**, 045125 (2014).

- [29] See J. L. Cohn, P. Boynton, J. S. Trivino, J. Trastoy, B. D. White, C. A. M. dos Santos, J. J. Neumeier, *Phys. Rev. B* **86**, 195143 (2012) and references therein.
- [30] J. L. Cohn, B. D. White, C. A. M. dos Santos, and J. J. Neumeier, *Phys. Rev. Lett.* **108**, 056604 (2012).
- [31] J.-F. Mercure, A. F. Bangura, X. Xu, N. Wakeham, A. Carrington, P. Walmsley, M. Greenblatt, and N. E. Hussey, *Phys. Rev. Lett.* **108**, 187003 (2012).
- [32] For additional data and analysis, see Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.112.186602>, which includes Refs. [38,39].
- [33] N. Kumar and A. M. Jayannavar, *Phys. Rev. B* **45**, 5001 (1992).
- [34] B. Fisher and M. Fibich, *Phys. Rev. B* **37**, 2820 (1988).
- [35] T. W. Silk, I. Terasaki, T. Fujii, and A. J. Schofield, *Phys. Rev. B* **79**, 134527 (2009).
- [36] Other materials with large  $Z_{xy}T$  include  $\text{CsBi}_4\text{Te}_6$  and  $\text{ReSi}_{1.75}$ . D.-Y. Chung, S. D. Mahanti, W. Chen, C. Uher, and M. G. Kanatzidis, *Mater. Res. Soc. Symp. Proc.*, **793**, S6.1.1 (2004); J-J Gu, K. Kuwabara, K. Tanaka, H. Inui, M. Yamaguchi, A. Yamamoto, T. Ohta, and H. Obara, *Mater. Res. Soc. Symp. Proc.* **753**, BB6.10.1 (2003); Y. Tang, B. Cui, C. Zhou, and M. Grayson (unpublished).
- [37] Since  $\rho_{xx}$  was not measured for the Peltier crystal, we computed it using the comprehensive results for  $\rho_b$  from N. Wakeham, A. F. Bangura, X. Xu, J.-F. Mercure, M. Greenblatt, and N. E. Hussey [*Nat. Commun.* **2**, 396 (2011)], linearly extrapolated to 450 K, and the  $\rho_c$  data for crystal B [Fig. 1(a)]. Using the appropriate tensor expressions (Ref. 2), this gave  $\rho_{xx} \approx 4.62 \times 10^{-5} \Omega \text{ m}$ . The linearity in  $\Delta T(I)$  (Fig. 3) implies that the actual  $\rho_{xx}$  for our specimen cannot be much larger than this value (we estimate not by more than 30%); a deviation from linearity (suppressed  $\Delta T$ ) that is quadratic in  $j$  would be the signature of joule heating from the second term in the heat flux equation [2].
- [38] H. Fritzsche, *Solid State Commun.* **9**, 1813 (1971).
- [39] V. A. Johnson and K. Lark-Horovitz, *Phys. Rev.* **92**, 226 (1953).