Anomalous thermal transport and strong violation of Wiedemann-Franz law in the critical regime of a charge density wave transition

Erik D. Kountz,1,2,3 Jiecheng Zhang,1,2,3 Joshua A. W. Straquadine,1,2,3 Anisha G. Singh,1,2,4 Maja D. Bachmann,1,2,4 Ian R. Fisher,1,2,4 Steven A. Kivelson,1,2,3 and Aharon Kapitulnik1,2,3,4

1Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA
2Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California 94305, USA
3Department of Physics, Stanford University, Stanford, California 94305, USA
4Department of Applied Physics, Stanford University, Stanford, California 94305, USA

(Received 12 March 2021; revised 24 June 2021; accepted 8 December 2021; published 22 December 2021)

DOI: 10.1103/PhysRevB.104.L241109

Unlike the standard paradigm [1,2], in more than one spatial dimension due to imperfect nesting, charge density wave (CDW) order (unlike superconducting order) only emerges for interactions greater than a critical strength. Generically, the “mechanism” involves strong electron-electron and electron-phonon interactions. Strong coupling is particularly reflected in large ratios of the induced gap to “mechanism” involves strong electron-electron and electron-phonon interactions. Strong coupling is particularly reflected in large ratios of the induced gap to
by a broad maximum and subsequent low-temperature drop as previously discussed [11]. Conversely, the critical anomaly in $\rho^c$ at $T_{CDW1}$ is much weaker, and neither component shows any clear nonanalyticity at $T_{CDW2}$. In contrast, the thermal diffusivity has a large sharp decrease at $T_{CDW1}$ along both the $a$ and $c$ directions, followed by a faster recovery along the $c$ direction. Also evident from Fig. 2(a), the thermal diffusivity more closely resembles the temperature derivative of the resistivity. (iii) Thermal diffusivity in both directions increases markedly below $T_{CDW2}$, which through suppression of this effect by weak Pd intercalation are argued to be electronic in origin (Fig. 3).

ErTe$_3$ samples were grown using a Te self-flux technique, ensuring melt purity, and producing large crystals with a high degree of structural order [12]. Being air sensitive, ErTe$_3$ must be stored in an oxygen and moisture-free environment. Crystal orientation was determined with x-ray diffraction (XRD). Thermal diffusivity and differential reflectivity ($dR/dT$) were measured using a photothermal microscope [13]. Details of specific heat, resistivity, and thermal diffusivity measurements are described in the Supplemental Material (SM) [14]. Figure 1(a) shows specific heat of two ErTe$_3$ crystals over a wide temperature range. The data closely follow the Debye approximation with $\theta_D \approx 160$ K, including above and below both CDW transitions saturating at the high-temperature Dulong-Petit value. Previous measurements of the specific-heat anomaly at $T_{CDW1}$ [10] find $\Delta c_p \approx 0.0144$ J/cm$^3$K, below the resolution of the present measurements, and surprisingly of “normal magnitude” given the large value of $2\Delta_f/\kappa_B T_{CDW1} \approx 15$ inferred from angle-resolved photoemission spectroscopy measurements [4]. By contrast, both CDW transitions produce large anomalies in the thermal diffusivity data on a same-batch crystal as shown in Fig. 2(a).
Particularly, at $T_{CDW1}$ diffusivity along both axes drops over a third from $\sim0.21$ to $\sim0.14$ cm$^2$/s.

Figure 1(b) shows resistivity data on same-batch crystals (see the SM [14] for determination of geometrical factors [16]). The trend in the data is similar to previously measured RT$_3$ crystals [17], particularly ErTe$_3$ [6,16], featuring a strong anomaly along the $a$ axis (perpendicular to the primary CDW direction) at $T_{CDW1}$ and only a weak wiggle along the $c$ axis near $T_{CDW2}$. In contrast, thermal diffusivity along both axes sharply decreases at $T_{CDW1}$ and gradually increases below $T_{CDW2}$ [Fig. 2(a)]. However, these thermal diffusivity anomalies resemble more the features of the derivative of the resistivity $d\rho/dT$ as seen in Fig. 2(b). Similarly, the magnitude (see the SM [14]) of the temperature derivative of the reflectivity $dR/dT$ at $h\nu \approx 1.5$ eV (820-nm wavelength) shows a large sharp decrease at $T_{CDW1}$, although here no anomaly is visible at $T_{CDW2}$.

Figure 3 demonstrates the effect of purposefully introduced weak disorder on the temperature dependence of thermal diffusivity. Focusing on the $a$ axis (no noticeable effects appear in the $c$ direction for this weak disorder [7]), we compare the diffusivity of Pd$_{0.005}$ErTe$_3$ to pure ErTe$_3$ [Fig. 2(a)]. Although $T_{CDW1}$ is suppressed to 250 K, the sharp drop in diffusivity is not affected. However, below $T_{CDW2}$ (here $\sim130$ K) there is a striking intercalation induced difference; the pronounced upturn of the diffusivity in the pure material vanishes.

ErTe$_3$ resistivity was measured before [16,17] and the temperature dependence understood in terms of the material band structure [11]. Specifically, when the primary CDW forms along the $c$ axis, the resistivity start increasing along the perpendicular $a$ direction. Likewise, when the secondary CDW forms along the $a$ axis, there is a larger change in $d\rho/dT$ along the $c$ direction.

In a photothermal measurement, we extract thermal transport information by analyzing the phase delay in the change of the heating spot guarantees very small heat and thermal diffusivity as is shown in Fig. 4 together with a best-fit guide to the eye curve. Assuming that WF law holds, we calculate the electronic thermal conductivity from the

$$\Delta R(v\tau) \text{ (e.g., by extending the Hagen-Rubens relation to near-IR corresponding to our probing light $R(v) \approx 1 - 2/\sqrt{\rho}$ with $\rho$ as the Drude resistivity); thus, } dR/dT \propto \sqrt{\kappa}/dT. \text{ In a seminal work, Fisher and Langer [9] showed that the leading (perturbative) effect of scattering of conduction electrons by classical (i.e., approximately static) critical modes leads to } d\rho/dT \propto c_{CDW}, \text{ where $c_{CDW}$ is the specific heat associated with critical fluctuations near a finite-$T$ phase transition. Examining the temperature derivative of the resistivity, particularly the } a \text{ direction, indeed, reveals what appears to be a broadened discontinuity at } T_{CDW1}, \text{ similar to the behavior of the reflectivity. This mean-field-like form agrees with the shape of the anomaly observed in direct measurements of specific heat [10,20], although the relative strength of the anomaly is much weaker in those measurements [essentially invisible in Fig. 1(a)]. Despite similar behaviors at } T_{CDW1}, \text{ at lower temperatures, } d\rho/dT \text{ and } dR/dT \text{ exhibit substantially different thermal evolutions. The former, but not the latter, recovers rapidly to values comparable to the CDW transition [21]. Furthermore, near } T_{CDW2}, \text{ both } d\rho/dT \text{ shows a relatively weak but still clear critical anomaly, whereas the effect of the second CDW transition is difficult to discern in } dR/dT. \text{ More insight between electrical and thermal transports is obtained using their respective Einstein relations, }

$$\sigma = \chi_{el}D_{el}; \quad \kappa = c_pD_Q,$$

with $\chi_{el}$ as the electronic compressibility, $c_p$ as the total specific heat, $D_{el}$ and $D_Q$ as the electronic and heat diffusivities, respectively. Although $\chi_{el}$ is a response function of only the electron system, the specific heat of the material, particularly at high temperatures, may be lattice dominated. A simple kinetic approach where electrons and phonons transport heat in parallel channels implies $\kappa = \kappa_{el} + \kappa_{gh} = c_{el}D_{el} + c_{gh}D_{gh}$, where $c_{el}$ and $c_{gh}$ are the electronic and lattice specific heats and $D_{el}$ and $D_{gh}$ are the respective diffusivities.

The total thermal conductivity along the $a$ and $c$ axes can be calculated following Eq. (1) and using the measured specific heat and thermal diffusivity as is shown in Fig. 4 together with a best-fit guide to the eye curve. Assuming that WF law holds, we calculate the electronic thermal conductivity from the
resistivity $\kappa_{el} = \frac{L_0T}{\rho(T)}$, also shown in Fig. 4. This allows us to define a “nonelectronic” contribution $\Delta\kappa \equiv \kappa - \kappa_{el}$. Although it is conventional to identify $\Delta\kappa$ with an independent phonon contribution $\Delta\kappa \leftrightarrow \kappa_{ph}$, it is apparent (discussed below) this is not plausible over much of the temperature range and especially in a region immediately below $T_{CDW1}$ (gray bar in Fig. 4).

We first consider room-temperature thermal conductivity, above the CDW transitions. The value of the total thermal conductivity is very high compared to other chalcogenide-based CDW materials: $\kappa = 0.06$ W/cm K for TaSe$_3$ [22], 0.07 W/cm K for NbSe$_3$ [23], 0.05 W/cm K for (TaSe$_4)_2$I [24], 0.1 W/cm K for 2H-TaSe$_2$ [25], 0.035 W/cm K for HfTe$_5$ [26], or 0.08 W/cm K at 370 K for 1T-TaS$_2$ [25]. By contrast, ErTe$_3$ exhibits $\sim$0.33 W/cm K at room temperature, more than three and up to ten times larger thermal conductivity than those compounds. However, using WF law and our measured resistivity to evaluate the electronic thermal conductivity, we obtain a value of $\Delta\kappa$ comparable in magnitude to these materials. Considering the much larger resistivities of these other materials, WF analysis yields a relative $\kappa_{el}/\kappa$ of around 20% to 25% for most compounds, reaching 45% for NbSe$_3$ nanowires [23]. In all cases $\kappa$ is very weakly $T$ dependent in this range of temperature. One naturally identifies $\Delta\kappa \approx \kappa_{ph}$ as an essentially independent phonon contribution to the thermal conductivity—as commonly assumed.

WF law is expected to work at temperatures comparable and above the Debye temperature ($\theta_D$), relying on quasielastic electron-phonon scattering applicable for modes whose characteristic frequencies, $\omega \ll k_B T/h$ and all nearly critical modes due to critical slowing down. Thus, analysis of the CDW transition region, particularly, the anomaly at $T_{CDW1}$, which is $\sim$100 K above $\theta_D$, implies a catastrophic breakdown of the WF approach. Although based on WF law, one would expect the critical anomaly in the total thermal conductivity to be weak similar to the resistivity, it is, in fact, pronounced and resembles the behavior of $d\rho/dT$. (Note the relatively weak specific heat anomaly at $T_{CDW1}$, primarily because the high transition temperature where the specific heat is already in the Dulong-Petit regime). More dramatically, if we use the WF law to subtract an electronic contribution to $\kappa$ in the critical regime, we would be forced to conclude that the lattice contribution $\Delta\kappa$ mysteriously vanishes, at least, within $\sim$30° below $T_{CDW1}$—indicated by the gray bar in Fig. 4. This sharp decrease in $\Delta\kappa$ in ErTe$_3$ and the strong violation of the WF law is quite different from other one-dimensional CDW materials including Lu$_2$Ir$_3$Si$_10$ [27], LaAgSb$_4$ [28], and CuTe [29] where the WF is followed through $T_{CDW}$ irrespective whether the electrical resistivity changes gradually or sharply. We know of no plausible physical mechanism that could produce such an effect. However, if inelastic scattering of the electrons from the critical modes plays a role in the breakdown of the WF law, this would be highly anomalous and suggests an unexpectedly intimate connection between the electronic and lattice degrees of freedom.

Below $\sim$240 K, $\Delta\kappa$ reaches $\sim$0.05 W/cm K, common to this type of materials, and, thus, again can be loosely interpreted as parallel lattice contribution. Using simple kinetic theory, our measured specific heat and typical longitudinal sound velocity of $\sim 2.8 \times 10^5$ cm/s [10,20], we obtain a mean free path of $\sim 35$ Å at $T = T_{CDW2}$, reduced from $\sim 80$ Å above $T_{CDW1}$. Although below the primary CDW transition the phonon mean free path might be expected to increase reflecting reduced phonon-electron scattering, CDW fluctuations in the transition region and CDW formation below that temperature could be additional sources of phonon scattering. (By contrast, in other chalcogenide-based CDW materials $\kappa$ is nearly constant with a slight tendency to increase with decreasing $T$ over the same temperature range.) Over the same temperature range, the total and electronic thermal conductivities reach an anisotropic value of $\kappa' \kappa'' \approx \kappa'' \approx 1.3$, reflecting the effect of the primary CDW transition at $T_{CDW1}$.

Interestingly, this anisotropy is only weakly reduced below the secondary CDW transition at $T_{CDW2}$ where the primary effect is an increase in all components of thermal transport. Although the increase in the putative lattice part below $T_{CDW2}$ could be from further gapping of electronic states that decrease the phonon-electron scattering rate, the electronic increase in thermal conductivity simply reflects the increase in the mean free path of the remaining itinerant electrons. We check this hypothesis by introducing additional electron disorder scattering with a small concentration of intercalated Pd atoms ($\lesssim 1\%$), which does not markedly change the carrier density [6]. See the SM for similar response in $\Delta\kappa$ when there is $\sim 0.3\%$ Pd intercalation of the material Pd$_{0.003}$ErTe$_3$ [14].

Figure 3 shows the effect of $\sim 0.3\%$ Pd intercalation on the thermal diffusivity. Note the decrease in the primary CDW transition that follows the phase diagram in Ref. [6]. Focusing on $\alpha$-axis transport where disorder shows a strong effect on the electronic structure [7], thermal diffusivity in Fig. 3 did not change much below $T_{CDW1}$, but the characteristic increase below $T_{CDW2}$ is missing, consistent with the increased scattering observed in resistivity [Fig. 1(b)]. Although this points to an electronic effect, incomplete gapping of electronic states may also affect phonon-electron scattering [7,8].

Often, transport properties of metals are successfully understood based on the response of weakly interacting elementary excitations—fermionic quasiparticles and bosonic phonons. In past decades, various transport regimes in certain “highly correlated” materials have been identified where the validity of this approach has been questioned. However, it remains highly controversial to what extent conventional quasiparticle ideas can be extended without fundamental changes in approach to strongly interacting regimes where the quasiparticle identity is “marginally” maintained, or if entirely new paradigms (e.g., some form of “non-Fermi liquid” or novel fractionalized quasiparticles) are needed.

One approach to attack this problem has been to investigate the breakdown of quasiparticle picture near a quantum critical point. However, even at classical (finite-$T$) critical points, the existence of nontrivial critical exponents describing behavior in the critical regime provides clear evidence that critical modes themselves cannot have a quasiparticle description. None-the-less, often, where, e.g., Fisher-Langer theory gives good account of transport anomalies, a treatment involving well-defined conduction electrons (and, presumably, phonons) weakly scattered by critical modes implies that the conventional mechanism of transport theory applies even in the critical regime.
The dramatic failure of this approach to adequately describe thermal transport in ErTe₃, most dramatically in the ∼30 K range below T_{CDW₁}, may potentially indicate a simpler context to study the quasiparticle paradigm breakdown. The discrepancies in the critical dependences of thermal conductivity and resistivity in this regime imply a complete breakdown of the WF law, the existence of independent electronic quasiparticles and phonon modes or both. Indeed, the observed behavior may more adequately be described as a strongly coupled electron-phonon critical "soup."

CDW formation is a common phenomenon in quasi-low-dimensional materials, arising from a variety of mechanisms. Although thermal transport measurements have not been widely performed for such materials, they exist for many well-known canonical examples, and in no cases has such dramatic violation of the WF law been deduced. This raises associated questions as why the effect should be so pronounced in this particular material system given the ubiquity of CDW compounds (for a recent survey of CDW systems, see, e.g., Ref. [30]). A wider survey of related materials might reveal that this effect is not unique to the rare-earth tritellurides, yet for now ErTe₃ occupies a unique position among known CDW compounds and presents an entirely new opportunity to explore unconventional transport properties of strongly interacting metals.

We would like to thank A. Fang for helpful discussions. This work was supported by the Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-76SF00515. The photothermal apparatus was built using a Grant from the Gordon and Betty Moore Foundation through Emergent Phenomena in Quantum Systems (EPiQS) Initiative Grant No. GBMF4529. J.A.W.S. was supported, in part, by an ABB Stanford Graduate Fellowship. A.G.S. was supported, in part, by an NSF Graduate Research Fellowship (Grant No. DGE-1656518). M.D.B. acknowledges partial support from the Swiss National Science Foundation under Project No. P2SKP2_184069, as well as from the Stanford Geballe Laboratory for Advanced Materials (GLAM) Postdoctoral Fellowship program. XRD measurements were performed at the Stanford Nano Shared Facilities (SNSF), supported by the National Science Foundation under Award No. ECCS-2026822.

[1] R. E. Peierls, Quantum Theory of Solids (Clarendon, Oxford, 1955).
[2] H. Fröhlich, On the theory of superconductivity: The one-dimensional case, Proc. R. Soc. A 223, 296 (1954).
[3] F. Pfunder, P. Lerch, J.-H. Chu, H.-H. Kuo, I. R. Fisher, and L. Degiorgi, Temperature dependence of the excitation spectrum in the charge-density-wave ErTe₃ and HoTe₃ systems, Phys. Rev. B 81, 195110 (2010).
[4] R. G. Moore, V. Brouet, R. He, D. H. Lu, N. Ru, J.-H. Chu, I. R. Fisher, and Z.-X. Shen, Fermi surface evolution across multiple charge density wave transitions in ErTe₃, Phys. Rev. B 81, 073102 (2010).
[5] B. F. Hu, B. Cheng, R. H. Yuan, T. Dong, A. F. Fang, W. T. Guo, Z. G. Chen, P. Zheng, Y. G. Shi, and N. L. Wang, Optical study of the multiple charge-density-wave transitions in ErTe₃, Phys. Rev. B 84, 155132 (2011).
[6] J. A. W. Straquadine, F. Weber, S. Rosenkranz, A. H. Said, and I. R. Fisher, Suppression of charge density wave order by disorder in Pd-intercalated ErTe₃, Phys. Rev. B 99, 235138 (2019).
[7] A. Fang, J. A. W. Straquadine, I. R. Fisher, S. A. Kivelson, and A. Kapitulnik, Disorder-induced suppression of charge density wave order: Stm study of pd-intercalated ErTe₃, Phys. Rev. B 100, 235446 (2019).
[8] A. Fang, A. G. Singh, J. A. W. Straquadine, I. R. Fisher, S. A. Kivelson, and A. Kapitulnik, Robust superconductivity intertwined with charge density wave and disorder in pd-intercalated ErTe₃, Phys. Rev. Research 2, 043221 (2020).
[9] M. E. Fisher and J. S. Langer, Resistive Anomalies at Magnetic Critical Points, Phys. Rev. Lett. 20, 665 (1968).
[10] M. Saint-Paul, G. Remenyi, C. Guttin, P. Lejay, and P. Monceau, Thermodynamic and critical properties of the charge density wave system ErTe₃, Physica B 504, 39 (2017).
[11] A. A. Sinchenko, P. D. Grigoriev, P. Lejay, and P. Monceau, Spontaneous Breaking of Isotropy Observed in the Electronic Transport of Rare-Earth Tritellurides, Phys. Rev. Lett. 112, 036601 (2014).
[12] N. Ru and I. R. Fisher, Thermodynamic and transport properties of YTe₃, LaTe₃, and CeTe₃, Phys. Rev. B 73, 033101 (2006).
[13] J. Zhang, E. M. Levenson-Falk, B. J. Ramshaw, D. A. Bonn, R. Liang, W. N. Hardy, S. A. Hartnoll, and A. Kapitulnik, Anomalous thermal diffusivity in underdoped YBa₂Cu₃O₆+δ, Proc. Natl. Acad. Sci. USA 114, 5378 (2017).
[14] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.104.L241109 for details of specific heat, resistivity, and thermal diffusivity measurements which includes Ref. [15].
[15] S. Mumford, T. Paul, E. Kountz, and A. Kapitulnik, Journal of Applied Physics 128, 175105 (2020).
[16] P. Walmsley and I. R. Fisher, Determination of the resistivity anisotropy of orthorhombic materials via transverse resistivity measurements, Rev. Sci. Instrum. 88, 043901 (2017).
[17] N. Ru, C. L. Condon, G. Y. Margulis, K. Y. Shin, J. Laverock, S. B. Dugdale, M. F. Toney, and I. R. Fisher, Effect of chemical pressure on the charge density wave transition in rare-earth tritellurides RTe₃, Phys. Rev. B 77, 035114 (2008).
[18] J. T. Fanton, D. B. Mitzi, A. Kapitulnik, B. T. Khuri-Yakub, G. S. Kino, D. Gazit, and R. S. Feigelson, Photothermal measurements of high tc superconductors, Appl. Phys. Lett. 55, 598 (1989).
[19] Z. Hua, H. Ban, and D. H. Hurley, The study of frequency-scan photothermal reflectance technique for thermal diffusivity measurement, Rev. Sci. Instrum. 86, 054901 (2015).
[20] M. Saint-Paul and P. Monceau, Phenomenological approach of the thermodynamic properties of the charge density wave systems, Philos. Mag. 101, 598 (2021).
[21] N. Lazarević, Z. V. Popović, R. Hu, and C. Petrovic, Evidence of coupling between phonons and charge-density waves in ErTe$_3$, Phys. Rev. B 83, 024302 (2011).

[22] B. Zawilski, R. Littleton IV, N. Lowhorn, and T. Tritt, Observation of a two level thermal conductivity in the low-dimensional materials, Solid State Commun. 150, 1299 (2010).

[23] L. Yang, Y. Tao, J. Liu, C. Liu, Q. Zhang, M. Akter, Y. Zhao, T. T. Xu, Y. Xu, Z. Mao, Y. Chen, and D. Li, Distinct signatures of electron-phonon coupling observed in the lattice thermal conductivity of NbSe$_3$ nanowires, Nano Lett. 19, 415 (2019).

[24] R. S. Kwok and S. E. Brown, Thermal Conductivity of the Charge-Density-Wave Systems K$_3$MoO$_3$ and (TaSe$_4$)$_2$I Near the Peierls Transition, Phys. Rev. Lett. 63, 895 (1989).

[25] M. D. Núñez-Regueiro, J. M. Lopez-Castillo, and C. Ayache, Thermal Conductivity of 1T – TaS$_2$ and 2H – TaSe$_2$, Phys. Rev. Lett. 55, 1931 (1985).

[26] B. M. Zawilski, R. T. Littleton, and T. M. Tritt, Description of the parallel thermal conductance technique for the measurement of the thermal conductivity of small diameter samples, Rev. Sci. Instrum. 72, 1770 (2001).

[27] Y.-K. Kuo, C. S. Lue, F. H. Hsu, H. H. Li, and H. D. Yang, Thermal properties of Lu$_5$Ir$_3$Si$_{10}$ near the charge-density-wave transition, Phys. Rev. B 64, 125124 (2001).

[28] C. S. Lue, Y. F. Tao, K. M. Sivakumar, and Y. K. Kuo, Weak charge-density-wave transition in LaAgSb$_2$ investigated by transport, thermal, and NMR studies, J. Phys.: Condens. Matter 19, 406230 (2007).

[29] C. N. Kuo, R. Y. Huang, Y. K. Kuo, and C. S. Lue, Transport and thermal behavior of the charge density wave phase transition in Lu$_5$Ir$_3$Si$_{10}$, Phys. Rev. B 102, 155137 (2020).

[30] M. Saint-Paul and P. Monceau, Survey of the thermodynamic properties of the charge density wave systems, Adv. Condens. Matter Phys. 2019, 2138264 (2019).