Thermodynamics of the thermoelectric working fluid close to the superconducting phase transition

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Abstract

The bottleneck in state-of-the-art thermoelectric power generation and cooling is the low performance of thermoelectric materials. While the adverse effects of lattice phonons on performance can be mitigated, the main difficulty remains to obtain a large thermoelectric power factor as the Seebeck coefficient and the electrical conductivity cannot be increased independently. Here, relating the thermoelastic properties of the electron gas that performs the thermoelectric energy conversion, to its transport properties, we analyze theoretically whether an electronic phase transition can enhance thermoelectric conversion and at what cost. More precisely, we consider the metal-to-superconductor phase transition in a model two-dimensional system, and we seek to quantify the contribution of the 2D fluctuating Cooper pairs to the power factor in the close vicinity of the critical temperature $T_c$. In addition, we provide experimental evidence of the rapid increase of the Seebeck coefficient without decreasing the electrical conductivity near $T_c$ in a 100-nm Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ thin film with high structural quality resulting in a power factor enhancement of approximately 300. This level of performance cannot be achieved in a system with low structural quality as shown experimentally with our sample degraded by ion bombardment as defects preclude the strong enhancement of the Seebeck coefficient near the phase transition. Finally, we theoretically discuss the ideal thermoelectric conversion efficiency (i.e. disregarding adverse phonon effects) and show that driving the electronic system to the vicinity of a phase transition may be an innovative path towards a strong performance increase but at the cost of a narrow temperature range of use of such materials.
1 Introduction

The growth of the semiconductor industry more than 60 years ago permitted significant progress in many solid-state device applications including lasers, photovoltaics, signal amplification, thermoelectricity, and detection, to name a few [1]. These applications are all commercialized by now, but clearly not on the same scale for all. Focusing on energy conversion, a quick comparison between thermoelectricity and photovoltaics shows the following: their study started during the first half of the 19th century; the two technologies benefited over several decades from the development of semiconductor physics and technology; while both may be considered on equal footing from the maturity viewpoint, thermoelectricity is not as widely deployed and integrated in power systems as photovoltaics is [2,3]. Thermoelectricity is often seen as a promising solution
for electrical power generation using the vast reservoir of waste heat, but as of yet it did not prove neither efficient nor scalable to fulfill this promise [4].

Both thermoelectric and photovoltaic technologies rely on the ability of their semiconductors’ electrons to perform the energy conversion [5, 6], but the latter proves nonetheless much more efficient than the former. From a thermodynamic viewpoint, an explanation of this difference lies in the nature of the boundary conditions under which the electronic working fluid is placed to produce work. If one feeds the electron system at temperature $T$ with energy from an external source, the variation of the internal energy reads: $\Delta U = W + Q = V \Delta q + T \Delta S$, where $V$ is the electrical potential difference across the system, $\Delta q$ the variation of the electric charge, and $\Delta S$ the system’s entropy variation. As thermoelectric generators require a thermal potential difference, i.e. a fixed temperature bias, to operate while photovoltaic converters operate under a photonic flux and isothermal conditions, the electron gas response is necessarily different.

In photovoltaic converters, the high-grade photonic energy transferred is mostly allocated to the promotion of the valence band electrons to conduction states as the photon frequency matches the energy gap, and comparatively little ends up as heating. In thermoelectric systems much of the low-grade thermal energy fed to the working fluid is dispersed among the electron gas’ individual degrees of freedom, simply heating the electron gas, while little goes to the collective response, i.e. electronic convective heat transport [7], hence the low efficiency. So, a path to thermoelectric conversion efficiency increase necessitates to subject the electron gas to suitable working conditions to enhance the thermoelectric coupling, either via band engineering [8] or by preparation in a particular thermodynamic state such as a phase transition either structural [9–13] or electronic [14, 15]. By doing so, more input energy is allocated to the collective response and the share of reversible entropy out of the total transported during the conversion process, is maximized.

In thermoelectricity performance is assessed against the dimensionless figure of merit $Z T$, which entails only the linear transport properties of the materials at temperature $T$ [16]:

$$Z T = \frac{\sigma \alpha^2}{\kappa} T = \frac{\alpha^2}{L(1 + \kappa_{\text{lat}}/\kappa_{\text{e}})}$$

where $\alpha$ denotes the Seebeck coefficient, $\sigma$ the electrical conductivity, and $\kappa$ the thermal conductivity. As conduction electrons and lattice transport heat by conduction in a semiconductor, the total thermal conductivity $\kappa$ reads: $\kappa = \kappa_{\text{e}} + \kappa_{\text{lat}}$; and $L = \kappa_{\text{e}}/\sigma T$ is the Lorenz number. Ideally, one aims to minimize heat transport by conduction, hence both $\kappa_{\text{lat}}$ and $\kappa_{\text{e}}$, while maximizing the Peltier term, which is related to heat transport by convection [7]. This useful mode of heat transport in thermoelectric systems can be characterized by the conductivity under zero electrochemical potential gradient $\kappa_{\text{conv}}$, which is related to $\kappa_{\text{e}}$ as follows: $\kappa_{\text{conv}} = (1 + Z T)\kappa_{\text{e}}$ [17]. While efforts are devoted to the increase of $Z T$ [18] or working conditions optimization [19], the question of whether or not there is an upper limit for $Z T$ is usually neglected. Further, an increase of $Z T$ at least up to $Z T = 4$, considered more than 20 years ago as elusive [20], remains largely inaccessible. Reaching this value would potentially yield a maximum efficiency about half the Carnot efficiency [21], thus making thermoelectric devices on par with widely used heat engines [4].

Now, since phonons effects cannot be arbitrarily reduced, one also seeks to maximize the power factor $\sigma \alpha^2$ [22]. Here, we look into the matter by searching for conditions that allow for a sizeable increase of the power factor $\sigma \alpha^2$, which would pave the way to a significant conversion efficiency increase. The power factor maximum is typically reached for carrier concentrations that correspond to heavily-doped semiconductors [23]. One problem is that an increase of $\alpha$ typically entails a decrease of $\sigma$. Interestingly, it was shown theoretically [24] and experimentally [25]
that as the electronic density of states of two-dimensional (2D) systems increases with decreasing a film's thickness so that it is much smaller than the de Broglie wavelength, the Seebeck coefficient increases too with no reduction of the electrical conductivity. Further, previous experimental works involving different families of superconducting compounds, showed that the temperature-dependence of the Seebeck coefficient exhibits a maximum after a significant increase close to the critical temperature \[26–28\]. Depending on the material, the variation can be either abrupt or gradual.

In this article, we concentrate on the conduction electron gas only as an idealization of thermoelectric systems, in the sense that we are interested in the conditions that boost the performance of the working fluid that performs the energy conversion in a heat engine. We establish a general link between the thermoelastic properties of the electronic working fluids and their transport properties. Principally considering two-dimensional electron systems (electron gas and fluctuating Cooper pairs), our numerical results show that close to the superconducting phase transition the power factor can significantly be augmented as \(\alpha\) increases while \(\sigma\) does not decrease owing to the transport properties of the 2D fluctuating Cooper pairs. These results are in good agreement with experimental data in the close vicinity of the critical temperature. To complement our analysis, we compute the maximal theoretical thermoelectric conversion efficiency of various electronic model systems: ideal 0-, 1-, and 3-dimensional electron gases, and 2D fluctuating Cooper pairs. We see that it saturates fairly quickly for all systems except that which undergoes a phase transition. Formulas and calculations not shown in the main are presented in a series of appendices.

2 Theory

2.1 Thermodynamics of the electron gas

Conduction electrons form a working fluid that can be ascribed thermodynamic variables from which thermoelastic coefficients may be defined [15,29] and a dimensionless thermodynamic figure of merit \(Z_{th,T}\) derived [15], providing a measure of the electronic working fluid's ability to perform energy conversion. Here, we adopt an approach “à la Carnot”, meaning that we concentrate on the working fluid assuming all else “ideal”, disregarding all other sources of dissipation negatively impacting performance, like heat leaks via the lattice and the coupling to the reservoirs. So, while phonons must be accounted for in the overall energy conversion efficiency calculation, we do not consider them in our thermodynamic analysis of the electronic working fluid; here, heat transfer by conduction reduces to the electronic contribution only: \(\kappa \equiv \kappa_e\) for the 2D electron gas (2DEG) and \(\kappa \equiv \kappa_{cp}\) for the 2D fluctuating Cooper pairs (2D FCP), so the notation \(ZT\) below corresponds to the figure of merit of the thermoelectric working fluid rather than that of the whole thermoelectric system.

In classical thermodynamics the isentropic expansion factor \(C_P/C_V\) is a measure of a working fluid's ability for heat-to-work conversion. The larger \(C_P\) is with respect to \(C_V\), the more heat is converted into mechanical work at constant pressure: the working fluid expands as it receives thermal energy while it cannot expand at constant volume in which case thermal energy simply heats up the system. The correspondence between the conjugate thermodynamic variables of a classical working fluid, volume \(V\) and pressure \(-P\), and those pertinent to the conduction electron gas, number of electrons \(N\) and electrochemical potential \(\mu\): \(V \implies N\) and \(-P \implies \mu\), yields the
thermoelectric heat capacity ratio $\gamma = C_\mu/C_N$ at temperature $T$ [15,29]:

$$
\frac{C_\mu}{C_N} = 1 + \frac{\beta^2 \chi T}{\ell} = 1 + \frac{\alpha_{th}^2}{\ell} = 1 + Z_{th}T \quad (2)
$$

where the heat capacities are defined as: $C_\mu N = T(\partial S/\partial T)_\mu$, which is the analogue to the specific heat at constant pressure, and $C_N N = T(\partial S/\partial T)_N$, which is the analogue to specific heat at constant volume, with $S$ being the electron system's entropy. Equation (2) is the definition of the thermodynamic figure of merit $Z_{th}T$, which contains $\alpha_{th} = \beta \chi T / q = (\partial \mu / \partial T)_N / q$, the thermoelectric coupling or entropy per carrier, characterizing the average capacity of the conduction electrons to carry both an electric charge $q$ and thermal energy $TS$. This coupling is related to two thermoelastic coefficients: $\beta N = (\partial N/\partial T)_\mu$, analogue to the thermal dilatation coefficient, and $\chi T N = (\partial N/\partial \mu)_T$, analogue to the isothermal compressibility. Note that $\ell = C_N/q^2 \chi T T$ is the thermostatic counterpart of the Lorenz number in coupled transport; as discussed in [15]: while the latter measures the system's ability to conduct thermal energy relative to its ability to conduct electricity, the former measures the system's ability to store thermal energy relative to its ability to gain conduction electrons. Hence, in the context of thermoelectricity, $\ell$ should be small so that the electron gas tends to minimize heat transfer by conduction, while $\alpha_{th}$ should be high so that the Peltier contribution to the heat flux, or heat transfer by convection [7,15], i.e. electrical charge transport, is maximized.

### 2.2 Transport coefficients near phase transition

Now, we pay a particular attention to the 2DEG just above the critical temperature $T_c$ and its thermoelectric properties driven by the 2D FCP [30]. A fluctuating Cooper pair can be treated as a carrier with charge $q = 2e$, where $e$ is the electron charge. Its typical size is in the $10^3$ to $10^4 \, \text{Å}$ range. The existence of fluctuating Cooper pairs above $T_c$ gives rise to paraconductivity, which is a pair contribution that enhances the electrical conductivity $\sigma_{cp} = e^2/16\pi\hbar$, where $\epsilon = \ln T/T_c \approx (T - T_c)/T_c$ [30,31]. The thermal conductivity $\kappa_{cp} = (k_B^2 \alpha_{GL} T_c^2 / 64 \pi \hbar) \epsilon \ln(1/\epsilon)$ of fluctuating Cooper pairs, with $\alpha_{GL}$, a dimensionless parameter in the Ginzburg-Landau free energy functional and $k_B$ the Boltzmann constant, can be calculated as the response to an applied temperature gradient [30,32]. The Seebeck coefficient can be found based from its basic definition $\alpha = \nabla \mu/q \nabla T = \alpha_{GL} k_B \ln \epsilon / 2e$ [33,34]. The thermoelectric figure of merit near $T_c$ thus reads:

$$
Z T = \frac{1}{\epsilon^2} \ln \frac{1}{\epsilon} \quad (3)
$$

which is diverging the closer the electron system gets to the critical temperature, i.e. as $\epsilon \rightarrow 0$. It is also instructive to calculate the Lorenz number for the 2D FCP $L_{cp} = \kappa_{cp}/(\sigma_{cp} T)$:

$$
L_{cp} = \frac{\alpha_{GL}^2}{4} \left( \frac{k_B}{e} \right)^2 \left( \frac{T - T_c}{T T_c} \right) \ln \left( \frac{T_c}{T - T_c} \right) \quad (4)
$$

As the system’s temperature tends to $T_c$, $L_{cp} \rightarrow 0$, which clearly deviates from the standard Lorenz number: $L = \kappa/(\sigma T) = \pi^2/3(k_B/e)^2$. The thermoelectric working fluid in the fluctuating regime, thus acquires the desired properties for increased conversion performance.
3 Experimental

As an experimental model system in this study, we selected an epitaxially grown 100-nm-thick Ba(Fe$_{0.90}$Co$_{0.10}$)$_2$As$_2$ thin film on a CaF$_2$ substrate that offered an extremely good structural and compositional quality. The superconducting properties of comparable samples were previously described in [35]. Here, the sample’s composition corresponds to the close-to-ideal doping case for these epitaxial growth conditions [36], reflected by a high transition temperature $T_c$ of 25.6 K. The thin film was prepared by pulsed laser deposition method in ultra-high vacuum of $10^{-9}$ mbar utilizing a KrF excimer laser. The pnictide thin film was grown with a frequency of 7 Hz at 700 °C, while its thickness was controlled by the number of pulses. Similar pnictide thin films were studied in detail in Refs. [35–37]. After the characterization of the transport properties, we purposefully introduced defects into the thin film by ion bombardment with 10 keV argon ions. The same yet degraded sample was then characterized again.

The thermoelectric properties of the sample were characterized by a Physical Property Measurement System of the Quantum Design DynaCool series (9 T), equipped with a thermal transport option. Utilizing the thermal transport option, the experimental parameters Seebeck coefficient and electrical resistivity were measured simultaneously and continuously as a function of temperature. Hereby, the sample was subjected to a thermal pulse, and its temperature and voltage responses were recorded. The Seebeck coefficient was extracted from these data, and the resistivity was characterized subsequently. Electrical contacts were made by a conducting silver-particle based two component epoxy glue that is recommended from Quantum Design for the thermal transport option. Note that both Seebeck coefficient and electrical resistivity could only be characterized in the normally conducting state of the sample, since $\alpha = 0$ and $\rho = 0$ in the superconducting state. The thermal transport option of the DynaCool, in principle, also provides thermal conductivity data. But for this thin film sample, these data were completely dominated by the thermal conductivity of the CaF$_2$ substrate, and are therefore not shown here.

3.1 X-ray diffraction characterization

The structure of the grown film was studied using X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with Co-K$_\alpha$ radiation for standard $\theta-2\theta$ measurements and a Panalytical XPert system with Cu-K$_\alpha$ radiation for texture measurements.

![XRD pattern](image)

Figure 1: Structural characterization. (a) XRD pattern of the standard Ba(Fe$_{0.90}$Co$_{0.10}$)$_2$As$_2$ film using Co-K$_\alpha$ radiation; (b) pole figure for the (103) plane of Ba(Fe$_{0.90}$Co$_{0.10}$)$_2$As$_2$; (c) analysis of the in-plane alignment using a $\phi$ scan through the (103) peaks.
XRD studies showed only (00\(\ell\)) peaks in the \(\theta - 2\theta\) scans indicating a clear c-axis orientation of the film (Fig. 1(a)). The c-axis lattice parameter was determined to 1.319 nm. Texture measurements revealed an epitaxial growth with a sharp in-plane alignment having a full width at half maximum (FWHM) value of 1.4\(^\circ\) (Fig. 1(b,c)). The results are almost identical to data published previously on Ba(Fe\(_{0.90}\)Co\(_{0.10}\))\(_2\)As\(_2\) films prepared under similar deposition conditions \([35]\). Therefore, we assume also a similar clean microstructure with a small reaction layer towards the substrate as shown by high resolution transmission electron microscopy in this work.

3.2 Ion bombardment

Figure 2: a) Simulated ion trajectories in a 25 nm thick Ba\(_2\)(Fe\(_{0.9}\)Co\(_{0.1}\))\(_2\)As\(_2\) compound as calculated with SRIM-2008. Left: The black arrow depicts the direction of the incoming Ar ion beam. Red dots depict projectile positions until the ion is finally stopped (black dot), here for 200 projectiles. For clarity, recoil atoms have been omitted. b) The extension of the damaged zone into the thin film can be estimated by overlaying a sufficient number of simulated trajectories, here 5000. Recoil atoms are plotted as well using the following colour code: Ba green, Fe blue, Co pink, As orange.

To introduce defects into the 100-nm-thick Ba(Fe\(_{0.90}\)Co\(_{0.10}\))\(_2\)As\(_2\) thin film deposited on the CaF\(_2\) substrate, it bombarded with argon ions with a kinetic energy of 10 keV and with a fluence of 8.5\(\times\)10\(^{12}\) ions per cm\(^2\) hitting the sample under an angle of incidence of 45\(^\circ\). In this energy regime, the damage is almost exclusively due to nuclear stopping, i.e. binary collisions between atoms. The resulting collisional cascades of ions (see Fig. 2a) and recoil atoms (see Fig. 2b) lead to the creation of a defective zone with an extension on the order of typically a few ten nanometers. To estimate the extent of ion-induced damage for the samples studied here we ran model calculations with the software package “Stopping and Range of Ions in Matter” (SRIM-2008) \([38]\) which computes the interactions of energetic ions with amorphous targets using a Monte Carlo approach. As input parameters, we used the above mentioned ion beam parameters, a density of 6.47 g cm\(^{-3}\) and the stoichiometry of the sample, in combination with generic values for the otherwise unknown lattice binding (3 eV) and displacement (25 eV) energies for all target
elements, and the respective elementary surface binding energies (Ba: 1.84 eV, Fe: 4.34 eV, Co: 4.43 eV, As: 1.26 eV) provided by SRIM-2008. We used the full cascade mode, in which the collisional damage to the target is analyzed by following every recoil atom until its energy drops below the lowest displacement energy of any of the target atoms. From these calculations, one may infer the extension of the defective zone into the film. Figure 2 shows that the bombardment of the film has led to a defective zone of \(\approx 30\) nm thickness. According to the simulations, the sputter yield for this system is \(\approx 12\) atoms per ion, i.e. in total one tenth of a monolayer is removed by the ion bombardment.

### 3.3 Transport properties

![Graph](image)

Figure 3: Thermoelectric transport characterization of the 100 nm \(\text{Ba(Fe}_{0.90}\text{Co}_{0.10})_2\text{As}_2\) thin film showing the Seebeck coefficient \(\alpha\) and electrical resistivity \(\rho\): a) high structural quality before ion bombardment, and b) low structural quality after ion bombardment.

Figure 3 shows the Seebeck coefficient and electrical resistivity of a 100-nm-thick relaxed \(\text{Ba(Fe}_{0.90}\text{Co}_{0.10})_2\text{As}_2\) pnictide thin film. In the upper panel, the measurements shown were performed on a high structural quality sample, while the lower panel shows the data of the same sample with low structural quality following ion bombardment. It is interesting to see that the structural quality has a limited impact on both the Seebeck coefficient and the electrical resistivity away from the superconducting phase transition region, here above 50 K, but that it strongly affects the Seebeck coefficient at lower temperature as shown by the drastic reduction of the magnitude of \(\alpha\), which contrasts sharply with the temperature dependence displayed in the upper panel. The role of the 2D fluctuating Cooper pairs in the thermoelectric coupling close to the phase transition is clearly mitigated by the structural defects.
4 Results

Figure 4: Parametric plots of $ZT$ vs $Z_{th}T$ of the 2D electron gas (with $\kappa \equiv \kappa_e$) and the 2D fluctuating Cooper pairs (with $\kappa \equiv \kappa_{cp}$). The lowest value here taken by $Z_{th}T$ corresponds to the temperature range imposed to be in the vicinity of the superconducting phase transition and for the model to be valid. Note the ultra-high values of $ZT$ of the 2D FCP system, which stem from its extremely strong dependence on the temperature, Eq. (3).

Thermoelectric conversion is possible because electron transport can take place under a temperature gradient, and ideally the process should be isentropic. The quantity $Z_{th}T$, which is directly related to the isentropic expansion factor $\gamma = C_{\mu}/C_N$, thus bridges the thermodynamic and the transport properties of the electronic working fluid at temperature $T$. Indeed, the relationship $\kappa_{conv} = (1 + ZT)\kappa_e$ [17] resembles that which defines $\gamma$ in Eq. (2), thus defining an isentropic expansion factor in the context of electron transport: $\gamma_{tr} = \kappa_{conv}/\kappa_e = 1 + ZT$. The correlation between $ZT$ and $Z_{th}T$ gives the deviation of $\gamma_{tr}$ from the standard $\gamma$ in thermostatics shown in Fig. 4 both in the normal thermodynamic regime and the fluctuating regime in 2D systems. The curves show a monotonic increase of $ZT$ against $Z_{th}T$. Note the different magnitudes between the case that involve a phase transition and that which does not. This clearly indicates that the power factor can reach extremely high values when suitable boundary conditions are imposed to the system.

We now turn to Fig. 5 where the power factor (normalized to its value at $T = 300$ K) calculated using the transport coefficients of the 2DEG and 2D FCP is shown and compared to experimental data obtained with a 100-nm-thick relaxed Ba(Fe$_{0.90}$Co$_{0.10}$)$_2$As$_2$ pnictide thin film with high and then low structural quality (following ion bombardment) on its CaF$_2$ substrate. While our 2D models are idealized and do not account for the finite thickness of the thin film, we assume that the physical phenomena discussed in our work, are sufficiently well described by the 2D models. More realistic numerical data would entail a density of states modified by a thickness-dependent form factor. This level of sophistication is not required in our work. Further, given the typical size of the Cooper pairs, the FCP motion is restricted along the direction of the growth axis, the experimental data is suitable to discuss the 2D FCP model in the close vicinity of the critical temperature.
Figure 5: Power factors $\sigma a^2$ normalized to their value at 300 K, of the 100 nm Ba(Fe$_{0.90}$Co$_{0.10}$)$_2$As$_2$ thin film before and after the ion bombardment, as functions of temperature. The transition region between the normal regime and the superconducting phase is influenced by the structural quality of the sample. Note the steep, nearly vertical slope computed for the ideal 2D FCP system, near $T_c = 25.6$ K.

In the close vicinity of $T_c$ we assume that the comparison with the 2D FCP model holds as the thin film has a quasi-2D character for the fluctuating Cooper pairs whose motion along the growth direction is restricted due to their size. The blue curve depicts the relative change of the power factor determined experimentally from $T = 300$ K down to $T_c$. When approaching the transition into the superconducting state, an increase in the Seebeck coefficient precedes this phase transition while the electrical resistivity of the sample remains almost unaffected as shown in Fig. 3. The observed increase clearly depends on the structural quality of the sample as shown by the green curve in Fig. 5. The closer the sample is to an ideal 2D system, the larger is the increase. The numerical simulations performed with the 2D electron gas model (black curve) and the 2D FCP model (grey curve) shown support this interpretation. The large increase of the Seebeck coefficient in the high-quality sample results in a dramatic increase of the power factor of this material before its transition into the superconducting state by a factor up to 300.

5 Discussion

An increase of the absolute value of the Seebeck coefficient before entering the superconducting regime was reported before in the literature. Quite sharp peaks of the Seebeck coefficient comparable to our experimental finding were measured in nearly ideally electron-doped La$_{2-x}$Ce$_x$CuO$_4$ thin films [27]. Both, sharp and broadened Seebeck peaks were evidenced for SmFeAsO$_{1-x}$F$_x$ and Fe$_{1+y}$Te$_{1-x}$Se$_x$ [28]. A large increase of the Seebeck coefficient of a series of pnictides in which the Sm-lattice position was substituted by Nd and La, was shown in [26]. This increase was accompanied by a strong enhancement of the power factor. Broadened Seebeck coefficient peaks
were found in varying pnictides compositions \([39,40]\), as well as in cuprates \([41]\). In the present work, our models focus only on the thermodynamics of the ideal electronic systems, and as shown in Fig. 5, they do not account for the structural quality of the thin films that has an impact on the Seebeck coefficient behavior as temperature varies leading the system from the normal regime to the fluctuating regime. Note that a steep increase of the Seebeck coefficient before entering the superconducting state is also well known for elementary superconductors, for instance Pb and Nb \([42,43]\). This effect traditionally explained by the phonon drag effect \([44,45]\). As we focus essentially on the electronic working fluid that does the thermoelectric energy conversion, we do not consider lattice phonons causing heat leaks. Disregarding the presence of phonons in the thermoelectric conversion process also leads us to not consider in the present study the phonon drag effects that can enhance the Seebeck coefficient in some temperature range. The effect of the coupling of 2D electrons and equilibrium 3D phonons on the Seebeck coefficient has been studied theoretically \([46,47]\).

So, to model our experimental data beyond the fluctuating regime is a particular task that requires a full separate work that would entail the study of the quasi-2D electrons (thin film) scattering by nonequilibrium 3D phonons (substrate) accounting for the thickness of the film and the lattice mismatch. The detailed knowledge of the band structure and of the phonon spectrum considering effects at the film/substrate interface would then be required. Note that the experimental data reported in the main text and further below here, show that after the sample is degraded by ion bombardment, the dependence of the Seebeck coefficient on temperature does not vary sharply as the temperature decreases because other processes such as the scattering of phonons by defects that suppresses the phonon drag effects on the one hand and the defects that preclude the appearance of fluctuating Cooper pairs on the other hand. Further, a study of phonon drag in thin films in the normal regime, shows that the Debye temperature of the substrate influences the position and magnitude of the phonon drag peak as the drag effect varies with temperature \([48]\). Interestingly, it was also shown that the phonon drag peak is strongly suppressed with the film thickness. Given that the film thickness in our sample is 100 nm, we can assume that though the drag effect certainly plays a role, this role is not the dominant one near \(T_c\). This is acceptable for the analysis of the behavior of the Seebeck coefficient and power factor in the vicinity of the critical temperature.

While this was not studied in further detail within the scope of this work, we suggest that the variation of the peak shape of the Seebeck coefficient, i.e. sharp or broadened, is a result of structural or compositional inhomogeneities in these samples. With a quite good structural and compositional integrity of our sample, the data here presented serves as a model system to underline the theoretical model. The Seebeck coefficient and the electrical conductivity evolve slightly differently as the systems approaches the critical temperature; Eq. (3) shows clearly the resulting temperature dependence of \(ZT\) close to the superconducting phase transition. This illustrates the difference between the transport of charges characterized by \(\sigma\), which is proportional to the carrier concentration, and the transport of entropy characterized by \(\alpha\), which varies logarithmically with the concentration. Being close to \(T_c\) favors a more rapid variation of \(\alpha\). We conclude here that the clear and distinct increase of the Seebeck coefficient observed in our experiment is a consequence of driving the subsystem of conduction electrons to the vicinity of the superconducting phase transition.

We end the discussion with an evaluation of the maximum thermoelectric conversion efficiency, \(\eta_{\text{max}}\), that the electronic working fluid can boast in a thermoelectric generator in (ideal) thermal contact with a heat source at temperature \(T_{\text{hot}}\), and a heat sink at temperature \(T_{\text{cold}} < T_{\text{hot}}\). \(\eta_{\text{max}}\)
is related to $\gamma$ as follows \cite{49,50}:

$$\eta_{\text{max}} = \frac{\sqrt{\gamma} - 1}{\sqrt{\gamma} + 1} \eta_C$$  \hspace{1cm} (5)

where $\eta_C = 1 - T_{\text{cold}}/T_{\text{hot}}$ is the Carnot efficiency. Owing to the relationship between $Z_{th}T$ and $ZT$, Eq. (5) confirms the well-known result that for a given set of boundary conditions, the larger $ZT$ the larger $\eta_{\text{max}}$.

![Figure 6: Maximum thermoelectric conversion efficiency attainable by all electronic working fluids considered in this work, as function of temperature. The dashed line shows when the 2D FCP model becomes invalid.](image)

The maximum efficiency scaled to the Carnot efficiency calculated for all model systems considered in this work, is reported in Fig. 6. The curves demonstrate that though ideal cases are considered (the focus being on the working fluid only, and a situation with no dissipative coupling between the generator and the thermal energy reservoirs), the Carnot efficiency cannot be reached; for this to occur, the isentropic expansion factor of the conduction gas would have to diverge, implying that it would have the capability to convert almost all of the thermal energy it receives into work, or convective heat transport \cite{7}. We saw in light of our thermodynamic analysis and experimental data, that bringing the electron gas close to a phase transition enhances the system’s power factor $\sigma\alpha^2$; hence by increasing both the thermoelectric coupling and electrical conductivity, thus favoring convective transport, the conversion of heat into work can be significantly boosted, albeit in a very limited temperature range in our study. Figure 6 also shows that while increasing the temperature of the electron systems that do not undergo a phase transition, yields an increase of $\eta_{\text{max}}$, their maximum efficiencies grow slowly and seem to saturate. For the system in the vicinity of a phase transition, the efficiency may tend to that of the ideal Carnot efficiency. Importantly, as we focused on the electronic working fluid only, the existence of an upper bound to $ZT$ accounting for the lattice thermal conductivity is demonstrated: for each system considered, the upper bound corresponds to that shown in Fig. 6.
6 Conclusion

Our thermodynamic study addresses why thermoelectric conversion is a fundamentally low-efficiency process across a wide range of systems and temperatures; it also shows that a path forward may lie in finding very specific working conditions such as placing the electron gas in the vicinity of a phase transition, but at the cost of narrowing down the wide applicability of efficient thermoelectric solutions for waste heat conversion. In other words, phase transitions impose that the system operates only close to the transition temperature and with small temperature bias. Depending on the degree of control of the working conditions, a high power factor obtained close to a phase transition might prove more useful for pumping heat rather than electrical power generation.

A Thermoelastic coefficients

As shown in Refs. [15, 51], the systems’ thermoelastic coefficients can be computed using the following formulas:

\[ \chi_{TN} = \int_0^\infty g(E) \left( -\frac{\partial f}{\partial E} \right) dE \]  \hspace{1cm} (6)

\[ \beta N = \frac{1}{T} \int_0^\infty g(E) (E - \mu) \left( -\frac{\partial f}{\partial E} \right) dE \]  \hspace{1cm} (7)

\[ C_{\mu N} = \frac{1}{T} \int_0^\infty g(E) (E - \mu)^2 \left( -\frac{\partial f}{\partial E} \right) dE, \]  \hspace{1cm} (8)

where \( f \) is the energy distribution function of the considered system with particle number \( N \), temperature \( T \), chemical potential \( \mu \), and density of state \( g \). The coefficient \( C_N \) may be simply found from Eq. (2) in the main text.

The case of the 2D fluctuating Cooper pairs is more involved and necessitates a different approach as shown in the Supplemental Material of Ref. [15]. The 2D fluctuating Cooper pairs chemical potential \( \mu_{cp} \) of a system with \( N_{cp} \) pairs is derived from the free energy \( F_{cp} \):

\[ F_{cp} = -\frac{A}{4\pi \xi^2} k_B T_c \epsilon \ln \epsilon \]  \hspace{1cm} (9)

\[ \mu_{cp} = F_{cp} \left( \frac{\partial^2 F_{cp}}{\partial \epsilon \partial N_{cp}} \right)^{-1} \]  \hspace{1cm} (10)

where \( \epsilon = \ln T/T_c \approx (T - T_c)/T_c \) with \( T_c \) the critical temperature of the superconducting phase transition, \( \xi \) is the coherence length, and \( A \) is the surface area of the 2D system.

The coefficient \( C_N \) reads:

\[ C_N = -\frac{T}{N_{cp}} \frac{\partial^2 F_{cp}}{\partial T^2} \]  \hspace{1cm} (11)

and \( \chi_T \) is given by:

\[ \chi_T = \frac{1}{N_{cp}} \left( \frac{\partial N_{cp}}{\partial \mu_{cp}} \right)_T \]  \hspace{1cm} (12)
B Transport coefficients in the relaxation time approximation

The transport coefficients for a variety of systems including low-temperature [52] and interacting systems [53,54] can be calculated using the Boltzmann equation. The simplest assumption is that of the relaxation time approximation for the electrons [55,56]. For the two-dimensional electron gas in a metallic system in particular, it is given by [57]

\[ \tau_e = \frac{\hbar^2}{\pi m A} = \frac{1}{g(E)}, \]  

(13)

where \(\hbar\) is the Planck constant, \(m\) is the electron rest mass, and \(A\) is the system’s surface.

In the relaxation time approximation, Onsager's kinetic coefficients can be calculated as follows:

\[ L_{11} = \frac{T}{d} \int_0^\infty \Sigma(E) \left( -\frac{\partial f}{\partial E} \right) dE \]

(14)

\[ L_{12} = L_{21} = \frac{T}{d} \int_0^\infty (E - \mu) \Sigma(E) \left( -\frac{\partial f}{\partial E} \right) dE \]

(15)

\[ L_{22} = \frac{T}{d} \int_0^\infty (E - \mu)^2 \Sigma(E) \left( -\frac{\partial f}{\partial E} \right) dE \]

(16)

where \(d\) is the system’s dimension, \(\Sigma(E) = \tau(E) v^2(E) g(E)\) is the transport distribution function with velocity \(v\) [58]; and the transport coefficients read [17]:

\[ \sigma = \frac{e^2 L_{11}}{T}, \]

(17)

\[ \alpha = \frac{L_{12}}{eTL_{11}}, \]

(18)

\[ \kappa_e = \frac{1}{T^2} \left[ L_{22} - \frac{L_{12}L_{21}}{L_{11}} \right], \]

(19)

where \(\sigma\) is the isothermal electrical conductivity, \(\alpha\) is the Seebeck coefficient, and \(\kappa_e\) is the thermal conductivity under zero electric current.

C Transport coefficients in the Landauer-Büttiker approach

In mesoscopic systems, the Landauer-Büttiker approach provides a means to calculate the transport coefficients accounting for the presence of scatterers [55,59]. The application of the Landauer-Büttiker approach leads to expressions similar to Eqs. (17)—(19) but with the electrical and thermal conductances, \(G\) and \(G_{th}\) respectively, instead of electrical and thermal conductivities, \(\sigma\) and \(\kappa\) [60]. The transmission function for two-terminal systems, coupled to two reservoirs, left (L) and right (R), is defined as

\[ T(E)_{LR} = \text{Tr} \{ \hat{f}_R \hat{\Sigma}^{+} \hat{G}^{-} \hat{f}_L \}, \]

(20)

where \(\hat{f}_{R,L} = 2\hbar / \tau_{R,L}^{el}(E)\) are the level width functions, describing the broadening of energy levels, and \(\tau_{R,L}^{el} = -\hbar / \text{Im} \{ \hat{\Sigma}_{R,L}^{+} \}\) is the “elastic lifetime”, i.e., the time between two collisions, with \(\hat{\Sigma}_{R,L}^{+}\)
being the self-energy operators and $\hat{G}^+$ and $\hat{G}^-$ are the advanced and retarded Green functions respectively [55].

From the experimental point of view, one considers electrical and transport conductances instead of electrical and transport conductivities. The reasons is that, for example, in a ballistic wire, the lack of backscattering inside it yields an infinite conductivity but a finite conductance [61].

**D Transport in the fluctuating regime**

Here, we consider the transport of 2D fluctuating Cooper pairs above the critical temperature in a superconductor [30]. The expression for the relaxation time of 2D fluctuating Cooper pairs reads:

$$\tau_{cp} = \frac{\tau_{GL}(\epsilon)}{1 + \xi(\epsilon)p^2}, \quad (21)$$

where $p$ is the momentum, $\xi$ is the fluctuating Cooper pair size, and $\tau_{GL} = \pi\hbar/8k_B(T - T_c)$ is the characteristic time in the time-dependent Ginzburg-Landau theory. In the vicinity of $T_c$, $\tau_{GL}$ is the fluctuating Cooper pair lifetime [30], and $\epsilon = \ln T/T_c \approx (T - T_c)/T_c$.

The existence of fluctuating Cooper pairs above $T_c$ yields to pair contribution to electrical conductivity $\sigma_{cp}$ [31], which is also called paraconductivity [30]. The thermal conductivity $\kappa_{cp}$ of fluctuating Cooper pairs can be calculated as the response to the applied temperature gradient [32]. However, one can calculate it more simply, based on the theory of heat transport [30]. The Seebeck coefficient can be found based from its basic definition $\alpha = \nabla\mu/q\nabla T$ [33,34]. Thus, the transport coefficients of fluctuating Cooper pairs above the critical temperature $T_c$ read:

$$\sigma_{cp} = \frac{e^2}{16\hbar} \frac{1}{\epsilon}, \quad (22)$$

$$\alpha_{cp} = \frac{\alpha_{GL}k_B}{2e} \ln \epsilon, \quad (23)$$

$$\kappa_{cp} = \frac{k_B^2\alpha_{GL}^2T_c}{64\hbar} \epsilon \ln \frac{1}{\epsilon}. \quad (24)$$

where $\alpha_{GL}$ is a dimensionless parameter in the Ginzburg-Landau free energy functional. Although the electrical $\sigma_{cp}$ and thermal $\kappa_{cp}$ conductivity are written similarly, $\sigma_{cp}$ shows a strong divergence in the vicinity of the critical temperature [30]. The thermal conductivity $\kappa_{cp}$ does not show any singularity near the transition [30,32].

**E Additional $ZT$ vs. $Z_{th}T$ curves**

The thermoelastic coefficients and the transport coefficients for all systems can be computed from the formulas given above and combined as shown in Eqs. (1) and (2) in the main text, to obtain $Z_{th}T$ and $ZT$ (with $\kappa \equiv \kappa_e$). As discussed in the main text, the parametric plot of $ZT$ against $Z_{th}T$ shows a clear correlation between the isentropic expansion factor and the thermoelectric figure of merit: the larger the former, the larger the latter.

All the curves depicted in fig. 7 show a monotonic behavior. It is interesting to note that for the 0D system, the correlation is linear implying that the isentropic expansion factor in the transport regime does not deviate from the heat capacity ratio at equilibrium, while it does for the small
values of $ZT$ and $Z_{th}T$ for finite-dimension systems. This originates in the energy dependence of the transport distribution functions and of the density of states in particular.

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