Thermoelectric power factor divergence close to phase transition in Co-doped epitaxial pnictide thin films

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The bottleneck in state-of-the-art thermoelectric power generation and cooling is the low performance of thermoelectric materials. The main difficulty is 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 show that the power factor can diverge in the vicinity of the metal-to-superconductor phase transition in two-dimensional systems. We provide experimental evidence of the rapid increase of the Seebeck coefficient without decreasing the electrical conductivity in a 100-nm Ba(Fe₁₋ₓCoₓ)₂As₂ thin film with high structural quality, as the sample temperature approaches the critical temperature, 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. We also theoretically discuss the thermoelectric conversion efficiency for a wide-range of model systems, and show that driving the electronic system to the vicinity of a phase transition may be an innovative path towards performance increase at the possible cost of a narrow temperature range of use of such materials.

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 macroscopic viewpoint, thermoelectricity is not as widely deployed and integrated in power systems as photovoltaics is [2] [3]. Thermoelectricity in particular is often invoked 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 response of the electron gas is necessarily different.

In the case of a photovoltaic converter, the high-grade photonic energy transferred is essentially 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.

The key quantity upon which rest most of the works in thermoelectricity is the dimensionless figure of merit \(ZT\), which entails only the linear transport properties of the materials at temperature \(T\) \[10\]:

\[
ZT = \frac{\sigma \alpha^2}{\kappa} T = \frac{\alpha^2}{L(1 + \kappa_{lat}/\kappa_e)}
\]

where \(\alpha\) denotes the Seebeck coefficient, \(\sigma\) the electrical conductivity, and \(\kappa\) the thermal conductivity. As both conduction electrons and lattice phonons may transport heat by conduction in a semiconductor, the total thermal conductivity \(\kappa\) reads: \(\kappa = \kappa_e + \kappa_{lat}\); and \(L = \kappa_e/\sigma T\) is the Lorenz number. Ideally, one aims to minimize heat transport by conduction, hence both \(\kappa_{lat}\) and \(\kappa_e\), 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 \(\kappa_{cond}\), which is related to \(\kappa_e\) as follows: \(\kappa_{cond} = (1 + ZT)\kappa_e\) \[17\].

While efforts are devoted to the increase of \(ZT\) \[18\] or working conditions optimization \[19\], the question of whether or not there is an upper limit for \(ZT\) is usually neglected. However, can \(ZT\) be increased, if not arbitrarily, at least significantly to reach a minimum value, say \(ZT = 4\), that would allow significant performance improvement placing thermoelectric devices on par with widely used heat engines \[3\]? Here, we look into the matter both theoretically and experimentally. We search 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. One problem is that an increase of \(\alpha\) typically entails a decrease of \(\sigma\). The power factor maximum as a function of carrier concentration is typically reached for concentrations that correspond to heavily-doped semiconductors \[20\]. Interestingly, it was shown theoretically \[21\] and experimentally \[22\] 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 \[23\]-\[25\]. Depending on the material, the variation can be either abrupt or gradual.

In this article, principally considering two-dimensional electron systems, we establish a link between the thermoelastic properties of the electronic working fluids and their transport properties. Our results and data show that close to the superconducting phase transition the power factor can significantly be augmented as \(\alpha\) increases while \(\sigma\) does not decrease. We then report our experimental measurements of the Seebeck coefficient and the resistivity in our Co-doped epitaxial pnictide thin films, which we discuss in light of our theoretical findings. Finally, to complement our analysis, we compute the maximal thermoelectric conversion efficiency of the model systems, as a function of temperature and see that it saturates fairly quickly for systems that do not undergo a phase transition. Calculations not shown in the main text also apply to a range of models: ideal 0-, 1-, and 3-dimensional electron gases presented in the appendices, where details on the experiments are also given.

**Theory**

Conduction electrons form a working fluid that can be ascribed thermodynamic variables from which thermoelastic coefficients may be defined \[15\]-\[26\]. Importantly, the dimensionless thermodynamic figure of merit \(Z_\Omega T\) introduced in \[15\], provides a measure of the ability of the electronic working fluid to perform energy conversion. Here, we adopt an approach “à la Carnot”, meaning that we essentially focus on the working fluid assuming all else “ideal”, i.e. disregarding all other sources of dissipation negatively impacting performance, notably heat leaks via the lattice phonons and the coupling to the reservoirs. Note that while Carnot’s efficiency is independent of the working fluid’s characteristics, the power produced by the engine is; this reflects the fact that a thermoelectric system transports both energy and entropy. 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, \(\kappa \equiv \kappa_e\).

In classical thermodynamics the isentropic expansion factor \(C_P/C_V\) is a measure of a working fluid’s conversion efficiency; indeed the larger \(C_P\) is with respect to \(C_V\), the more heat is used for mechanical work as 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. Hence, establishing a correspondence between the conjugate thermodynamic variables of a classical working fluid, volume \(V\) and pressure \(-P\), and those pertinent to a conduction electron gas, number of electrons \(N\) and electrochemical potential \(\mu\): \(V \longrightarrow N\) and \(-P \longrightarrow \mu\), the thermoelectric heat capacity ratio \(\gamma = C_\mu/C_N\) at
temperature $T$ reads [15] [26]:

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

where $C_\mu, N = T (\partial S / \partial T)_{\mu}$ is the analogue to the specific heat at constant pressure, and $C_N, N = T (\partial S / \partial T)_{N}$ is the analogue to specific heat at constant volume, with $S$ being the electron system’s entropy. This expression is the definition of the thermodynamic figure of merit $Z_{th} T$. In Eq. (2), $\alpha_{th} = \beta \chi_T / q = (\partial \mu / \partial T)_{N} / q$ is the thermoelectric coupling or so-called entropy per carrier, which describes from the thermodynamic viewpoint the average capacity of the conduction electrons to carry both an electric charge $q$ and thermal energy $TS$. This coupling is characterized by 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 is a measure of 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 thermoductivity, $\ell$ 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, $\gamma_C$, i.e. electrical charge transport, is maximized.

Thermoelectric conversion is possible only because of electron transport can take place, and ideally the process should be isentropic. The quantity $Z_{th} T$, which is directly related to the heat capacity ratio $\gamma = C_\mu / C_N$, thus bridges the thermodynamic and the transport properties of the electronic working fluid at temperature $T$. Indeed, we may remind that the relationship $\kappa_{conv} = (1 + ZT) \kappa_C$ [17] resembles that which defines $\gamma$ in Eq. (2), thus defining an isentropic expansion factor in the context of electron transport: $\gamma_{tr} = \kappa_{conv} / \kappa_C = 1 + ZT$. The correlation between $ZT$ and $Z_{th} T$ gives the deviation of $\gamma_{tr}$ from the standard $\gamma$ in thermostatics. Figure 1 shows this correlation between $ZT$ and $Z_{th} T$ both in the normal thermodynamic regime and the fluctuating regime close to a superconducting phase transition 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.

**Experimental** As experimental model system for 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 [27]. Here, the sample’s composition corresponds to the close-to-ideal doping case for these epitaxial growth conditions [28], 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. Pulsed laser deposition films were studied in detail in Refs. [27, 29]. 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.

The blue curve in Fig. 2 shows the relative change of the power factor of a 100-nm-thick relaxed Ba(Fe$_{0.90}$Co$_{0.10})_2$As$_2$ pnictide thin film with high
FIG. 2. Power factors $\sigma_\alpha^2$ normalized to their value at 300 K, of the 100 nm Ba(Fe$_{0.9}$Co$_{0.1}$)$_2$As$_2$ thin film before and after the ion bombardment, as functions of temperature. The blue curve shows the experimental data obtained with the high structural quality sample before ion bombardment, and the green curve, the data obtained with the low structural quality sample after ion bombardment. The transition region between the normal regime and the superconducting phase is mostly governed by the structural quality of the sample. The black and grey curves are numerically obtained from the models that simulate the ideal 2DEG and 2D FCP systems respectively. Note the steep slope computed for the ideal 2D FCP system, near $T_c = 25.6$ K.

and then low structural quality (i.e. before irradiation) on its substrate. 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 (see Fig. 6 in the Appendix for the Seebeck and electrical resistivity data). The observed increase clearly depends on the structural quality of the sample as shown by the green curve in Fig. 2. The closer the sample is to an ideal 2D system, the larger is the increase. The numerical simulations performed with the 2D electron gas (2DEG) 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.

**Discussion.** Generally, an increase of the absolute value of the Seebeck coefficient before entering the superconducting regime was reported before in the literature. For instance, 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 [24]. Both, sharp and broadened Seebeck peaks were evidenced for SmFeAsO$_{1-x}$F$_x$ and Fe$_{1+y}$Te$_{1-x}$Se$_x$ [25]. 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 by Pinsard-Gaudart et al. [23]. This increase was accompanied by a strong enhancement of the power factor. Broadened Seebeck coefficient peaks were found in varying pnictides compositions [30, 31], as well as in cuprates [32]. In the present work, our models focus only on the thermodynamics of the ideal electronic systems, and as shown in Fig. 2 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 [33, 34]. This effect is traditionally explained by the phonon drag effect [35, 36].

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 (see the experimental data in Fig. 6 in the Appendix). With a quite good structural and compositional integrity of our sample, the here presented data serves as model system to underline the theoretical model. The Seebeck coefficient and the electrical conductivity evolve slightly differently as the systems approaches the critical temperature; the model summarized in the Appendix 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 the superconducting phase transition 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 $T_h$, and a heat sink at temperature $T_c < T_h$. The efficiency $\eta_{\text{max}}$ is related to $\gamma$ as follows [37, 38]:

$$\eta_{\text{max}} = \frac{\sqrt{\gamma - 1}}{\sqrt{1 + \gamma}} \eta_C$$  \hspace{1cm} (3)

where $\eta_C = 1 - T_h/T_c$ is the Carnot efficiency.

Owing to the relationship between $ZT_{th}T$ and $ZT$, Eq. 3 confirms the well-known result that for a given set of boundary conditions, the larger $ZT$ the larger $\eta_{\text{max}}$. The
maximum efficiency scaled to the Carnot efficiency calculated for all model systems considered in this work, is reported in Fig. 3. The curves clearly show that even 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 is not 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. We saw in light of our experimental results and thermodynamic analysis, that bringing the electron gas close to a phase transition enhances the system’s power factor $\sigma^2$; 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 3 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, note that as we focused on the electronic working fluid only, the existence of an upper bound to $ZT$ accounting for the lattice thermal conductivity is thus shown: for each system considered, the upper bound corresponds to that shown in Fig. 3.

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.

APPENDIX

The mathematical and experimental details omitted in the main text are summarized in this appendix. We show the $Z_{\text{th}} T$ vs $ZT$ curves computed numerically for the 0D, 1D, 3D models not discussed in the main text, as well as the simulated ion trajectories during bombardment of the sample, and the resulting damage zone. We also show transport properties measurement data, Seebeck coefficient and electrical resistivity of the sample, before and after ion bombardment.

Thermoelastic coefficients

As shown in Refs. [15, 39], the systems’ thermoelastic coefficients can be computed using the following formulas:

$$\chi T N = \int_0^\infty g(E) \left( -\frac{\partial f}{\partial E} \right) dE$$

$$\beta N = \frac{1}{T_a} \int_0^\infty g(E) (E - \mu_a) \left( -\frac{\partial f}{\partial E} \right) dE$$

$$C_\mu N = \frac{1}{T_a} \int_0^\infty g(E) (E - \mu_a)^2 \left( -\frac{\partial f}{\partial E} \right) dE,$$

where $f$ is the energy distribution function of the considered system with particle number $N$ and density of state $g$. The coefficient $C_\mu$ may be simply found from Eq. (2).

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 $\mu_{\text{cp}}$ of a system with $N_{\text{cp}}$ pairs is derived from the free energy $F_{\text{cp}}$. 

FIG. 3. Maximum thermoelectric conversion efficiency attainable by all electronic working fluids considered in this work, as function of temperature. The 2D fluctuating Cooper pairs system is numerically shown here to boost the largest efficiency, which can potentially reach the Carnot efficiency but on the condition to have the system’s temperature very close to $T_c$. The dashed line shows when the 2D FCP model becomes invalid.
\[ F_{cp} = -\frac{A}{4\pi^2} k_B T_c \varepsilon \ln \varepsilon \]  
\[ \mu_{cp} = \frac{F_{cp}}{\varepsilon} \left( \frac{\partial N_{cp}}{\partial \varepsilon} \right)^{-1} \]

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

The coefficient \( C_N \) reads:

\[ C_N = -\frac{T}{N_{cp}} \frac{\partial^2 F_{cp}}{\partial T^2} \]

and \( \chi_T \) is given by:

\[ \chi_T = \frac{1}{N_{cp}} \left( \frac{\partial N_{cp}}{\partial \mu_{cp}} \right)_T \]

**Transport coefficients in the relaxation time approximation**

The transport coefficients for a variety of systems including low-temperature [40] and interacting systems [41, 42] can be calculated using the Boltzmann equation. The simplest assumption is that of the relaxation time approximation for the electrons [43, 44]. For the two-dimensional electron gas in a metallic system in particular, it is given by [45]

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

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:

\[ L_{11} = \frac{T}{d} \int_0^\infty \Sigma(E) \left( -\frac{\partial f}{\partial E} \right) dE \]  
\[ L_{12} = L_{21} = \frac{T}{d} \int_0^\infty (E - \mu) \Sigma(E) \left( -\frac{\partial f}{\partial E} \right) dE \]  
\[ L_{22} = \frac{T}{d} \int_0^\infty (E - \mu)^2 \Sigma(E) \left( -\frac{\partial f}{\partial E} \right) dE \]

where \( d \) is the system’s dimension, \( \Sigma(E) = \tau(E) \nu^2(E) g(E) \) is the transport distribution function with velocity \( \nu \) [40], and the transport coefficients read [47]:

\[ \sigma = \frac{e^2 L_{11}}{T}, \]
\[ \alpha = \frac{L_{12}}{e TL_{11}}, \]
\[ \kappa_c = \frac{1}{T^2} \left( L_{22} - \frac{L_{12} L_{21}}{L_{11}} \right), \]

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

**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 [43, 48]. The application of the Landauer-Büttiker approach leads to expressions similar to Eqs. (15)–(17) but with the electrical and thermal conductances, \( G \) and \( G_{th} \) respectively, instead of electrical and thermal conductivities, \( \sigma \) and \( \kappa \) [49]. The transmission function for two-terminal systems, coupled to two reservoirs, left (L) and right (R), is defined as

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

where \( \hat{\Gamma}_R \) and \( \hat{\Gamma}_L \) are the overlap functions, \( \hat{G}^+ \) and \( \hat{G}^- \) are the advanced and retarded Green functions respectively [43].

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 [50].

**Transport in the fluctuating regime**

Here, we consider the transport of 2D fluctuating Cooper pairs above the critical temperature in a superconductor [51]. A fluctuating Cooper pair can be treated as a carrier with charge \( q = 2e \), where \( e \) is the charge of the electron.

The expression for the relaxation time of 2D fluctuating Cooper pairs reads:

\[ \tau_{cp} = \frac{\tau_{GL}(\varepsilon)}{1 + \xi(\varepsilon) |p|^2}, \]

where \( p \) is the momentum, \( \xi \) is the fluctuating Cooper pair size, and \( \tau_{GL} = \pi \hbar / 8 k_B (T - T_c) \) 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 [51], and \( \varepsilon = \ln T/T_c \approx (T - T_c)/T_c \).

The existence of fluctuating Cooper pairs above \( T_c \) yields to a pair contribution to electrical conductivity \( \sigma_{cp} \), which is also called paraconductivity [51]. The thermal conductivity \( \kappa_{cp} \) of fluctuating Cooper pairs can be
calculated as the response to the applied temperature gradient [53]. However, one can calculate it more simply, based on the theory of heat transport [51]. The Seebeck coefficient can be found based from its basic definition $\alpha = -\frac{\mu}{k_B}$. Thus, the transport coefficients of fluctuating Cooper pairs above the critical temperature $T_c$ read:

$$\sigma_{cp} = \frac{e^2}{16\hbar} \frac{1}{\varepsilon}$$ \hspace{1cm} (20)

$$\alpha_{cp} = \frac{\alpha_{GL} k_B}{2e} \ln \frac{\varepsilon}{\epsilon}$$ \hspace{1cm} (21)

$$\kappa_{cp} = \frac{k_B^2 \alpha_{GL}^2}{64\hbar} T_c \ln \frac{1}{\varepsilon}$$ \hspace{1cm} (22)

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 [51]. The thermal conductivity $\kappa_{cp}$ does not show any singularity near the transition [51][53].

The combination of Eqs. (20)-(22) leads to the figure of merit $Z_{cp}T$:

$$Z_{cp}T = \frac{1}{\varepsilon^2} \ln \frac{1}{\varepsilon}$$ \hspace{1cm} (23)

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

$$L_{cp} = \frac{\alpha_{GL}^2}{4} \left( \frac{k_B}{e} \right)^2 \times \left( \frac{T - T_c}{T_c} \right)^2 \ln \left( \frac{T_c}{T - T_c} \right)$$ \hspace{1cm} (24)

which clearly deviates from the standard Lorenz number: $L = \kappa/(\sigma T) = \pi^2/3(k_B/e)^2$. As $T \to T_c$, $L_{cp} \to 0$.

**Additional ZT v. $Z_{th}T$ curves**

The thermoelectric 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) to obtain $Z_{th}T$ and $Z T$. 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. 4 show a monotonic behavior. It is interesting to note that for the OD 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.

To introduce defects into the 100-nm-thick Ba(Fe0.90Co0.10)2As2 thin film deposited on the CaF2 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. 5a) and recoil atoms (see Fig. 5b) 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) 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 5 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.

Figure 5 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.

\[ \text{FIG. 5. a) Simulated ion trajectories in a 25 nm thick } \text{Ba}_2(\text{Fe}_{0.90}\text{Co}_{0.10})_2\text{As}_2 \text{ compound as calculated with SRIM-2008. Left: The black arrow depicts the direction of the incoming Ar ion beam. Red dots depict projectile positions until the ion is finally stopped (black dot), here for } 200 \text{ projectiles. For clarity, recoil atoms have been omitted. b) The extension of the damaged zone into the thin film can be estimated by overlaying a sufficient number of simulated trajectories, here 5000. Recoil atoms are plotted as well using the following colour code: Ba green, Fe blue, Co pink, As orange.} \]

\[ \text{FIG. 6. Thermoelectric transport characterization of the 100 nm } \text{Ba(Fe}_{0.90}\text{Co}_{0.10})_2\text{As}_2 \text{ thin film showing the Seebeck coefficient } \alpha \text{ and electrical resistivity } \rho \text{. a) high structural quality before ion bombardment, and b) low structural quality after ion bombardment.} \]
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