

Enhancement of the Na_xCoO_2 thermopower due to electronic correlations

P. Wissgott,¹ A. Toschi,¹ H. Usui,² K. Kuroki,² and K. Held¹

¹*Institute for Solid State Physics, Vienna University of Technology, 1040 Vienna, Austria*

²*University of Electro-Communications, 1-5-1 Chofugaoka, Chofu-shi, Tokyo 182-8585, Japan*

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Using the merger of local-density approximation and dynamical mean-field theory, we show how electronic correlations increase the thermopower of $\text{Na}_{0.7}\text{CoO}_2$ by 200%. The newly revealed mechanism is an asymmetric shift of (quasi) electrons and holes away from the Fermi level, concurrent with an asymmetry of the respective (group) velocities. Exploiting this effect in band structure and correlation engineering may lead to a substantial increase in the thermoelectric figure of merit.

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Climate change and the prospective oil peak necessitate the discovery of new green-energy sources. One possibility in this context is to convert hitherto unused excess heat into electrical energy using thermoelectrics.¹ For a real breakthrough and a widespread application of this technology, however, thermoelectric figures of merit $ZT \geq 3$ are needed.^{2,3} Recently, some advance was brought about through phonon⁴ and band-structure engineering⁵ so that $ZT \geq 1$ could be achieved. Pushing ZT much higher requires, however, a thermoelectric leap, which is most likely brought about by discovering a new class of materials, at least in the case of (high- T) superconductivity scientific progress went along this line with the discovery of novel correlated materials. At commercially available $ZT \lesssim 1$, thermoelectrics are already applied in niche markets such as radioisotope power systems for satellites⁶ where reliability is more important than efficiency and the car industry is taking encouraging first steps to use thermoelectrical generators.⁷ The materials presently used in industry are mainly Te based and have been investigated most thoroughly⁸ with respect to optimizing their thermoelectric properties, including the aforementioned phonon⁴ and band-structure engineering.⁵

The good thermoelectric properties of Te-based materials are related to their physics of slightly doped semiconductors with a low-effective mass and high mobility of the charge carriers.^{2,8} A possible improvement are compounds with a pudding-mold type of band structure as those of Na_xCoO_2 (Ref. 9) and LiRh_2O_4 ,¹⁰ two oxides with remarkably good thermoelectric properties.¹¹⁻¹⁴

Another route to good thermoelectric properties is through electronic correlations^{15,16} which can renormalize bands most substantially so that narrow quasiparticle bands with a high density of states emerge. The renormalization factor is most dramatic in heavy-Fermion systems which have particularly narrow Kondo resonances, modeled, e.g., by a periodic Anderson model.¹⁷ While one might expect the narrowest resonances to be most suitable for thermoelectrics, there is a trade-off since increasing the temperature T above the Kondo temperature (essentially the resonance width) will eventually smear out the resonance itself.

In this Rapid Communication, we demonstrate by means of Na_xCoO_2 , which already has a favorable pudding-mold band structure, that the complementary effect of electronic correlations can dramatically increase the thermopower, see Fig. 1. Needed are inequivalent orbitals or sites so that elec-

tronic correlations can change the “particle-hole balance” of the system drastically, shifting more electrons away from the Fermi level than holes.

For treating electronic correlations and band-structure effects on an equal level, we employ the LDA+DMFT, i.e.,

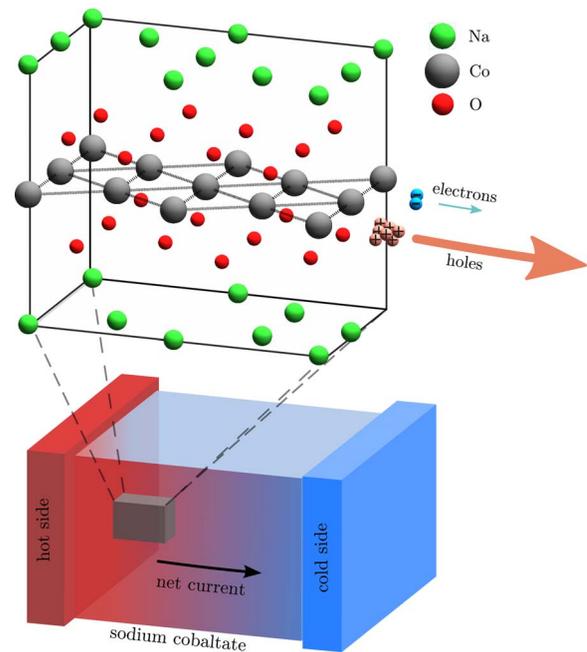


FIG. 1. (Color online) Scheme of a Na_xCoO_2 thermoelectric module and its crystal structure. The charge carriers are confined to the hexagonal layers of Co atoms, which are inequivalent because of the (disorderly distributed) Na ions above and below. If we apply a heat gradient, electrons, and holes alike are diffusing from the hot to the cold side resulting typically in a very small net current. For a good thermoelectric, we need however a large net current, i.e., a huge asymmetry between electron and hole diffusion. Due to the pudding-mold band structure in Na_xCoO_2 , the group velocity of the holes is already considerably larger than that of the electrons, as indicated by the larger arrow. Electronic correlations additionally shift electrons away from the Fermi level, as visualized by the fewer electrons and the narrower width of the arrow. As both effects add up, the electron is much smaller than the hole current leading to the net current displayed and hence to the good thermoelectric properties of Na_xCoO_2 .

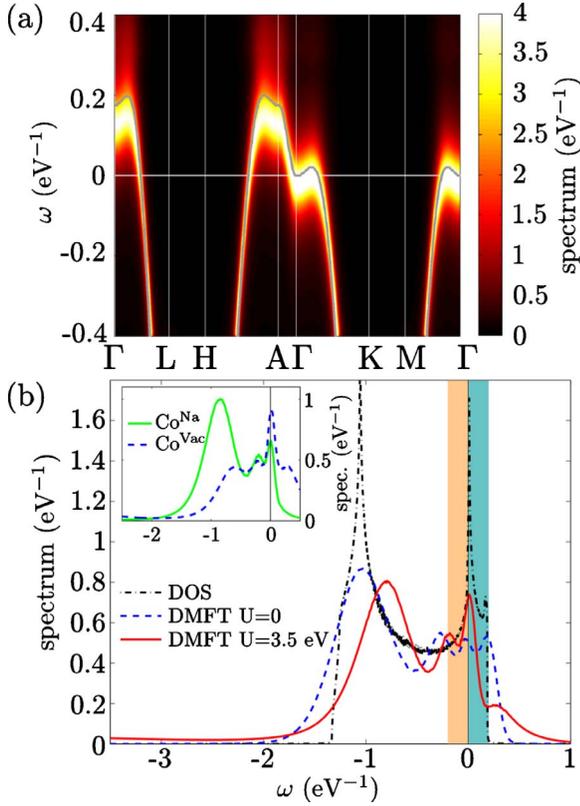


FIG. 2. (Color online) (a) LDA+DMFT k -resolved spectrum of $\text{Na}_{0.7}\text{CoO}_2$ at 290 K around the chemical-potential level ($\omega \equiv 0$), along with the tight-binding band extracted from the LDA calculation (light gray). (b) LDA+DMFT k -integrated spectra for $T=290$ K and $x=0.7$ with and without interaction U and disorder potential $\Delta\varepsilon$ (dashed-dotted line: $U=0$, $\Delta\varepsilon=0$; dashed line: $U=0$, $\Delta\varepsilon=0.55$ eV; and solid line: $U=3.5$ eV, $\Delta\varepsilon=0.55$ eV). For fixed $U=0$, an increasing disorder potential $\Delta\varepsilon=0 \rightarrow 0.55$ eV leads to more symmetric but lower spectral weight in the highlighted interval $\pm 8k_B T$ around the Fermi level. For fixed $\Delta\varepsilon=0.55$ eV, increasing $U=0 \rightarrow 3.5$ eV recovers spectral weight on the hole side $\omega < 0$ whereas electrons $\omega > 0$ lose spectral weight in the relevant (highlighted) area. The inset shows the k -integrated spectra at the two inequivalent lattice sites with and without an adjacent Na^+ ($T=290$ K, $U=3.5$ eV, and $\Delta\varepsilon=0.55$ eV).

the merger of local-density approximation (LDA) and dynamical mean-field theory (DMFT)^{18–20} and calculate thermoelectric response functions as described in Ref. 21. Previous LDA+DMFT calculations for Na_xCoO_2 (Refs. 22–24) focused on the spectral function, whereas we naturally aim at the transport properties of this material. Starting point is a tight-binding fit to the LDA band structure²⁵ for the Co a_{1g} band within the hexagonal CoO_2 layers, see Fig. 1. Considering transport properties (e.g., the thermopower S), the other d bands can be neglected at a first approximation. In fact, LDA predicts already that these bands are almost filled and this result is also confirmed experimentally since e_g hole pockets are absent in angular-resolved photoemission spectroscopy.^{26,27} There are $x < 1$ Na^+ ions per formula unit, which we consider to be randomly distributed with a Na atom or vacancy in trigonal prismatic coordination to the Co sites. As it has been suggested in Ref. 23, this gives rise to a

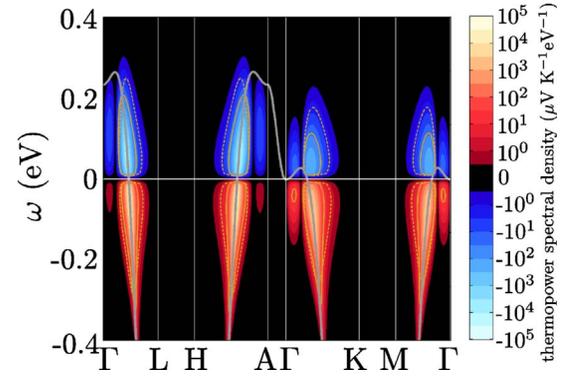


FIG. 3. (Color online) Thermopower spectral density $s(k, \omega)$ for $T=290$ K, $U=3.5$ eV, and $\Delta\varepsilon=0.55$ eV together with the tight-binding band extracted from the LDA data (gray solid line). Positive values $s > 0$ (red for $\omega < 0$) contributed by holes dominate negative values $s < 0$ (blue for $\omega > 0$) contributed by electrons. The electronic contribution is more sensitive to correlation which is emphasized by the values $s = \pm 10^2 \mu\text{V K}^{-1} \text{eV}^{-1}$ highlighted by an isocurve, comparing $U=3.5$ eV (solid) and $U=0$ (dashed).

disorder potential on the Co sites since the positively charged Na^+ attracts the Co electrons. This disorder potential is of essential importance for the strong electronic correlations of the Co d electrons and as in Ref. 23, we take a disorder potential of $\Delta\varepsilon=0.55$ eV. Our resistivity calculation (inset of Fig. 4) *a posteriori* confirms that a disorder potential of this strength is present; otherwise the experimental value of the resistivity at room temperature, mainly due to the disorder (and not to the electron-electron scattering) could not be explained.²⁸ Our model Hamiltonian hence reads

$$H = - \sum_{(ij),\sigma} t_{ij} c_{j\sigma}^\dagger c_{i\sigma} + U \sum_i c_{i\uparrow}^\dagger c_{i\uparrow} c_{i\downarrow}^\dagger c_{i\downarrow} + \Delta\varepsilon \sum_{i \in \text{vac},\sigma} c_{i\sigma}^\dagger c_{i\sigma},$$

where $c_{i\sigma}^\dagger$, $c_{i\sigma}$ are creation and annihilation operators of the a_{1g} electrons with i the site index and σ the spin index and t_{ij} denotes the hopping parameter from site i to site j , obtained from a tight-binding fit to LDA data.^{25,29} For the Coulomb repulsion within the a_{1g} orbitals we take a value $U=3.5$ eV and for the Na-disorder potential $\Delta\varepsilon=0.55$ eV as in Ref. 23. As a DMFT impurity solver we use quantum Monte Carlo simulations, where the Na disorder is included at the level of the coherent-potential approximation. For the calculation of the response functions we proceed as in Ref. 21 using a Taylor fit to extract the low-energy behavior of the self-energy on the real axis.

Figure 2 shows our k -resolved and k -integrated spectral function. For example along path $\text{H}\Gamma\text{K}$ through the Brillouin zone, the LDA band structure $\varepsilon(k)$ [gray line in Fig. 2(a)] vaguely resembles the form of a pudding mold. The advantage of the pudding-mold band structure is the highly asymmetric group velocity of the electrons and holes above and below the Fermi level, respectively. This velocity is given by the slope $v_g(k) = \partial\varepsilon(k)/\partial k$ which, because of the pudding mold, dramatically changes at the Fermi level at least in the ΓK direction (not so much along HA). The LDA density of states, on the other hand, is higher above the Fermi level (for electrons) than below (for holes), see Fig.

TABLE I. Thermoelectric and transport properties for single-crystalline Na_{0.7}CoO₂ at 290 K. For the computed figure of merit $Z = S^2/\rho(\kappa_{ph} + \kappa_e)$, we take the experimental phononic thermal conductivity $\kappa_{ph} = 66$ mW/cm K (Ref. 32). The electronic part of the thermal conductivity κ_e is calculated with the correlation functions from Eq. (1) and estimated experimentally by the Wiedemann-Franz law. Note that there are no free parameters and that only disorder ($\Delta\epsilon$) and correlation (U) together describe all experimental values reasonably well.

Parameters	ρ (m Ω cm)	S (μ V/K)	κ_e (mW/cm K)	S^2/ρ (μ W/K ² cm)	Z (10 ⁻³ K)	ZT
$U=0, \Delta\epsilon=0$	0.21	54	36.8	13.8	0.135	0.039
$U=3.5$ eV, $\Delta\epsilon=0$	0.31	66	27.4	13.7	0.146	0.042
$U=0, \Delta\epsilon=0.55$ eV	2.51	25	2.9	0.2	0.004	0.001
$U=3.5$ eV, $\Delta\epsilon=0.55$ eV	1.37	63	6.5	2.9	0.040	0.012
Experiment	1.04 (Ref. 31)	64 (Ref. 13)	4.0 (Ref. 32)	3.9 (Refs. 13 and 31)	0.053 (Refs. 13, 31, and 32)	0.015 (Refs. 13, 31, and 32)

2(b). Hence, the asymmetry in v_g which increases the thermopower S is partially compensated by the asymmetry in the density of states. In Fig. 1 there would be, on the LDA level, more electrons than holes contributing.

The thermoelectric figure of merit is defined as $ZT = S^2/(\rho\kappa)T$ with the temperature T , the electrical resistivity ρ , and the thermal conductivity $\kappa = \kappa_{el} + \kappa_{ph}$ where κ_{el} , κ_{ph} denote the electronic and phononic contributions, respectively. By use of Kubos formulas in DMFT,³⁰ one finds $\rho = 1/K_0$, $S = -\frac{k_B K_1}{T K_0}$, and $\kappa_{el} = (K_2 - K_1^2/K_0)/T$ with the correlation functions

$$K_n = (-1)^{n+1} \frac{2\pi e^{2-n}}{V} \sum_k v_g^2(k) \int d\omega A^2(k, \omega) \frac{\partial f}{\partial \omega} \omega^n, \quad (1)$$

where V is the unit-cell volume, $f(\omega)$ is the Fermi-Dirac distribution function. Comparing Eq. (1) for $n=0$ and $n=1$, it becomes clear that due to the factor ω in K_1 , electron ($\omega > 0$), and hole contributions ($\omega < 0$) push S in opposite directions. A high-electron-hole asymmetry is hence mandatory for getting a large $|S|$.

Before turning to the electronic correlations, let us first discuss the effect of disorder [dashed line of Fig. 2(b)], not yet switching on the interaction U . As one can see, the spectral weight around the Fermi energy is smeared out because of the disorder and the spectral weight is most dramatically reduced. As one might expect from Eq. (1), this is very unfavorable for the thermopower. Actually, it is reduced from the disorder-free value⁹ to only $S = 25$ μ V/K without interaction U . In Fig. 1, we visualize this by a narrower arrow for both electron and hole contribution and a smaller net current.

This radically changes if electronic correlations are taken into account. Their effect can be best understood by hands of the inset of Fig. 2(b), which shows the k -integrated Co spectrum locally resolved for sites with and without an adjacent Na⁺ ion. The Coulomb interaction drive the vacancy-adjacent Co sites more toward half filling. Consequently, electronic correlations become stronger which reflects in the sharp quasiparticle resonance and Hubbard-like side bands. In contrast, the Na⁺-adjacent Co sites become almost completely filled and are only weakly correlated. Together, the shift of the Na⁺-adjacent Co spectrum below the Fermi en-

ergy and the strong renormalization of the vacancy-adjacent Co sites yields a higher spectral weight on the hole than on the electron side. This asymmetry now *adds* to the $v_g(k)$ asymmetry, in stark contrast to the original LDA spectral weight. Note, that the velocities itself are, to first order, not renormalized by the electronic correlations since these are a property of the underlying LDA orbitals. A complete overview of the effect of disorder and correlation on the transport properties is given in Table I.

To further illustrate the changes induced by correlation, we introduce a thermopower spectral density $s(k, \omega) = -\frac{k_B}{TK_0} \frac{2\pi e}{V} v_g^2(k) A^2(k, \omega) \frac{\partial f(\omega)}{\partial \omega} \omega$, which integrated over k and ω yields the thermopower S (Fig. 3). The contour lines show that, upon (artificially) switching on the proper U , thermopower spectral weight is taken away from the electron side. As one can see in Fig. 2(b) it is transferred further away from the Fermi level. In contrast, the reduction in spectral weight on the hole side is much smaller and close to the Γ point $s(k, \omega)$ is even enhanced. This correlation-induced electron-hole imbalance strongly enhances the thermopower (S increases by 200% with respect to the case of $U=0$).

Finally, we present in Fig. 4 the calculated thermopower S as a function of T for various doping; the corresponding

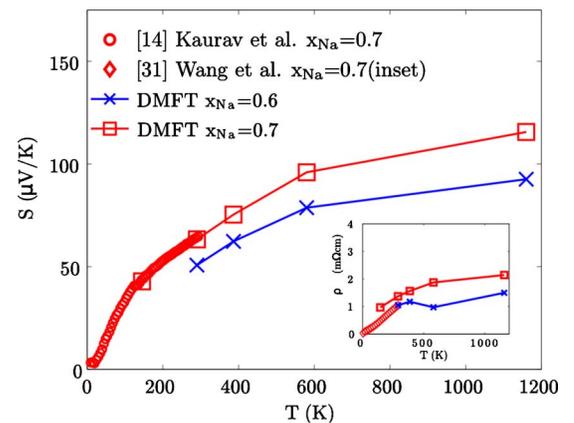


FIG. 4. (Color online) Thermopower S as a function of temperature for different doping $x=0.6, 0.7$ showing good agreement to the experiment of Kaurav *et al.* (Ref. 13). The inset shows the corresponding result for the resistivity compared to experiments by Wang *et al.* (Ref. 31).

resistivity is shown in the inset. Our LDA+DMFT results agree well with experiment for both quantities including the doping and T dependence. The large thermopower of Na_xCoO_2 originates from the pudding-mold band structure and is further enhanced by electronic correlations. The physical mechanism for the large resistivity on the other hand, is the disorder scattering.

From our calculations we conclude that Na_xCoO_2 is far from optimal for thermoelectric properties. On the band-structure side, there is still no strong electron-hole asymmetry for the group velocities in the $\bar{\Gamma}\text{L}$ and $\bar{\text{H}}\text{A}$ direction due to the three dimensionality, see Fig. 2. Hence, the electron contribution [blue, $\omega > 0$ in Fig. 3] still reduces the thermopower considerably. This can be improved by band-structure engineering the pudding-mold form, e.g., by expanding the c -axis length via intercalation. Second, disorder broadens the LDA substantially and dramatically decreases the Seebeck coefficient as well as the conductivity $\sim 1/\rho$. There is hence a high potential for further increasing S , e.g., by realizing a similar physical situation on the basis of inequivalent orbitals or superstructures without disorder. Last, but not least, we have

shown the crucial role correlation can play, not only because of the narrowing of the coherent excitations but also in strengthening the particle-hole imbalance. Given the high sensitivity of correlated systems to small changes in the external conditions and recent advances in engineering man-made heterostructures of correlated materials, there is plenty of room for improving this correlation effect further.

We can thus conclude from our study of transport properties in Na_xCoO_2 that, if properly combined, band structure and correlation effects (as those present in transition metal d and rare earth f orbitals) can considerably improve the thermoelectric properties of materials. Jointly, engineering band structure and correlations hence opens a new route to further enhance S (and possibly ZT) up to the levels required for a widespread technological applications.

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