Effects of electronic correlations and disorder on the thermopower of Na$_2$CoO$_2$

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For the thermoelectric properties of Na$_2$CoO$_2$, we analyze the effect of local Coulomb interaction and (disordered) potential differences for Co-sites with adjacent Na-ion or vacancy. The disorder potential alone increases the resistivity and reduces the thermopower, while the Coulomb interaction alone leads only to minor changes compared to the one-particle picture of the local density approximation. Only combined, these two terms give rise to a substantial increase of the thermopower: the number of (quasi-)electrons around the Fermi level is much more suppressed than that of the (quasi-)holes. Hence, there is a particle-hole imbalance acting in the same direction as a similar imbalance for the group velocities. Together, this interplay results in a large positive thermopower. Introducing a thermoelectric spectral density, we located the energies and momenta regions most relevant for the thermopower and changes thereof.

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The efficient conversion between different forms of energy represents a primary task in technical applications. Thereby the arguably most valuable form is electrical energy. On the other hand, heat energy is widely used in power plants to produce mechanical energy which is then further converted to electricity. The reason for the widespread application of this multiple-step process is based on the lack of an efficient direct alternative.

A direct heat-electricity conversion is possible by the thermoelectric effect or thermopower. The (dimensionless) thermoelectric figure of merit $ZT$ has been established as a benchmark to compare different materials. Values of $ZT \sim 3$ appear to be necessary to trigger an extensive industrial use of thermoelectric devices, which could then not only replace traditional methods of energy production but could also increase the efficiency of existing technical implementations such as car or power plants via the conversion of excess heat to electricity.

The development of novel thermoelectric applications follows two routes: First, there is the search for new materials with a large intrinsic $ZT$ which can either be achieved by optimizing features of already known compounds (via e.g. bandstructure engineering) or by the discovery of new classes of materials with peculiar properties (e.g. Kondo system). Second, one tries to diminish phonon losses of the thermopower which can be done by avoiding collective excitations of the crystal by a specific structural arrangement (phonon engineering) such as heterostructures.

Opposed to other transport properties, as for example the electrical conductivity, the magnitude of the thermoelectric effect depends on an asymmetry between the two charge carriers holes and electrons. This asymmetry usually manifests itself in different velocities and/or spectral densities in the vicinity of the chemical potential.

In this paper, we investigate the thermoelectric properties of Na$_2$CoO$_2$ taken as a representative compound where the already favorable single-electron features are enhanced by the combination of strong electronic correlations and disorder. We extend the analysis of a previous work$^9$ exploring the dependence of the thermopower on various parameters, one at a time as well as combinations of two of them, e.g. disorder and correlation strength at the same time.

As a non-interacting starting point we used the local density approximation (LDA) result from Ref.$^{10}$ fitted to a tight-binding bandstructure. Already at the level of LDA the thermoelectric performance of Na$_2$CoO$_2$ was found to be high and was understood in terms of the pudding mold shape of the decisive $a_{1g}$ band.$^{11}$ Here, we want to analyze the effects of electronic correlation in this compound and therefore we have combined LDA with dynamical mean field theory (DMFT). The LDA+DMFT approach is described in Refs.$^{12,13}$ and we proceed as in Ref.$^{18}$ to compute the thermoelectric response. We focused on the low-energy excitations which give the main contributions to the thermopower. Earlier LDA+DMFT studies on the spectral properties of Na$_2$CoO$_2$ can be found in Refs.$^{19,23}$

In Fig.$^1$ we show a summary of the main results described in this study: Considering neither disorder nor correlations, the charge carrier properties are described by the “pudding mold” band which favors electrons in terms of spectral density, but favors holes with respect to group velocity. The latter effect is larger so that hole transport dominates and we get a positive value of the thermopower $S$, Fig.$^1$ (left panel). Introducing disorder to the system increases the scattering rate of both charge carriers thus diminishing $S$, Fig.$^1$ (middle panel). If we additionally take into account electronic correlations, the hole spectral density is recovered and can be even over-compensated whereas the number of electrons is further decreased which overall yields a high thermoelectric response, Fig.$^1$ (right panel). For a more quantitative picture, refer to Fig.$^2$ where the change of $S$ in the parameter space of correlation $U$ and disorder $\Delta \varepsilon$ is visualized.
FIG. 1: (Color online) Qualitative effect of disorder and electronic correlations on the charge carrier densities and the thermopower in Na\textsubscript{x}CoO\textsubscript{2}. On the vertical axis, energy in arbitrary units is shown with the Fermi level E\textsubscript{F} and electrons above and holes below. The horizontal axis schematically indicates the movement through the material with velocities and charge carrier density according to the length and width of the arrow, respectively. The presence of disorder and electronic correlations is visualized by scattering centers \(\Delta \varepsilon\) and the encirclement of the charge carriers accompanied by U, respectively.

FIG. 2: (Color online) Change of the thermopower S in the parameter space of local Coulomb repulsion U and disorder potential \(\Delta \varepsilon\) for Na\textsubscript{0.7}CoO\textsubscript{2} at \(T = 290\) K. The highlighted regions indicates realistic parameter values for this material. It can be seen that drastic changes happen for example for \(\Delta \varepsilon = 0.55\) eV where an increasing U leads to an enhancement of S by 200%. Moreover, for even larger values of \(\Delta \varepsilon\) and \(U = 3.5\) eV we found the maximal values of \(S = 80\) \(\mu\)V/K in the tested parameter space. Note that the system shows insulating tendency for similar values of \(\Delta \varepsilon \gtrsim 0.55\) eV and \(U = 0\). This implies that in correlated materials disorder effects may be exploited to enhance the thermopower.

The structure of this paper is as follows: In Sec. I we introduce the Hamiltonian of the model and describe how standard LDA+DMFT can be expanded by means of coherent potential approximation (CPA) to include disorder. In Sec. II we depict the linear response formalism to compute the thermopower S as a functional of spectral density, group velocity and temperature. Both sections present the necessary details for following our result which were naturally missing in the short paper Ref. [9].

Sec. III provides an insight to the structural and spectral properties of Na\textsubscript{x}CoO\textsubscript{2} missing in Ref. [9]. Additionally to the lattice structure, the employed tight-binding approximation is explained in detail. Confirming previous results from Ref. [11] the third nearest neighbor hopping appears to play a key role for the transport properties of this triangular compound. Disentangling the spectral contributions and the self energy from the two non-equivalent lattice sites due to disorder, it is shown that one of the two sites exhibits a much larger correlation effect than the other. A comparison of low energy spectral properties to experiment concludes this section. In Sec. IV the main results for the thermopower are presented. The method of visualization of spectral contributions to the thermopower introduced in Ref. [9] is described in detail as well as new ways to simplify the theoretical thermoelectric analysis. In an effort to distinguish between the parameters temperature, disorder and electronic correlation, we investigate their influence on the thermopower with the respective other parameters fixed. It is revealed that the system is very sensitive to small changes of disorder. The impact of correlations on the transport properties is directly connected to the strength of the disorder which can be seen in a detailed spectral analysis. Towards the end of this section, the dependence of the thermopower on a change of the sodium doping is delineated. Increasing the doping within the investigated doping region appears to increase the thermoelectric effect which is also supported by experimental results. Finally, we give a conclusion in Sec. V.

I. LDA+DMFT APPROACH INCLUDING CPA

We aim to model Na\textsubscript{x}CoO\textsubscript{2} with binary disorder, which corresponds to consider two different sites \(a, b\) with an occurrence of \(x_a, x_b = 1 - x_a\). In comparison to the standard one-band Hubbard model[23] the disorder
Hamiltonian

\[ H_{\text{dis}} = -\sum_{ij,\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \Delta \varepsilon \sum_{i \in b} n_i \]  

(1)

includes a term contributing only on the site \( b \) by a disorder potential \( \Delta \varepsilon \). Here, \( c_{i\sigma}^{\dagger} \) and \( c_{i\sigma} \) create and annihilate an electron on site \( i \) with spin \( \sigma \), respectively, \( n_{i\sigma} := c_{i\sigma}^{\dagger} c_{i\sigma} \) is the electron density on site \( i \) for the spin \( \sigma \), \( U \) is the local Coulomb interaction.

For disordered systems the Coherent Potential Approximation (CPA) provides a way to treat inequivalent sites in the same spirit as DMFT. In the CPA, the sites \( a, b \) are assumed to be surrounded by a self-consistently determined effective medium. Both sites experience the same dynamical mean field, i.e. see the same (averaged) environment given by an impurity Greens function \( G_0^{-1} \) as defined in Ref. [17] or equivalently the same (coherent) potential represented by a self energy \( \Sigma \). Even though the mean field \( G_0^{-1} \) is the same, the disorder manifests in two different on-site energies \( \varepsilon_a = 0, \varepsilon_b = \Delta \varepsilon \) on the sites \( a \) and \( b \), respectively (Fig. 3).

In DMFT the dynamical mean field \( G_0^{-1} \) determines an action

\[ \mathcal{A} := \sum_{\sigma \omega_m} \psi_\sigma^{\dagger}(\omega_m) G_0^{-1}(\omega_m) \psi_\sigma(\omega_m) 
- U \sum_{\sigma} \int_0^\beta d\tau \psi_\sigma^\dagger(\tau') \psi_\sigma(\tau') \psi_\sigma^\dagger(\tau') \psi_\sigma(\tau'). \]  

(2)

where \( \psi^\dagger, \psi \) are creation and annihilation operators, respectively, \( \sigma \) is a spin index, \( \beta \) is the inverse temperature and \( \omega_m \) are Matsubara frequencies (see e.g. Ref. [17]). The inclusion of (disorder) CPA into DMFT is straightforward (see Fig. 3 for a schematic visualization): Assume for the moment that the effective medium \( G_0^{-1}(\omega_m) \) is known. Then, the local Greens functions \( G_a(\ell = 0, i\omega_m), G_b(\ell = 0, i\omega_m) \) can be determined via the action \( \mathcal{A} \) from (2) by replacing the standard \( G_0^{-1}(\omega_m) \) by \( (G_0^{-1}(\omega_m) - 2 \varepsilon_a) \) with different on-site energies \( \varepsilon_a = 0, \varepsilon_b = \Delta \varepsilon \). The local Greens functions \( G_a, G_b \) are the local interacting propagators of electrons starting at \( a, b \) and returning to the same site \( a \) or \( b \), respectively. Then, the total Greens function \( G(\ell = 0, i\omega_m) \) is given by the weighted mean

\[ G(i\omega_m) = x_a G_a(\omega_m) + (1 - x_a) G_b(\omega_m) \]  

(3)

such that both propagators \( G_a, G_b \) are taken into account according to the stoichiometric appearance of the corresponding site \( x_a \) or \( x_b \) in the lattice.

For the CPA expansion of the DMFT, the effective dynamic medium \( G_0^{-1}(\omega_m) \) is determined self-consistently. For a given \( G_0^{-1} \), we obtain the local Greens functions \( G_a, G_b \) by two Hirsch-Fye quantum Monte Carlo (HF-QMC) calculations with different on-site potentials \( \varepsilon_a = 0, \varepsilon_b = \Delta \varepsilon \). Then, the weighted \( G(i\omega_m) \) from Eq. (3) can be used to compute the new self energy \( \Sigma(\omega) \) or equivalently the new effective field \( G_0^{-1} \) via Dyson’s equation

\[ \Sigma(i\omega_m) = G_0^{-1}(i\omega_m) - G^{-1}(i\omega_m). \]  

(4)

With this approach we can include both correlations and disorder in a dynamical mean field scheme.

\section{Linear Response and DMFT Expressions for the Thermopower}

In linear response, the thermopower is defined as a ratio of two correlation functions \( K_1 \) and \( K_0 \)

\[ S = \frac{k_B}{T} \frac{K_1}{K_0} \]  

(5)

Here and throughout, \( T \) denotes the temperature. The determination of the correlation functions usually requires a representation of current operators in terms of the electric field operators \( \psi^\dagger, \psi \). The electrical current in imaginary time reads

\[ \tilde{j}(\tau, \tau') = \frac{i|e|}{2m} \left[ \psi^\dagger(\tau, \tau') \nabla \psi(\tau, \tau') - \nabla \psi^\dagger(\tau, \tau') \psi(\tau, \tau') \right], \]  

(6)

which can be found in many textbooks. On the contrary, the representation for the heat current has many subtleties and is derived via a continuity equation following Ref. [30]

\[ \tilde{\Theta}(\tau, \tau') = -\frac{1}{2m} \left[ \psi^\dagger(\tau, \tau') \nabla \psi(\tau, \tau') + \nabla \psi^\dagger(\tau, \tau') \psi(\tau, \tau') \right] \]  

(7)

where the dot denotes an (imaginary) time derivative. Then, the electrical-current-electrical-current correlation
function evaluates to (as vertex corrections are absent in single-band DMFT)

\[
K_0 = -\frac{2e^2 \pi \hbar}{V} \sum_k |\nabla \varepsilon(k)|^2 \int d\omega A^2(k,\omega) \frac{\partial f(\omega)}{\partial \omega}
\]

with \( V \) the unit cell volume, \( \hbar \nabla \varepsilon = \partial \varepsilon / \partial k \) the group velocity of the charge carriers, \( A(k,\omega) \) the electron spectral function and \( f(\omega) \) the Fermi function. Note that \( K_0 = \sigma \) has units of a conductivity \([A V^{-1} m^{-1}]\). On the other hand, the heat-current-electric-current correlation function reads

\[
K_1 = \frac{2|e|c_{\text{e}}V}{V} \sum_k |\nabla \varepsilon(k)|^2 \int d\omega A^2(k,\omega) \omega \frac{\partial f(\omega)}{\partial \omega}
\]

where \( c_{\text{e}}V = 11600 \text{ K/eV} \) and \( K_1 \) has units \([A J^{-1} K \text{m}^{-1}]\). Combining \( K_0 \) and \( K_1 \) leads to the thermopower

\[
S = \frac{-k_B \beta \sum_k |\nabla \varepsilon(k)|^2 \int d\omega A^2(k,\omega) \omega \frac{\partial f(\omega)}{\partial \omega}}{|e| \sum_k |\nabla \varepsilon(k)|^2 \int d\omega A^2(k,\omega) \frac{\partial f(\omega)}{\partial \omega}}.
\]

Note that this result is expressed in the correct units \([V/K] = [A J^{-1} K \text{m}^{-1}]\) (\( \beta \) times the fraction of \( K_1 \) and \( K_0 \) remains dimensionless).

For the integral in the denominator of Eq. \( \text{(10)} \), i.e. \( K_0 \), the contributions with respect to \( k \) and \( \omega \) enter additively, i.e. an asymmetry of \( |\nabla \varepsilon(k)| \) with respect to \( k \) or \( A(k,\omega) \) with respect to \( k, \omega \) is not important. The integral in the numerator of Eq. \( \text{(10)} \) \( (K_1) \) has an additional \( \omega \) and since \( df/d\omega \) is negative, \( |\nabla \varepsilon(k)|^2 A^2(k,\omega) \omega df/d\omega \) is positive for \( \omega < 0 \) (holes) and negative for \( \omega > 0 \) (electrons)\(^\text{24}\). Consequently, asymmetry of the group velocity \( |\nabla \varepsilon(k)| \) as well as the corresponding asymmetry of the spectrum \( A(k,\omega) \) are decisive for a high thermopower\(^\text{20}\).

In our model material \( \text{Na}_x\text{CoO}_2 \) this is accomplished by a low group velocity \( \nabla \varepsilon(k) \) for electrons, whereas holes move much faster through the system. For the band structure this means we have a flat region directly above \( \omega > 0 \) the Fermi level at \( \omega = 0 \) and a steep slope directly below \( \omega < 0 \). This is the feature usually denoted by “pudding mold” (cf. Ref. \( \text{11} \)).

From Eq. \( \text{(6)} \) it becomes clear that \( K_0 \) is always positive, since \( \partial f/\partial \omega \) is negative for all \( \omega \) and the other quantities only enter quadratically. At the same time \( K_1 \) may be either positive or negative depending whether the hole contribution \( \omega < 0 \) or electron contribution \( \omega > 0 \) dominate. This reflects obviously in the sign of the thermopower \( S \).

### III. Structure and Spectral Properties of Sodium Cobaltate

In 1997, Terasaki and coworkers\(^\text{11}\) identified \( \text{NaCo}_2\text{O}_4 \) (= \( \text{Na}_{0.5}\text{CoO}_2 \)) as a promising candidate for thermoelectric applications. Other publications confirmed the results of a positive thermopower of the order of \( 100 \mu \text{V/K} \) even for other sodium contents\(^\text{22}\). With appearance of superconductivity in the \( \text{H}_2\text{O} \) intercalated compound\(^\text{35,36}\), the material \( \text{Na}_x\text{CoO}_2 \) once again proved to exhibit surprising features.

Recently, Kuroki et al\(^\text{11}\) argued in favor of band structure properties playing the most important role in determining the thermopower in \( \text{Na}_x\text{CoO}_2 \). In their study, Kuroki and co-workers used Boltzmann’s equation to compute the Seebeck coefficient \( S(T) \). Here, we go beyond that approach and propose an “ab initio” method to compute \( S \) by means of linear response theory including correlations by DMFT and disorder by CPA (cf. Sec. \( \text{11} \) and \( \text{1} \) respectively). As representative compound, we choose a doping of \( x_{\text{Na}} = 0.7 \), i.e. \( \text{Na}_{0.7}\text{CoO}_2 \).

#### A. Lattice structure

In Fig. \( \text{4} \) we plot the crystal structure of the system. Sodium cobaltate \( \text{NaCo}_2\text{O}_4 \) consists of alternating layers of sodium and cobaltate \( \text{CoO}_2 \). The Co atoms are arranged in a trigonal lattice structure with a nearest-neighbor distance of 2.84 \( \text{Å} \), see Ref. \( \text{37} \). Each cobalt atom is surrounded by 6 oxygen atoms in form of a tilted oc-
FIG. 5: (Color online) The breakup of the degeneracy of the $d$ orbitals: First, the $5$ $d$ basis energetically split up in $3$ $t_{2g}$ orbitals and $2$ $e_g$ orbitals in an octahedral configuration. Second, the $3$ $t_{2g}$ orbitals split up in one $a_{1g}$ and $2$ $e_g'$ due to the distortion of the oxygen octahedra. The energy differences shown in this plot are symbolical. We also visualize the occupancy of the orbitals in the different situations, where oxidation state of the cobalt atom in the compound is $\text{Co}^{3+}$ ($\text{Co}^{4+}$) if a Na partner is (not) present. This additional electron whose presence depends on a sodium donor is shown as an arrow with different color.

tahedron. The Na atoms are located in their own layer half way between the CoO$_2$ layers.

The exact lateral position of the sodium atoms within their layer and mutual shifts of the CoO$_2$ layers, depend non-trivially on doping, temperature, etc. For example, Huang\cite{29} reports a change of the Na positions for $x_{Na} = 0.75$ around $T = 320$ K. On the other hand, an earlier work of Yakabe\cite{33} finds three typical phases of Na$_x$CoO$_2$ as $x_{Na}$ changes from $0.55$ to $1$. Since almost all of the transport takes place in the CoO$_2$ layers, mutual shifts of the cobaltate layers only weakly influence the thermopower results. We therefore assume the CoO$_2$ layers to be all equivalent, i.e. there is no structural shift. The lateral position of Na in the compound, on the other hand, is a delicate topic. Many Na coordinates have been reported, mainly the position directly above the Co atom ($x = 0$, $y = 0$) and a position which is aligned to the O atoms ($x = 2/3$, $y = 1/3$). Moreover, the former reference also suggests movement of the sodium ions.

For lower temperatures Zandbergen\cite{38} found two different types of Co atoms, namely $\text{Co}^{3+}$ and $\text{Co}^{4+}$. We therefore assume that the cobaltate system shows binary disorder, even if the sodium atoms are distributed on multiple sites. As we are interested in relatively high temperatures for thermoelectric applications, a possible ordering of the Na ions does not appear to be relevant\cite{39}. For simplicity, we assume the Na to be located on the ($x = 0$, $y = 0$, $z = 1/2$) site directly above the cobalt. Thus, we can still assign a Na atom to one specific Co site. This corresponds to the same ”virtual crystal approximation” which has been used for the underlying band structure calculation\cite{39}. For a doping of $x_{Na} = 0.7$, 70% of the sodium sites are actually occupied and we consequently have 30% vacancies in the sodium layers. The thereby inequivalent Co sites in the cobaltate layers are denoted by $\text{Co}_{Na}$ ($\approx \text{Co}^{3+}$) and $\text{Co}_{Vac}$ ($\approx \text{Co}^{4+}$) depending on whether they have a close sodium atom or not. As we will show below, electrons of one band with little $k_z$ dispersion are responsible for transport. We denote the filling of this band at the two different sites by $n_{Na}$ and $n_{Vac}$, respectively. Due to the disorder, these electrons tend to be at cobalt sites $\text{Co}_{Na}$ with a sodium partner, by means of simple electrostatic attraction to the Na$^+$ ionic cores. The strength of this tendency is governed by the disorder potential $\Delta\varepsilon$, i.e. the difference of the on-site potential of the two non-equivalent sites. Additionally, many-body effects can influence the movement of electrons and holes in the disordered crystal.

To determine the relevant energy bands in this material, it is vital to understand the crystal field splitting of the NaCoO$_2$ lattice. In this light, as part of a thought experiment, the gradual transition between the Co atomic orbitals and their bulk material analogs can be useful: The $5$ atomic $d$-orbitals can be classified according to $\epsilon_g$, $\epsilon_g'$ and $\epsilon_{2g}$ respectively. The basis energetically split up in $3$ $\epsilon_g$, $2$ $\epsilon_g'$, and $3$ $\epsilon_{2g}$ orbitals, but, on the other hand, the $\epsilon_{2g}$ orbitals pointing towards the oxygen octahedra become less favorable for electrons to occupy than in the atomic case.

Moreover, the O octahedra which surround the Co atom are distorted, cf. Fig. 1. One can show, that this does not lift the degeneracy of the $\epsilon_g$, but, on the other hand, the $\epsilon_{2g}$ states split up in $1$ $a_{1g}$ and $2$ energetically lower $\epsilon_g'$ orbitals. These $a_{1g}$ and $\epsilon_g'$ states do not correspond any longer to single $t_{2g}$ orbitals, but are rather linear combinations thereof. These considerations lead to the orbital structure visualized in Fig. 5.

When we go beyond a single Co site, the picture of local orbitals is not fully valid any more, but is rather replaced by bands representing a certain dispersion relation. Still, we can look for bands in the band structure which have predominant $a_{1g}$, $\epsilon_g'$, or $\epsilon_g$ orbital character and which arrange in the same energetic order as the orbitals in Fig. 5.

The band structure from Singh\cite{38} provided the starting point for the tight-binding approximation. To mimic dis-
order at the level of LDA, Singh used a NaCo$_2$O$_4$ supercell with twice as many bands due to the doubling of the unit cell. Following a different approach, we extract an approximation for one single $a_{1g}$ band of NaCo$_2$O$_4$ from the LDA result and include the disorder in a second step at the level of the DMFT algorithm, cf. Sec. II.

Corresponding to atomic valence orbitals, one also finds valence bands within a solid state compound. Analogously, very tightly bound “core bands” and, in the ground state unoccupied, “conductance bands” may be identified. In cobaltite, the valence bands are the 3 oxygen p-orbitals and the 3 cobalt d-$t_{2g}$-orbitals. Due to high electronegativity, the p-bands of O are well below the Co bands. On the other hand, the sodium s-orbitals belong to the conductance bands and are even above the unoccupied Co $e_g$-bands. The number of bands considered in the LDA+DMFT model strongly influences the computational effort necessary to solve it. Whereas the decrease to the complexity for the tight-binding approximation is not decisive, the effort for the DMFT calculations heavily depends on the number of bands. We aim therefore to minimize the number of orbitals, without losing (too much) physically relevant information.

The oxidation state of Co in the compound is +3 in NaCo$_2$O$_4$ and +4 in CoO$_2$, respectively. Thus, of the 9 valence electrons 6 and 5, respectively, actually fill the cobalt d bands. For transport properties a rather small energy interval of the order of $\mathcal{O}(k_B T)$ around the Fermi edge is important, since electrons in this regime can be thermally activated. Only the $t_{2g}$ bands are located within that interval (under normal conditions). In the following, we will assume that the hybridization of $e_g$ and $a_{1g}$ bands is negligible. With this assumption, the crystal field splitting visualized in Fig. 5 guarantees that the $e_g$ orbitals remain filled and that, for transport calculations, restricting to the partly occupied $a_{1g}$ orbital is sufficient.

To extract the two effective $a_{1g}$ bands from the band structure of NaCo$_2$O$_4$, Kuroki and Usui made a tight-binding fit, which is shown in Fig. 6. Since we aim to include only one $a_{1g}$ band in the DMFT, we have to find the corresponding single tight-binding band for NaCo$_2$O$_4$. Though NaCo$_2$O$_4$ is similar to NaCo$_2$O$_4$, there are subtle differences: Since the super cell for NaCo$_2$O$_4$ contains two Co atoms the corresponding Brillouin zone has half the size of the one for NaCo$_2$O$_4$ in z direction. Thus, the single $a_{1g}$ band will not match exactly one of the two bands for NaCo$_2$O$_4$ of the original fit. The lower band of the two highlighted bands mainly belongs to the cobalt site in NaCo$_2$O$_4$ with a sodium partner. As an approximation, we therefore take the tight-binding parameters for this band, but use the (larger) Brillouin zone of NaCo$_2$O$_4$ in DMFT. The final $a_{1g}$ band is shown in Fig. 6 together with the corresponding group velocities $\nabla \varepsilon^{TB}(k) = \{\vec{v}_x, \vec{v}_y, \vec{v}_z\}$.

In the following, we discuss the applied tight-binding approximation: Let the $a_{1g}$ band have the dispersion relation $\varepsilon^{LDA}(k)$ given by the data points which are the output of the LDA calculation. We now aim to replace $\varepsilon^{LDA}(k)$ by an analytic expression, which then can be easily used to obtain the group velocity $\nabla \varepsilon^{LDA}(k)$. To this end, we make a tight-binding ansatz with 9 parameters

$$
\varepsilon^{LDA}(k) \approx \varepsilon^{TB}(k) = \sum_{n=1}^{9} t_n \sum_{j=1}^{\#NN} e^{i \vec{k} \cdot \vec{r}_{jn}}, \quad (11)
$$

where $\#NN$ denotes the number of nearest-neighbors of $n$th order and $\vec{r}_{jn}$ enumerates the corresponding $n$th nearest-neighbor position. Due to inversion symmetry the
exponential function in (11) can be simplified as
\[ \varepsilon_{LDA}(k) \approx \varepsilon_{TB}(k) = 2 \sum_{n=1}^{9} t_n \sum_{j=1}^{N_{NN}} \cos(k \cdot r_{jn}). \] (12)

Here, \( N_{NN} \) means that the pairs of atoms connected by inversion symmetry are counted only once. The first 4 parameters \( t_1, \ldots, t_4 \) describe the hopping between nearest-neighbors within one Co-plane. The fifth parameter \( t_{z0} \) measures the probability of Co-interplane hopping from a cobalt atom to another cobalt directly above (below). The final 4 parameters \( t_{z1}, \ldots, t_{z4} \) describe processes of combined interplane and nearest-neighbor hopping.

The fitted set of parameters are listed in Table I. The final tight-binding fit of the a\( \Gamma \) regime this is the standard behavior for van-Hove peaks, up to the third nearest-neighbor is necessary to obtain the important upper van-Hove-like peak, which will play a role for the explanation of the large thermopower below. If we also consider interplane hopping (i.e. \( t_{z,i} \neq 0 \) the peak above \( \omega = 0 \) is less pronounced. Leaving the 2d regime this is the standard behavior for van-Hove peaks, which are usually damped in 3d with respect to lower dimensions. The final DOS is dominated by two major peaks which are approximately 1 eV apart.

| notation | intra/interlayer | NN | values(par.fit) |
|----------|-----------------|----|----------------|
| \( t_1 \) | intralayer | 1st | 0.1800 |
| \( t_2 \) | intralayer | 2nd | -0.0388 |
| \( t_3 \) | intralayer | 3rd | -0.0270 |
| \( t_4 \) | intralayer | 4th | 0.0004 |
| \( t_{z,0} \) | interlayer | - | -0.0180 |
| \( t_{z,1} \) | interlayer | 1st | -0.0049 |
| \( t_{z,2} \) | interlayer | 2st | -0.0016 |
| \( t_{z,3} \) | interlayer | 3rd | 0.0011 |
| \( t_{z,4} \) | interlayer | 4th | 0.0005 |

TABLE I: Tight-binding parameters obtained by a parameter fit to LDA data.

FIG. 8: (color online) Top: k-integrated spectra \( A(\omega) \) obtained by DMFT and maximum entropy method compared to the non-interacting DOS \( N(\omega) \). Bottom: he self energy \( \Im \Sigma(\omega) \) on the imaginary axis. Note that sodium and vacancy contributions are resolved.

B. LDA+DMFT self energy and spectrum of \( \text{Na}_{0.7}\text{CoO}_2 \)

With the tight-binding dispersion relation \( \varepsilon_{TB} \), we now run the DMFT algorithm depicted in Sec. IV For given temperature \( T \), correlation \( U \), doping \( x_{\text{Na}} \), and disorder potential \( \Delta \varepsilon \), we obtain the self energy \( \Sigma(\omega_m) \) at the Matsubara frequencies \( \omega_m = (2m + 1)\pi/T \), and the Greens function \( G(\tau) \). Here, and throughout this work, \( \beta \) denotes the inverse temperature in eV\(^{-1} \) defined by \( \beta := 11600/T \) eV\(^{-1} \). From the imaginary part of the self energy \( \Im \Sigma(\omega) \) we can extract information about the strength of correlation and disorder effects in the system. For example, a divergent
\[ \lim_{\omega \to 0^+} \Im \Sigma(\omega) = \pm \infty \] (14)
indicates that the charge carriers are localized which leads to an insulating phase. On the other hand, a correlated metal usually yields
\[ \lim_{\omega \to 0^+} \Im \Sigma(\omega) = 0, \] (15)
with a quasiparticle weight \( Z \neq 1 \).

In Fig. 8(bottom), we plot the self energy \( \Im \Sigma \) over the
Matsubara frequencies $\omega_m$ for our set of initial parameters

$$\{T = 290 \text{ K}, U = 3.5 \text{ eV}, x_{Na} = 0.7, \Delta \varepsilon = 0.55 \text{ eV}\}. \tag{16}$$

Note that here we employ similar parameters as in a previous LDA+DMFT calculation for Na$_x$CoO$_{22}$ which did, however, not analyze transport properties$^{13,14}$ At the first glance, the overall $\Sigma_{tot}$ shows characteristics of a bad metal since in the whole temperature range considered it neither diverges nor converges to 0 for $\omega \to 0$. Hence, the separation of correlation and disorder effects on $\Sigma$ needs further investigation. As a first step, we can also visualize the contributions of the two sites Co$_{Na}$ and Co$_{Vac}$ to the self energy $\Sigma_{tot}$. Following Sec. II, these contributions are computed via Dyson’s equation with the corresponding Greens function, i.e.

$$ \Sigma_{Na} = -G^{-1}_{0} + \Delta \varepsilon - G^{-1}_{Na}, \tag{17} $$

$$ \Sigma_{Vac} = -G^{-1}_{0} - G^{-1}_{Vac}, \tag{18} $$

$$ \Sigma_{tot} = -G^{-1}_{0} - G^{-1} \tag{19} $$

where $G = x_{Na}G_{Na} + x_{Vac}G_{Vac}$. We observe that the self energy $\Sigma_{Na}$ for the sites Co$_{Na}$ is metallic, the other contribution $\Sigma_{Vac}$ for Co$_{Vac}$ showing insulating tendency. Analogous to the self energy $\Sigma(i\omega)$ connected to the influence of correlation and disorder, the Greens function $G(\tau)$ provides information about the many-body excitations of the system, as the k-integrated spectrum $A(\omega)$ is given implicitly by

$$ G(\tau) = \int d\omega \frac{e^{\tau(\mu-\omega)}}{1 + e^{\beta(\mu-\omega)}} A(\omega). $$

To calculate the spectral functions, we employ the maximum entropy method (see for example Ref. 43,44). In Fig. 8 (top), we plot the total spectrum $A_{tot}(\omega)$ for the $a_{1g}$ band and compare it to the contribution of the two sites Co$_{Na}$,Co$_{Vac}$ as well as to the non-interacting density of states (DOS) $N(\omega)$. Note that we do not show here the lower Hubbard band at $\omega \approx -U = -3.5$ eV. At the first glance, the changes between the $N(\omega)$ to $A_{tot}(\omega)$ are not significant. But since two contributions $A_{Na}$, $A_{Vac}$ with two different electron fillings

$$ n_{Na} = 2 \cdot 0.91, n_{Vac} = 2 \cdot 0.71 \quad (n_{tot} = 2 \cdot 0.85 = 1 + x_{Na}) \tag{20} $$

mix, a separate investigation of the two spectra is useful (note that $n_{Na}x_{Na} + n_{Vac}x_{Vac} = n_{tot}$). On Co$_{Na}$ sites, the $a_{1g}$ band is almost filled, whereas on Co$_{Vac}$ the value is closer to half filling, where correlation effects are expected to be stronger. In fact, as can be seen in Fig. 9 the formation of a quasiparticle peak at $\omega = 0$ and a lower Hubbard band at $\omega \approx -U = -3.5$ eV in the spectrum $A_{Vac}$ for the sites Co$_{Vac}$ can be observed. Especially the Fermi liquid behavior for small $\omega$, may be a decisive ingredient for higher thermopower, since the spectral weight in the thermally activated energy interval is crucial as already discussed in Sec. II. This analysis indicates that disorder enhances the effect of correlations in the compound driving the sites Co with Na vacancy, closer to half filling. As a consequence, the quasiparticle peak for a given correlation $U$ is more pronounced than in the case without disorder.

Analogously to the filling, one can also investigate the
approximate renormalization of the two bands

\[ Z_{\text{Na}} = 0.88, Z_{\text{Vac}} = 0.36 \quad (Z_{\text{tot}} = 0.48), \]

which was obtained from \( 3 \Sigma(i \omega_n) \) by using the tangent of the two Matsubara frequencies closest to the origin. This values should be considered with caution, since the disorder perturbs the Fermi liquid behavior at both sites \( \text{CoNa} \) and \( \text{CoVac} \). However, as Fig. [0] indicates, \( \text{Na}_{0.7}\text{CoO}_2 \) can be interpreted as a system consisting of sites with large correlations \( \text{CoVac} \), and sites \( \text{CoNa} \) where correlation effects are weak.

Apart from the k-integrated spectrum \( A(\omega) \), we are also interested in the k-resolved quantity \( A(k, \omega) \), that is inserted in Kubo’s formula [10]. Therefore, we need an analytic continuation \( \Sigma(i \omega_n) \rightarrow \Sigma(\omega) \), which is, in general, non-trivial. The behavior of \( \Sigma(\omega) \) further away from the Fermi level is not important for transport properties and a Taylor fit is hence sufficient. With the self energy \( \Sigma(\omega) \) the spectrum is calculated as

\[ A(k, \omega) = -\frac{1}{\pi} \frac{\Im(\Sigma(k, \omega))}{[\omega + \mu - \epsilon(k) - \Re(\Sigma(k, \omega))]^2 + [\Im(\Sigma(k, \omega))]^2}, \]

where \( \mu \) is the chemical potential from the DMFT calculation.

A visualization of the approximation for \( A(k, \omega) \) compared to the tight-binding band can be found in Fig. [10].

Let us remark here that it cannot be expected that the electronic structure or spectra match the experimental results (inset taken from Ref. [45]). The two slopes in the inset with the experimental results shows.

![Fig. 11: (color online) Top: Comparison of the spectrum \( A(\omega) \) to ARPES results, inset taken from Ref. [45]. In experiment, the peaks correspond to \( a_{1g} \) excitations. Bottom: k-integrated spectrum \( A(\omega) \) and corresponding experimental results (inset taken from Ref. [45]). The two slopes in the inset are spectra for different photon energies. For comparison, a linear background signal for \( \omega < -0.2 \) eV has been added by hand to the numerical results.](image)

### IV. THERMOPOWER

In order to understand the influence of temperature, disorder, correlations and doping on the self energy and the thermopower, in this section we will investigate their effect separately with the other parameters kept fixed. For disorder and correlations, however, it is revealed that their effect strongly depends on the respective other parameter. We therefore discuss combined effects of disorder and correlations in an own subsection. Before starting with the first parameter, let us introduce some helpful quantities which will be helpful in the analysis. In Sec. [1] we derived the expression \( S(T) \sim K_1/K_0 \) for the thermopower. The pivotal quantity which we now focus on, is \( K_1 \) depicted in Eq. [9] and therein especially the kernel as a function of \( (k, \omega) \). In most of the cases, changes of \( K_1 \) directly reflect on the thermopower \( S \). If we separate the factors in the kernel for the initial parameters [16], we arrive at contributions visualized in Fig. [12]. Investigating these contributions can lead to a deeper understanding of the important processes in thermoelectric transport. In order to factorize the total kernel \( K_{\text{tot}} \), we define 5...
auxiliary functions of $k$ and $\omega$

$$K_1(k, \omega) := \frac{\partial f(\omega, T)}{\partial \omega},$$  \(23\)

$$K_2(k, \omega) := \frac{\partial f(\omega, T)}{\partial \omega},$$  \(24\)

$$K_3(k, \omega) := |\nabla \varepsilon(k)|^2, \quad \omega, \quad \quad 25\)

$$K_4(k, \omega) := |\nabla \varepsilon(k)|^2 \frac{\partial f(\omega, T)}{\partial \omega} \omega, \quad \omega, \quad \quad 26\)

$$K_5(k, \omega) := A^2(k, \omega) \frac{\partial f(\omega, T)}{\partial \omega}, \quad \omega, \quad \quad 27\)

$$K_{tot}(k, \omega) := \frac{k_B}{TK_0} 2\pi e \frac{\varepsilon}{V} |\nabla \varepsilon(k)|^2 A^2(k, \omega) \frac{\partial f(\omega, T)}{\partial \omega} \omega. \quad \omega. \quad \quad 28\)

where we included all prefactors in $K_{tot}$ such that $S = \sum_k \int d\omega K_{tot}(k, \omega)$. The total kernel $K_{tot}$ may thus be interpreted as a “thermopower spectral density” determining the contribution to $S$ in $(k, \omega)$-space. In the following we restrict ourselves to in-plane transport, i.e. we set $|\nabla \varepsilon(k)|^2 = \varepsilon^2 = \varepsilon^2 + \varepsilon^2$. In Fig. 12 a visualization of $K_1, \ldots, K_5, K_{tot}$ for $\{T = 290 K, \ U = 3.5 eV, \ \Delta \varepsilon = 0.55 eV\}$ is shown. The derivative of the Fermi function $K_1$ constitutes an energy interval around the Fermi edge, where electrons are thermally activated. There will be no electronic transport outside of this interval. The different sign of the charge carriers electrons (negative) and holes (positive) is accounted for by the factor $\omega$ in $K_2$. Thus, Fig. 12 (top,right) shows the charge carriers activated for transport with respect to sign. On the other hand, the group velocity $K_3$ is a quantity which only depends on the band structure. As a consequence, $K_3$ will be large whenever the slope of $\nabla \varepsilon(k)$ is steep, cf. Fig. 12 (middle,left). Combining the latter three contributions leads to $K_4$ shown in Fig. 12 (middle,right). We observe that the values are still distributed symmetrically with respect to the Fermi level. The effect of the temperature and spectrum without the group velocity is encoded in $K_5$. There appear to be more contributions from the electrons $\omega > 0$ (Fig. 12 (bottom,left)). Finally, the thermopower spectral density $K_{tot}$ indicates the regions of $(k, \omega)$ space which contribute to the thermopower, cf. Fig. 12 (bottom,right). The function $K_{tot}$ yields both positive (holes) and negative (electrons) contributions to the thermopower, which may in principle also annihilate each other. In fact, that is the usual behavior for most materials where the thermopower $S$ is therefore only of the order of $\pm O(1) \mu \text{V/K}$. In our example, the electron contributions are significantly smaller than hole contributions, and this imbalance reflects itself on a positive thermopower $S$.

A. Effects of the temperature

Before considering the numerical results of the model system $\text{Na}_0.7\text{CoO}_2$, we discuss the effects of temperature to the thermopower $S$ by a rather general approach analyzing the thermal dependence of the kernel $K_{tot}(k, \omega)$. Let us assume for the moment the extreme case that the spectrum $A(k, \omega) \approx A(k)\Theta(-\omega)$, i.e. only holes contribute to the thermopower. Then, we can solve the integral

$$I(\beta) := \int_{-\infty}^{0} d\omega \frac{\partial f(\omega, \beta)}{\partial \omega} \omega$$  \(29\)

to obtain an approximation of the thermal dependence of the thermopower $S$: \[\]

$$I(\beta) = f(\omega, \beta) \omega |\infty - \int_{-\infty}^{0} d\omega f(\omega, \beta) = \frac{\ln(2)}{11600} T [eV].$$

Analogous considerations for the conductivity $\sigma = K_0$ yield a factor $\beta$ which cancels with $\beta$ from the definition of $S = k_B\beta e^{-1} K_1 K_0^{-1}$. Thus, a linear dependence $S \propto T$ represents a first approximation for the thermopower. Since extreme asymmetries as assumed in Eq. (29) will typically not persist for larger $T$ the linear dependence will be reduced for higher temperatures. For low temperatures $T$, the spectrum $A$ inside of the thermally activated energy interval will become symmetric with respect to $\omega$, i.e. $A(k, \omega) \approx A(k)$. Then, the integral

$$I(\beta) = \int_{-\infty}^{\infty} d\omega \frac{\partial f(\omega, \beta)}{\partial \omega} \omega = 0$$

vanishes, since the integrand is an odd function. Thus, for small $T \rightarrow 0$, the thermopower $S$ is expected to converge to 0.

After these general considerations, we now return to $\text{Na}_0.7\text{CoO}_2$: In Fig. 13 we plot the imaginary part of the self energies $\Im \Sigma(\omega)$ on the Matsubara axis and the $k$-integrated spectra $A(\omega)$ for various temperatures $T$. The high energy tail of $\Im \Sigma(\omega)$ is determined by a sum rule, and is therefore almost temperature independent. In the vicinity of $\omega = 0$, we observe a variation of $\Im \Sigma(\omega)$ with respect to temperature. This has several reasons: First, the highest Matsubara $\omega_m$ moves closer to $\omega = 0$ by definition and therefore we obtain a finer resolution. On the other hand, incoherent effects due to electron-electron scattering decrease with lower temperature. The $k$-integrated spectrum plotted in Fig. 13 (top), shows less spectral weight of $A(\omega)$ in the vicinity of the Fermi edge for increasing temperature $T$. This is a usual effect of higher temperatures: the dampening of narrow peaks in the spectrum. In addition, there are no indications for a phase change to an insulator of the material in the investigated temperature interval $145–1160 K$ originated in the electronic structure, since the qualitative spectral distribution remains more or less unchanged. However, the result for $\beta = 20 [eV^{-1}]$ is puzzling, because it shows a deviation of the general temperature behavior with respect to the other results. The same behavior is also observed
FIG. 12: (color online) Contributions $K_1,\ldots, K_5, K_{\text{tot}}$ to the thermopower $S$ for $T=290$ K according to Equations (23)-(28). Positive values are emphasized by bright (yellow) domains, negative contributions are visualized by dark (red) domains. The units of the kernels $K_1,\ldots, K_5$ are arbitrary, but domains with brighter or darker scale (intenser red or blue colors) correspond to larger positive or negative values, respectively. As a dashed line, we also plot the LDA band structure. The solid line shows the isovalues $\pm 10^2 \mu V K^{-1} eV^{-1}$ for the thermopower spectral density.
for other doping $x_{Na} = 0.6, 0.8$. Most probably this result is connected to the numerical error in the employed Maximum Entropy Method (MEM) as two spectral peaks merge into one.

In Fig. 14 we show how the k-resolved spectra and the thermopower spectral density $K_{tot}$ changes with temperature. We observe that the spectral weight is in fact decreasing in the thermally activated energy interval. Thus, the linear approximation for $S(T)$ has to be adapted for the spectra of Na$_{0.7}$CoO$_2$. The linear increase will be dampened with increasing temperature leading to a flattening of $S(T)$. This can also be seen in the final results in Fig. 25 where we plot the thermopower $S(T)$ for various doping $x_{Na}$.

B. Effects of the disorder

Separating the effects of correlation and disorder is a highly non-trivial task. Generally, correlations seem to have a larger impact on the thermopower $S$ than disorder in Na$_{0.7}$CoO$_2$. With the aim of understanding, we first set $U = 0$ eV and gradually increase the disorder potential $\Delta \varepsilon = 0 \rightarrow 1$ eV. In the next section the opposite case, namely no disorder and increasing correlation, will be investigated.

The probability for a charge carrier to be scattered from one site Co$_{Na} \leftrightarrow$CoVac to the other is obviously proportional to the doping $x_{Na}$. On the other hand, the strength of the scattering event is determined by the disorder potential $\Delta \varepsilon$. In fact, $\Delta \varepsilon$ can be interpreted as an “electron affinity”, since a larger $\Delta \varepsilon$ will lead to more electrons occupying the sites Co$_{Na}$ by means of the electrostatic attraction of the sodium ions.

In Sec. III.B the importance of the self energy $\Sigma(i \omega)$ on the imaginary axis has been discussed. With no correlation $U = 0$, we can observe the pure scattering effects of the disorder. In Fig. 15 the imaginary part of the self energy $\mathfrak{Re}(\Sigma)$ is shown. The value $\lim_{\omega \rightarrow 0} \mathfrak{Re}(\Sigma)$ gradually increases as $\Delta \varepsilon = 0 \rightarrow 1$ eV, which can be understood as follows: With the Greens function $G := G(0)$ and the Weiss field $\mathcal{G}_0 := G(0)$, we make a CPA ansatz

$$G = \frac{x_{Na}}{\mathcal{G}_0^{-1} + \Delta \varepsilon} + \frac{1 - x_{Na}}{\mathcal{G}_0^{-1}}. \quad (30)$$

This means that the total (local) Greens function consists of contributions corresponding to the sub lattice Co$_{Na}$ and CoVac, where the former is energetically lowered by the disorder potential $\Delta \varepsilon$. As in the atomic limit, the task is to extract the self energy $\Sigma = \Sigma(0)$ by expressing $G$ of Eq. (30) with the corresponding Dyson equation

$$G = \frac{1}{\mathcal{G}_0^{-1} - \Sigma}. \quad (31)$$

After some algebra, we find

$$\Sigma = x_{Na} \Delta \varepsilon \left[ \frac{1 - x_{Na}}{1 - (1 - x_{Na}) \Delta \varepsilon} \mathfrak{Im}\mathcal{G}_0 + i(1 - x_{Na}) \Delta \varepsilon \mathfrak{Re}\mathcal{G}_0 \right]$$

$$= \frac{1}{\left[ 1 - (1 - x_{Na}) \Delta \varepsilon \mathfrak{Re}\mathcal{G}_0 \right]^2 + [(1 - x_{Na}) \Delta \varepsilon \mathfrak{Im}\mathcal{G}_0]^2}$$

$$= \frac{x_{Na} \Delta \varepsilon \mathfrak{Re}\mathcal{G}_0 + i(1 - x_{Na}) \Delta \varepsilon \mathfrak{Im}\mathcal{G}_0}{[1 - (1 - x_{Na}) \Delta \varepsilon \mathfrak{Re}\mathcal{G}_0]^2 + [(1 - x_{Na}) \Delta \varepsilon \mathfrak{Im}\mathcal{G}_0]^2} \quad (32)$$

To obtain an approximation of the Weiss field $\mathcal{G}_0^{-1}$, we use the Fourier transform of the non-interacting local Greens function $G_0(\omega = 0)$

$$\mathcal{G}_0 \approx \mathcal{P} \int d\varepsilon \frac{N(\varepsilon)}{-\varepsilon} + i\pi N(0), \quad (33)$$

where we used the Sokhatsky-Weierstrass theorem and $N(\varepsilon)$ denotes the non-interacting DOS. Note that we used the advanced version of the theorem, which means we will restrict to the part $\omega_m < 0$ of the self energy $\Sigma(i \omega_m)$. Now, we assume a constant and symmetric DOS.
FIG. 14: (color online) k-resolved spectra $A(k, \omega)$ (left) and corresponding thermopower spectral densities $K_{tot}$ (right) for various temperatures $T$. The color code is given by the colorbar. The dashed line on the spectral images is the tight-binding fit. The spectral weight around the Fermi edge is decreasing with temperature. Thus, the increase of the contribution to the thermopower gets dampened and is therefore not linear.
FIG. 15: (color online) The imaginary part of the self energy $\Im \Sigma(i\omega)$ on the Matsubara axis for $T = 290$ K and $U = 0$ eV for various values of the disorder potential $\Delta \varepsilon = 0 \rightarrow 1$ eV. A gradual increase of $\Im \Sigma(i\omega)$ with respect to $\Delta \varepsilon$ is observed. The values $\lim_{\omega \rightarrow 0} \Im \Sigma(i\omega)$ obtained by the approximate formula (34) and by DMFT. For small disorder $\Delta \varepsilon$ the approximation is in good agreement with the DMFT data.

$N(\varepsilon) \approx N(0) \Theta(\varepsilon - \varepsilon_0) \Theta(\varepsilon_0 - \varepsilon)$ with $N(0) \approx 0.8$ eV$^{-1}$ from Eq. (33) and together with Eq. (32) we arrive at

$$\lim_{\omega \rightarrow 0} \Im \Sigma(i\omega) \approx \pi x_{Na}(1 - x_{Na}) \Delta \varepsilon^2 N(0) \left[ 1 + \pi (1 - x_{Na}) \Delta \varepsilon N(0) \right].$$  

(34)

The values of $\lim_{\omega \rightarrow 0} \Im \Sigma(i\omega)$ as a function of $\Delta \varepsilon$ are plotted as an inset in Fig. 15 and compared to the self-consistently determined DMFT+CPA results. The DMFT+CPA data indicate quadratic dependence with respect to $\Delta \varepsilon$, which is properly approximated by our simple considerations.

The approximate formula (34) indicates a direct connection between the disorder $\{x_{Na}, \Delta \varepsilon\}$ and the self energy at low frequency $\lim_{\omega \rightarrow 0} \Im \Sigma(i\omega)$. In fact, the value $\Im \Sigma(0)$ can be interpreted as an inverse time $\tau^{-1}$, the average time which an electron spends at a site Co$_{Na}$ or Co$_{Vac}$, before scattering to the respective other site.

The increased scattering rate due to disorder is affecting both $K_0$ and $K_1$. Numerical results indicate that $K_1$ is stronger suppressed than the conductivity $K_0$ which corresponds to an overall drastic decrease of the thermopower $S$ which is visualized in Fig. 16.

FIG. 16: (color online) The thermopower $S$ as a function of the disorder potential $\Delta \varepsilon$ without correlation ($U = 0$) for $T = 290$ K. The inset shows the corresponding values for the resistivity $\rho$. The magnitude of $S \sim K_1/K_0$ becomes smaller with larger $\Delta \varepsilon$, which can be traced back to a decrease of the current-heat correlation function $K_1$ dominating the increasing $\rho = 1/K_0$. 

$N(\varepsilon) \approx N(0) \Theta(\varepsilon - \varepsilon_0) \Theta(\varepsilon_0 - \varepsilon)$ with $N(0) \approx 0.8$ eV$^{-1}$ from Fig. 7. To that end, the principle value term drops in Eq. (33) and together with Eq. (32) we arrive at

$$\lim_{\omega \rightarrow 0} \Im \Sigma(i\omega) \approx \pi x_{Na}(1 - x_{Na}) \Delta \varepsilon^2 N(0) \left[ 1 + \pi (1 - x_{Na}) \Delta \varepsilon N(0) \right].$$  

(34)
C. Effects of electronic correlation

After considering disorder without correlation in the previous section, we now focus on the effects of electron-electron correlation and assume that there is no disorder. At half filling \( n/2 = 1/2 \), it is well known that for increasing correlation \( U \), a Mott metal-insulator transition can be observed (see e.g. Ref. 13). Away from half filling \( n/2 < 1/2 \), an electron occupying a certain site simply hops to a neighboring empty site without the necessity of a double occupancy (which would cost the energy \( U \)). Thus, we additionally obtain standard conduction channels. An equivalent picture is also applicable for holes for \( n/2 > 1/2 \) as in our model material Na\(_8\)CoO\(_2\). Without disorder, we have a mean filling of \( n/2 = 0.85 \), which is rather far away from \( n/2 = 1/2 \). For \( U = 3.5 \) eV, a renormalization of the non-interacting energy band of \( Z = 0.77 \) is obtained. Consequently, without disorder, electronic correlations are only intermediate strong. However, it pays to investigate the effect of correlation on the self energy to compare with the case of combined disorder and correlation. In Fig. 17 we plot the imaginary part of the self energy \( \Sigma(i\omega) \) for different values of the correlation \( U \). Several features can be observed: First, the maximum \( \Sigma(i\omega) \) occurs at \( U \). Second, the limit \( \lim_{i\omega \to 0} \Sigma(i\omega) \neq 0 \) and the value depends on \( U \). This behavior can be explained by means of Landau’s Fermi Liquid Theory, which predicts a dependence \( \lim_{i\omega \to 0} \Sigma(i\omega) \propto (U/T)^2 \). A visualization of the values \( \lim_{i\omega \to 0} \Sigma(i\omega) \) as a function of \( U \) can be found in the inset in Fig. 17.

In Fig. 18 we show the thermopower and the resistivity as a function of \( U \) with \( \Delta \varepsilon = 0 \). Larger \( U \) appears to increase \( \rho \) which reflects on the thermopower \( S \). However, the change of \( S \) is much smaller than in the case of non-zero disorder \( \Delta \varepsilon > 0 \) below. Correlation effects are small without the simultaneous consideration of disorder. When we include disorder, one of the two sites, namely Co\(_{\text{Vac}}\), will be driven closer to half filling. Then, the formation of a quasiparticle peak can be observed, which eventually leads to a higher thermopower.

D. Effects of combined disorder and correlation

The pure effects of disorder and correlation on self energy and spectra were discussed in the previous two sections. Whether the observed characteristics of disorder and correlation remain qualitatively unchanged in the presence of the other parameter, i.e. correlation or disorder, respectively, is yet to be investigated. We therefore fix either \( U = 3.5 \) eV or \( \Delta \varepsilon = 0.55 \) eV and vary the respective other parameter \( T = 290 \) K and \( x_{Na} = 0.7 \).

In Fig. 19 the imaginary part of the self energy \( \Sigma(i\omega) \) for different values of the disorder potential \( \Delta \varepsilon = 0 \) to \( 1.5 \) eV and fixed \( U = 3.5 \) eV is shown. Two main energy regions can be identified: In the high energy region \( \omega \gtrsim -4 \) eV the behavior of the self energy is governed by the correlation \( U \), which again can be explained by sum rules, cf. Ref. 46. On the other hand, between \(-4 \) eV and \( 0 \) eV, the slope of \( \Sigma(i\omega) \) changes decisively with increasing \( \Delta \varepsilon \). However, the latter part of the slope may again be explained by the arguments of Sec. 14B since the values of \( \lim_{i\omega \to 0} \Sigma(i\omega) \) again depends approximately quadratically on the disorder \( \Delta \varepsilon \) and agrees for small \( \Delta \varepsilon \). For \( \Delta \varepsilon = 1.5 \) eV \( \gtrsim t \), the system is already insulating, which is emphasized by an almost divergent \( \Sigma \) in the vicinity of \( \omega = 0 \).
Another interesting numerical result is the filling of the $a_{1g}$ orbital on the two sub lattices $Co_{Na}$ and $Co_{Vac}$ as a function of $\Delta \varepsilon$, as visualized as an inset in Fig. [19].

The filling $n_{Na}$ rises in the analyzed $\Delta \varepsilon$-interval basically linearly to 1 as the disorder potential $\Delta \varepsilon$ increases, whereas $n_{Vac}$ decreases. For very large disorder $\Delta \varepsilon = 1.5$ eV the fillings approach their maximum and minimal values $n_{Na} = 1$ and $n_{Vac} = 0.5$, respectively.

After the self energy, we investigate the spectrum for increasing disorder potential $\Delta \varepsilon$. The k-integrated spectra $A(\omega)$ can be found in Fig. [20] (top). For $\Delta \varepsilon = 0 \rightarrow 1$ eV the spectral weight at the Fermi edge decreases, but the asymmetry of the spectral distribution with respect to $\omega = 0$ increases. A further increase $\Delta \varepsilon \gtrsim 1$ eV leads to the formation of a band gap and a alloy band splitting created by disorder.

Though less spectral weight implies decreasing thermopower contributions for both electrons and holes (see $\kappa_{tot}$ in [28] and Fig. [1]), asymmetry in the spectrum with respect to the Fermi edge $\omega = 0$ enhances $S$, and the thermopower thus non-trivially depends on the disorder. In Fig. [20] (bottom), we show the numerical results for the thermopower $S$ as a function of the disorder potential $\Delta \varepsilon$. The slope shows a flat maximum of the thermopower $S = 80\mu V/K$ for $\Delta \varepsilon \sim 0.7$ eV. For larger $\Delta \varepsilon \gtrsim 0.9$ eV, transport gets more and more suppressed as the spectral weight is shifted away from $\omega = 0$ an alloy band gap forms. Again, the k-resolved spectra and contributions to the thermopower shown in Fig. [23] enhance the understanding of these effects: For no disorder $\Delta \varepsilon = 0$ eV, we obtain a weak renormalization as discussed in Sec. [16]. With a disorder of $\Delta \varepsilon = 0.7$ eV all the charge carriers get scattered, which can be seen in a more diffuse k-resolved spectrum (corresponding to a larger $\Im \Sigma(i\omega_n)$). However, as the corresponding contribution to the thermopower reveals, electrons become scattered stronger than holes. Therefore the net enhancement for the transport property $S$ in Fig. [20] (bottom), can be explained by an increase of spectral weight for the holes $\omega < 0$ compared to the purely disordered model, which is larger than the, also observed, increase of spectral weight for electrons ($\omega > 0$). But for $\Delta \varepsilon > 0.8$ eV the contribution of holes to the thermopower starts to diminish by a larger amount than can be accounted for by less negative contribution of the electrons. All charge carriers then are scattered at a high rate, the thermopower $S$ consequently drops as the system becomes insulating.

After the numerical results for increasing disorder, we now fix $\Delta \varepsilon = 0.55$ eV and gradually increase the correlation $U = 0 \rightarrow 5$ eV. In Fig. [21] we plot the corresponding imaginary part $\Im \Sigma(i\omega)$. Surprisingly, the value $\lim_{\omega \rightarrow 0} \Im \Sigma(i\omega)$ first drops from 0.15 eV below 0.1 eV and then stabilizes around 0.1 eV for increasing correlation $U$.
FIG. 21: (color online) The imaginary part of the self energy \( \Im \Sigma(i\omega) \) on the Matsubara axis for \( T = 290 \text{ K}, \Delta \varepsilon = 0.55 \text{ eV} \) and increasing values of the correlation \( U \). The black lines in the magnification are parabolic fits of the slopes. Note that the slopes converge to similar values for \( \omega \rightarrow 0 \), yet increase with larger \( U \). For \( U < \Delta \varepsilon \), the value of \( \lim_{\omega \rightarrow 0} \Im \Sigma(i\omega) \) appears to be governed by the disorder, while for larger \( U \) the shape of \( \Im \Sigma(i\omega) \) is mainly determined by correlation effects.

This indicates a rather non-trivial impact of a changing \( U \) on an already disorder system (the situation is further complicated since the Luttinger theorem does not hold due to disorder, and non-zero temperature, and the van-Hove like peak around the Fermi edge appears to react very sensitive to changes of \( U \)).

The effect of increasing correlation on the k-integrated spectrum is shown in Fig. 22 (top). A shift of spectral weight from just above to just below the Fermi level can be observed. This indicates an increase of the thermopower for larger \( U \), which is indeed found as it is shown in Fig. 22 (bottom), where we show \( S \) function of \( U \). The enhancement of \( S = 25 \rightarrow 64 \mu \text{V/K} \) is extreme as \( U = 0 \rightarrow 3 \text{ eV} \). However, the growth of \( S \) gets saturated for \( U \geq 5 \text{ eV} \).

To further improve our understanding, we again investigate the k-resolved spectra and corresponding contributions to the thermopower, cf. Fig. 23. Without correlation \( U = 0 \), there is little spectral weight directly around the Fermi edge. However, in that energy interval a larger \( U \) effectively packs spectral weight to larger extent for holes than for electrons. Thus, the drastic enhancement of \( S \) can be understood. For larger \( U \sim 5 \text{ eV} \), the change at the Fermi edge is not decisive, resulting in the saturation of the thermopower \( S \) with respect to \( U \) shown in Fig. 22 (bottom).

E. Effects of the doping

The considerations of the previous sections are mostly thought experiments to identify the important effects in the model compound Na_{0.7}CoO_2. On the other hand, the typical external parameters one can control in experiment, are the temperature \( T \) and the doping \( x_{\text{Na}} \). The gradual change or replacement of specific elements within a chemical compound has been used since ancient times. During the course of the 20th century, doping has become a major tool in technical applications and experimental materials science.

In semiconductor applications, one usually dopes by replacement: In addition to the main contents (e.g. Si), a similar element is added which leaves the crystal structure in principle unchanged and takes the position of a fraction of the main chemical component(s). In the band structure, this procedure creates new bands which are energetically close to the ones of the desired charge carrier, and can therefore be much easier thermally activated than in the pure compound.

In contrast to replacement, Na_{0.7}CoO_2 is doped by
FIG. 23: (color online) k-resolved spectra $A(k,\omega)$ (left) and corresponding thermopower spectral densities $K_{tot}$ (right) for various values for the disorder potential $\Delta \varepsilon = \{0 \text{eV}, 0.7 \text{eV}, 1 \text{eV}\}$ at $T = 290$ K. The color code is given by the colorbar and the tight-binding fit is visualized as dashed line. The electronic contribution $\omega > 0$ to the thermopower is increased for $\Delta \varepsilon = 0.7 \text{eV}$, but the hole contribution $\omega < 0$ is enhanced even more. For large values of $\Delta \varepsilon = 1 \text{eV}$ spectral weight is diminishing above and below the Fermi edge.
FIG. 24: (color online) k-resolved spectra \( A(k, \omega) \) (left) and corresponding thermopower spectral densities \( \kappa_{\text{tot}} \) (right) for various values for the correlation \( U = \{0 \text{ eV}, 2 \text{ eV}, 5 \text{ eV} \} \) at \( T = 290 \text{ K} \). The color code is given by the colorbar and the tight-binding fit is shown as a dashed line. Spectral weight is shifted from above, directly below the Fermi edge \( \omega = 0 \) as \( U = 0 \rightarrow 2 \text{ eV} \), which increases the hole contributions to \( S \) while decreasing the electron contribution. This effect is even stronger for \( U = 5 \text{ eV} \).
changing the sodium content, cf. Refs. 32,34 Since the single electron of the alkali Na becomes a valence electron in the cobaltate CoO₂ layers, this corresponds to shifting the Fermi energy $E_F$ within the $a_{1g}$ band of the non-interacting band structure (Fig. 2). As discussed in Sec. II and in Ref. 11, the “pudding mold”-like slope of the $a_{1g}$ band is expected to be a very important feature for a high thermopower $S$. The closer the Fermi energy $E_F$ is to the flat top of the band, the larger the effect will be. Then, one charge carrier highly outmatches the other in terms of group velocity $\vec{v}(k)$. We therefore expect the thermopower to increase for higher $x_{Na}$. In fact, as can be seen in Fig. 25, the computations yield a larger thermopower $S$ as the doping $x_{Na}$ increases from 0.6 → 0.8. Here, we plot the thermopower $S$ over temperature $T$ for various doping $x_{Na}$ and compare to experiment (see Ref. 9 for a corresponding comparison of the resistivity). The experimental results are in good agreement with our data, even though a direct comparison is made difficult, by the (in this case) unknown orientation of the crystal in the experiment. The result of larger thermopower $S$ with increasing $x_{Na}$ can be qualitatively explained by band structure arguments. Still, there can be additional effects due to correlations and disorder. The k-integrated spectra in Fig. 26 indicate that spectral weight is shifted from electrons $\omega > 0$ to holes $\omega < 0$ as $x_{Na} = 0.6 \rightarrow 0.8$. This further enhances the “pudding mold” effect of the group velocity $\nabla \varepsilon$. The k-resolved spectra in Fig. 27 show another result: The “pudding mold” contribution of the k-path in the xy-plane $\Gamma \rightarrow K$ important for $x_{Na} = 0.6,0.7$ is joined by the $k_x \neq 0$ contribution $A \rightarrow H$ as the Fermi level moves down. That provides an explanation why the dampening of the linear increase of the thermopower $S$ becomes smaller as $x_{Na} = 0.7 \rightarrow 0.8$. 

FIG. 25: (color online) The thermopower $S$ over the temperature $T$ for $U = 3.5$ eV, $\Delta \varepsilon = 0.55$ eV and various doping $x_{Na}$ computed by DMFT compared to experiment. Transport in x-direction is assumed, $\vec{v}_y = \vec{v}_x + \vec{v}_y$. The thermopower increases non-linearily with temperature $T$ as discussed in Sec. IV A. For increasing doping $x_{Na}$, the thermopower increases for all temperatures $T$.

FIG. 26: (color online) k-integrated spectra for $U = 3.5$ eV, $\Delta \varepsilon = 0.55$ eV, $T = 290$ K and various doping $x_{Na}$. For $x_{Na} = 0.6$ the Fermi liquid peak is the most pronounced as the filling of the site CoV₁₃₂ is closest to 1/2. In the vicinity of the Fermi edge, spectral weight is shifted from $\omega > 0$ to $\omega < 0$ as $x_{Na} = 0.6 \rightarrow 0.8$. (bottom) The imaginary part of the self energy $\Sigma(i\omega)$ on the Matsubara axis for $U = 3.5$ eV, $\Delta \varepsilon = 0.55$ eV, $T = 290$ K and various doping $x_{Na} = \{0.6,0.7,0.8\}$. (inset) Magnification around $\omega = 0$ and corresponding tangents (black). All slopes converge to similar values which are independent of the disorder $x_{Na}$, but dependent on the disorder potential $\Delta \varepsilon$ and $U$. 
FIG. 27: (color online) k-resolved spectra $A(k, \omega)$ (left) and corresponding thermopower spectral densities $K_{\text{tot}}$ (right) for $U = 3.5 \text{ eV}$, $\Delta \varepsilon = 0.55 \text{ eV}$ and various values of the doping $x_{\text{Na}}$. The color code is given by the colorbar and the tight-binding fit is visualized by a dashed line. The (negative) electronic contribution to the thermopower is smaller as $x_{\text{Na}} = 0.6 \rightarrow 0.8$, thus the thermopower $S$ shows a net increase. For $x_{\text{Na}} = 0.8$ also the "pudding molds" between $A \rightarrow H$ and $A \rightarrow L$ becomes important.
In Na$_2$CoO$_2$ two distinct effects enhance the hole current in comparison to the electron one: a larger group velocity and a larger number of holes or, more precisely, a larger hole spectral weight, also see Fig. 1. As both effects point in the same direction, we obtain a large electron-hole imbalance. Consequently, a temperature gradient results in a higher hole current, and, hence, a large positive thermopower $S$. The larger group velocity of the holes can be understood already from a one-particle LDA point of view. It is caused by the particular pudding-mold type of bandstructure, In this paper we analyzed the second mechanism which is a genuine correlation effect. The microscopic origin is a complex interplay of Coulomb repulsion $U$ and a (disordered) potential $\Delta \epsilon$ due to the Na vacancies. We have hence taken $U$ and $\Delta \epsilon$ as free parameters (not \textit{ab initio} ones as in Ref. [9]). The Coulomb repulsion alone (without disorder) has only a rather minute impact. This is due to the filling of 1.7 electrons per Co site. With 0.3 holes in an otherwise filled Co $a_{1g}$ orbital, chances to have 2 holes on the same Co site are very small. Hence the impact of the Coulomb repulsion, whose main effect is to suppress such configurations, is small. Without the vacancy potential, electronic correlations in Na$_2$CoO$_2$ would therefore be very weak. Without Coulomb repulsion on the other hand, the vacancy disorder smears out the spectrum and particularly enhances the resistivity less than the current–heat-current correlation function is diminished, so that the thermopower actually decreases. The story becomes very different if Coulomb repulsion and disorder potential are combined. Then, the disorder potential gives rise to two inequivalent lattice sites. Since the number of holes in the $a_{1g}$ exactly corresponds to the number of sites with a higher potential for the electrons, we end up with a situation close to two electrons on the Co site with adjacent Na-ion and one electron on the Co site with adjacent vacancy. In this situation, electronic correlations can be very strong for the half-filled Co sites with an adjacent vacancy. Because of this, we get a strongly renormalized spectrum with a sharp peak at the Fermi level, see Fig. 9. The other sites, with adjacent Na-ions, on the other hand, have only a sizeable spectral weight on the hole-side of the Fermi level. Taken together, we have more (quasi-)holes but nonetherless sharp peaks in the spectrum. In this situation, the thermopower increases up to 80 $\mu$V/K with interaction. For a larger value of the disorder potential, the Coulomb interaction can even (counter intuitively) change the behavior from an insulator with a very small thermopower to a metal with a big one.

For tracing down the energy and momentum of the quasiparticles responsible for positive and negative thermopower alike, we have analyzed the various contributions to the thermopower separately. In Fig. 12 we show for which $k$ and $\omega$ we have a significant contribution from the group velocity, the spectral weight, and for which interval holes and electrons can be thermally activated. We also introduced a thermoelectric spectral weight which combines these terms and hence provides for a $k$- and $\omega$-resolved analysis of the thermopower. The biggest contributions naturally stem from those $k$-vectors which have the largest group velocity, albeit the quantitative contribution is changing in comparison to the non-interacting case. Most interestingly, also hole contributions appear which, without interaction, were not present at certain $k$-points. Generally, electronic correlations change the energies and momenta with big contributions to the thermopower quite substantially.

As the vacancy (disorder) potential $\Delta \epsilon$ is most crucial for the thermopower and the physical properties of Na$_2$CoO$_2$ in general, it is worthwhile to have a closer inspection of this parameter. Actually, in LDA calculations, $\Delta \epsilon$ is rather small, i.e., $\sim 0.05$ eV (Ref. [10]). This value is way too small to provide for the aforementioned charge disproportionation and the resulting strong electronic correlations on the Co sites with vacancy. Marianetti and Kotliar, argued that LDA overestimates screening so that the actually $\Delta \epsilon$ is much larger, i.e., $\sim 0.55$ eV. This is also the value we have considered in our paper as the physically relevant one. Besides the overestimation of screening, we think that the electron-phonon coupling is an important source for the effective increase of $\Delta \epsilon$ by $\sim g^2/\omega_0$ ($g$: electron phonon coupling strength; $\omega_0$: phonon frequency).

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