

Thermopower of the electron-doped manganese pnictide LaMnAsO

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Upon chemical substitution of oxygen with fluor, LaMnAsO has been electron-doped in experiments, resulting in samples with remarkably high Seebeck coefficients of around $-300 \mu\text{VK}^{-1}$ at room temperature and 3% doping. Within the framework of density functional theory plus dynamical mean-field theory (DFT + DMFT) we not only are able to reproduce these experimental observations, but also can provide a thorough investigation of the underlying mechanisms. By considering electronic correlations in the half-filled Mn-3d shells, we trace the high Seebeck coefficient back to an asymmetry in the spectral function, which is due to the emergence of an incoherent spectral weight under doping and a strong renormalization of the unoccupied states. This is only possible in correlated systems and cannot be explained by DFT-based band structure calculations.

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I. INTRODUCTION

In times of a drastic increase in energy consumption, the possibility of converting otherwise wasted heat into electric energy through thermoelectric devices becomes increasingly important [1,2]. In addition to already commercially used narrow-gap semiconductors, like Pb(Se, Te) and Bi₂Te₃, research on thermoelectricity is also devoted to correlated materials, as it has been shown in recent years that electronic correlations can have a strong influence on the thermopower [3–9].

A class of strongly correlated materials for which experiments have repeatedly reported high thermopowers (Seebeck coefficients) is the manganese pnictides [10–18]. We focus on one example of this material class, electron-doped LaMnAsO, where doping can be accomplished experimentally by a fractional replacement of the O atoms with F [18,19]. The experimental facts to be explained by theory are the following: The room-temperature Seebeck coefficient of polycrystalline LaMnAsO_{1- δ} F _{δ} samples changes from about $-290 \mu\text{VK}^{-1}$ at 3% doping to $-190 \mu\text{VK}^{-1}$ at 7% doping but jumps to only $-30 \mu\text{VK}^{-1}$ at 10% doping [18].

On the theoretical side fairly little is known about the origin of the high Seebeck coefficients in manganese pnictides. Only for BaMn₂As₂, the Seebeck coefficient was calculated within density functional theory (DFT) and the constant scattering time approximation, which resulted in values of around $-150 \mu\text{VK}^{-1}$ for electron doping at 300 K [20]. However, the underlying microscopic details have not been studied yet. Moreover, it has been pointed out in earlier works that the strong electron-electron interaction in nominally half-filled Mn-3d shells is an important factor to understand the physical properties of manganese pnictides [21–24]. In that sense, one also needs to take into account electron-electron interactions when studying thermoelectricity.

In this work, we use *ab initio* density functional theory electronic structure calculations coupled to dynamical mean-field theory (DFT + DMFT) [25] to develop a theoretical understanding of the Seebeck coefficient in electron-doped LaMnAsO. Using the virtual crystal approximation (VCA) to simulate electron doping, not only the magnitude of the Seebeck coefficient, but also its doping dependence can be understood from the picture of a doped correlated insulator under the emergence of an incoherent spectral weight due to inelastic electron-electron scattering. Such a description is not possible on the level of DFT but requires at least local electronic correlations in the Mn-3d shells which are taken into account in DFT + DMFT. We emphasize that all calculations are performed without adjustable doping-dependent parameters. The interaction parameters U and J are fixed to their values in our previous study [24], where excellent agreement between theory and experiment for optical properties was found.

After an outline of the theoretical framework, we briefly review the necessary ingredients for high Seebeck coefficients from an electronic structure point of view, before we turn to the numerical calculations and comparisons between theoretical and experimental results.

II. METHODOLOGY

To describe the electronic structure and the transport properties of electron-doped LaMnAsO we carry out fully charge self-consistent DFT + DMFT calculations using the TRIQS/DFTTOOLS package [26–29] in combination with WIEN2k [30,31]. In addition to the following outline we refer the reader to our previous work [24] for further computational details.

For the DFT calculation we use 10000 **k** points in the full Brillouin zone and the standard Perdew-Burke-Ernzerhof (PBE) [32] generalized gradient approximation for the exchange-correlation functional. We use the crystal structure of the undoped compound (measured at 290 K in

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Ref. [33]) for all calculations. A test calculation with the experimental crystal structure at 10% electron doping [18] showed no substantial changes in our results. For all magnetic calculations we consider the C-type antiferromagnetic (AFM) ordering as determined experimentally for the undoped compound [34]. We treat electron doping using the virtual crystal approximation in DFT by modifying the atomic numbers of the substituted atoms according to the desired doping levels. We assess the quality of this approximation by a comparison to supercell calculations (see the Appendix). The doping is of course taken into account also in the DMFT part of the calculation by adjusting the chemical potential to the corresponding electron count.

From the DFT Bloch states we construct projective Wannier functions for the Mn-3d orbitals in an energy window from -5.50 to 3.25 eV around the Fermi energy for the undoped compound, but adjust the upper boundary such that the same number of states at each doping level is included. In DMFT we work with a full rotationally invariant Slater Hamiltonian for the five Mn-3d orbitals with a Coulomb interaction $U = F^0$ of 5.0 eV and a Hund's coupling $J = (F^2 + F^4)/14$ of 0.9 eV ($F^4/F^2 = 0.625$) [24]. We choose the fully localized limit as double-counting correction [35], where we use the electron charge in the 3d orbitals calculated from the fully self-consistently determined charge density. The TRIQS/CTHYB solver [36], which is based on continuous-time quantum Monte Carlo in the hybridization expansion [37,38], is used to solve the impurity model on the Matsubara axis at an inverse temperature $\beta = 40$ eV $^{-1}$, corresponding to room temperature. We use the Beach's stochastic method [39] for the analytic continuation of the self-energy to the real-frequency axis by constructing an auxiliary Green's function, $G_{\text{aux}}(z) = (z - \Sigma(z) + \Sigma(\infty) + \mu)^{-1}$.

Transport properties are evaluated within the linear response Kubo formalism (neglecting vertex corrections). The static conductivity tensor $\sigma_R^{\alpha\alpha'}$ and the Seebeck tensor $S^{\alpha\alpha'}$ are given by [40,41]

$$\sigma^{\alpha\alpha'} = K_0^{\alpha\alpha'} \quad \text{and} \quad S^{\alpha\alpha'} = -(K_0^{-1})^{\alpha\gamma} K_1^{\gamma\alpha'}, \quad (1)$$

with $\alpha, \alpha', \gamma \in \{x, y, z\}$ and kinetic coefficients

$$K_n^{\alpha\alpha'} = N_\sigma \pi \int d\omega (\beta\omega)^n \left(-\frac{\partial f(\omega)}{\partial \omega} \right) \Gamma^{\alpha\alpha'}(\omega, \omega), \quad (2)$$

where N_σ is the spin degeneracy and $f(\omega)$ the Fermi function. The transport distribution is defined as

$$\Gamma^{\alpha\alpha'}(\omega) = \frac{1}{V} \sum_{\mathbf{k}} \text{Tr}[v^\alpha(\mathbf{k})A(\mathbf{k}, \omega)v^{\alpha'}(\mathbf{k})A(\mathbf{k}, \omega)], \quad (3)$$

with the unit cell volume V . In multiband systems the interacting (correlated) spectral function $A_{\nu\nu'}(\mathbf{k}, \omega)$ and the velocities $v_{\nu\nu'}^\alpha(\mathbf{k})$ are Hermitian matrices in the band indices ν and ν' , which we have omitted in the equations above. The velocities (matrix elements of the momentum operator) are calculated with the WIEN2k *optic* code [42], $v_{\nu\nu'}^\alpha(\mathbf{k}) = -i \langle \psi_\nu(\mathbf{k}) | \nabla^\alpha | \psi_{\nu'}(\mathbf{k}) \rangle / m_e$, from the charge self-consistent Bloch states.

For a crystal symmetry demanding diagonal rank 2 tensors, as is the case for LaMnAsO, the Seebeck coefficient in direc-

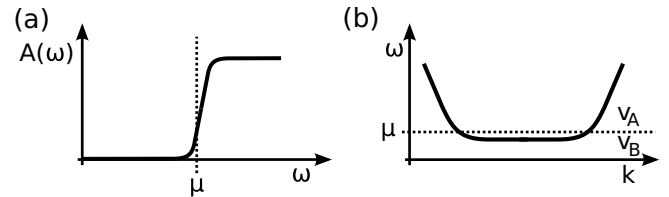


FIG. 1. Sketch of two scenarios promoting a high Seebeck coefficient. (a) Particle-hole asymmetry in the spectral function $A(\omega)$. (b) Asymmetry in the velocities $v_A \gg v_B$ due to a high dispersion above the chemical potential μ and the flat portion of the band below, respectively.

tion α is given by

$$S^\alpha = -\frac{K_1^{\alpha\alpha}}{K_0^{\alpha\alpha}} = -\frac{K_1^{\alpha\alpha}}{\sigma^{\alpha\alpha}}. \quad (4)$$

As all synthesized samples of LaMnAsO (doped and undoped) are polycrystalline, we simulate a ‘‘polycrystalline’’ Seebeck coefficient by averaging over the three Cartesian coordinates [43]:

$$S_{\text{av}} = \frac{S^{xx}\sigma^{xx} + S^{yy}\sigma^{yy} + S^{zz}\sigma^{zz}}{\sigma^{xx} + \sigma^{yy} + \sigma^{zz}}. \quad (5)$$

III. INGREDIENTS FOR A HIGH SEEBECK COEFFICIENT

Due to the ω factor in the kinetic coefficient $K_1^{\alpha\alpha'}$, Eq. (2), electron contributions ($\omega > 0$) and hole contributions ($\omega < 0$) influence the Seebeck coefficient S in opposite ways. Thus, getting a high $K_1^{\alpha\alpha'}$, and in turn a high S , requires a high electron-hole asymmetry around the chemical potential μ , i.e., a strongly asymmetric transport distribution $\Gamma^{\alpha\alpha'}$, Eq. (3). There are two mechanisms to promote a strong asymmetry in $\Gamma^{\alpha\alpha'}$, as there are likewise two quantities entering $\Gamma^{\alpha\alpha'}$: the velocity matrices $v^\alpha(\mathbf{k})$ and the spectral function $A(\mathbf{k}, \omega)$.

The first scenario, shown in Fig. 1(a), is to have an asymmetric spectral function, e.g., with a steep slope of the spectrum close to the chemical potential μ [44–46]. A high positive Seebeck coefficient is expected if there is much more spectral weight below μ than above, and a high negative Seebeck coefficient for cases with much more spectral weight above μ than below. In the context of strongly correlated systems this picture was also discussed with regard to a sharp Kondo peak directly above or below the chemical potential [4,5].

In the second scenario a high Seebeck coefficient is obtained from a strong asymmetry directly in $v(\mathbf{k})$, which can occur due to peculiar band shapes [6,7,47]. If we assume a constant isotropic scattering time τ_s , an approximation for the kinetic coefficients is [6]

$$K_0 \sim \sum_{\mathbf{k}} (v_A^2(\mathbf{k}) + v_B^2(\mathbf{k})), \quad (6)$$

$$K_1 \sim \sum_{\mathbf{k}} (v_A^2(\mathbf{k}) - v_B^2(\mathbf{k})). \quad (7)$$

Here, the summation runs only over states in the range of $|\omega - \mu| \lesssim 1/\beta$. The velocities v_A are characteristic velocities for states above (A) μ and v_B for states below (B) μ . For example, a linear dispersion in the vicinity of μ corresponds to $v_A^2 \approx v_B^2$,

and thus K_1 will be small, as is the case for ordinary metals [6]. The optimal situation for a high S are “pudding mold”-like bands, which are, for instance, nondispersive or only weakly dispersive below μ and show a strongly dispersive behavior above μ ; see Fig. 1(b). If μ is located close to the flat portion of such a band and the temperature is high enough, we find $v_A^2 \gg v_B^2$, and consequently $K_1 \sim v_A^2$. For a band with its flat portion below μ this results in a negative S .

Of course, $v(\mathbf{k})$ and $A(\mathbf{k}, \omega)$ are intertwined, and for real materials the influence of the electronic structure on the thermoelectric properties should always be considered as an interplay of these two ingredients [8,48]. A band structure showing a strong asymmetry in $v(\mathbf{k})$ usually comes with an asymmetry in $A(\mathbf{k}, \omega)$, too. This can be such that it partially compensates for the effect of the asymmetry in $v(\mathbf{k})$, as demonstrated for $\text{Na}_{0.7}\text{CoO}_2$ [48]. We show below that also the opposite behavior, where $A(\mathbf{k}, \omega)$ and $v(\mathbf{k})$ contribute with the same sign to S , is possible. Coming back to the sketch in Fig. 1(b), this happens when the corresponding asymmetry in $A(\mathbf{k}, \omega)$ is such that the derivative of the Fermi function in the kinetic coefficient [Eq. (2)] picks up more spectral weight above μ than below. Then the asymmetries in $A(\mathbf{k}, \omega)$ and $v(\mathbf{k})$ both contribute with a negative sign to S .

An indicator, which we use in this work, to measure the influence of the asymmetry in the spectral function on S , is to evaluate Eqs. (1)–(3) with $v^\alpha(\mathbf{k}) = \text{const.} \times \mathbb{1}$. In this case, the velocities drop out and we end up with

$$S^{v=\mathbb{1}} = - \frac{\int d\omega \beta \omega (\partial f(\omega)/\partial \omega) \sum_{\mathbf{k}} \text{Tr}[A^2(\mathbf{k}, \omega)]}{\int d\omega (\partial f(\omega)/\partial \omega) \sum_{\mathbf{k}} \text{Tr}[A^2(\mathbf{k}, \omega)]}. \quad (8)$$

If $S^{v=\mathbb{1}}$ is significantly different from S , we can infer that the asymmetry in the velocities is important for the Seebeck coefficient. If $S^{v=\mathbb{1}} \approx S$, the velocities are of less importance, and a high Seebeck coefficient is driven mainly by the asymmetry in the spectral function.

IV. RESULTS

We start with the discussion of the Seebeck coefficient S_{av} of LaMnAsO at 5% electron doping, which was experimentally determined to be $-240 \mu\text{V K}^{-1}$ [18]. First, we calculate S_{av} directly from spin-polarized (AFM) DFT assuming a constant isotropic scattering time τ_s (const.- τ_s approximation) [49]. This approximation results in a high negative value of $S_{\text{av}} = -170 \mu\text{V K}^{-1}$. On the contrary, when setting the velocity matrices $v(\mathbf{k}) = \mathbb{1}$ [Eq. (8)] we only obtain $S_{\text{av}}^{v=\mathbb{1}} = -70 \mu\text{V K}^{-1}$, showing the importance of the asymmetry in $v(\mathbf{k})$. This is also apparent in the DFT band structure (Fig. 2, top). The DFT picture is that of a band insulator which becomes metallic under doping as the Fermi energy is “shifted” into the unoccupied states. The doping mainly affects the hole pockets of xz/yz orbital character at the A and M points. At the M point the bands are rather flat, resembling a moldlike shape, with the bottom of the xz/yz bands lying below the Fermi energy. This is the origin of the strong influence of $v(\mathbf{k})$ on S_{av} . The associated asymmetry in the density of states (DOS) (see bottom panel in Fig. 2) does not compensate the $v(\mathbf{k})$ asymmetry but, rather, gives a contribution with the same sign and implies that at room temperature more relevant states above the Fermi energy than

below contribute to S_{av} . We conclude that on the DFT level the asymmetries in the DOS and $v(\mathbf{k})$ are both of similar relevance for S_{av} .

This picture drastically changes when we calculate S_{av} from the AFM DFT + DMFT solution instead of using the DFT + const.- τ_s approximation. The resulting S_{av} is $-230 \mu\text{V K}^{-1}$, which is in remarkably good agreement with the experimental value. Setting $v(\mathbf{k}) = \mathbb{1}$ leads to only a slight reduction in $|S_{\text{av}}|$ by about 15%. In sharp contrast to the DFT + const.- τ_s result, this reveals that the asymmetry in the DFT + DMFT spectral function is the major factor, whereas the influence of the velocity asymmetries is negligible.

To gain a better understanding of this observation, we discuss how electronic correlations shape the spectral function under doping (Fig. 3, bottom). In comparison to undoped LaMnAsO (dashed line), doping has two major effects: First, the edge of the spectral function between 0.0 and 0.25 eV in the undoped compound is pushed towards $\omega = 0.0$ eV with increased doping. Although the slope of this edge is steeper in comparison to the undoped spectral function, it does not substantially change for the different doping levels. Second, the insulating state is suppressed and the spectral weight at and below the chemical potential emerges. The spectral weight below the chemical potential increases with the doping level and develops into a shoulder, well visible at 10% doping. We emphasize that this spectral weight is not a result of the displacement of quasiparticle states but is entirely incoherent and originates from inelastic scattering due to electronic correlations.

This is also visible in the \mathbf{k} -resolved spectral function (Fig. 3, top), where the chemical potential cuts through the incoherent spectral weight of the unoccupied states. However, the most prominent spectral features at the A and M points lie above the chemical potential, which leads to a considerable spectral weight asymmetry. This is clearly different from the DFT band structure, where the coherent bands cross the Fermi energy (see Fig. 2, top). Additionally, around the A and M points we find a spectral weight which has a stronger pronounced flat part than the corresponding DFT bands (cf. the path from M to Γ in the top panels in Figs. 2 and 3). In general, spectral features are much less dispersive in the DFT + DMFT result as a consequence of the overall renormalization of the unoccupied states.

Additionally, we show in the bottom panel in Fig. 3 the spectral functions which are generated by a rigid shift of the undoped spectral function according to the different doping levels (dotted black lines). The fact that not much spectral weight is present in the first 0.05 eV above the chemical potential results in a substantial shift already at the lowest doping level of 3%. A further increase in the doping leads to only small additional shifts. However, these simple energy shifts do not correctly reproduce the doped DFT + DMFT results, demonstrating the importance of separate fully charge self-consistent DFT + DMFT calculations at each doping level.

Now, we turn to the doping dependence of the Seebeck coefficient (Fig. 4). The DFT + DMFT S_{av} in the AFM phase is $-290 \mu\text{V K}^{-1}$ at 3% doping and increases up to $-190 \mu\text{V K}^{-1}$ at 10% doping (blue circles). At a doping of 3% the calculated value coincides with the experimental data [18] (black circles)

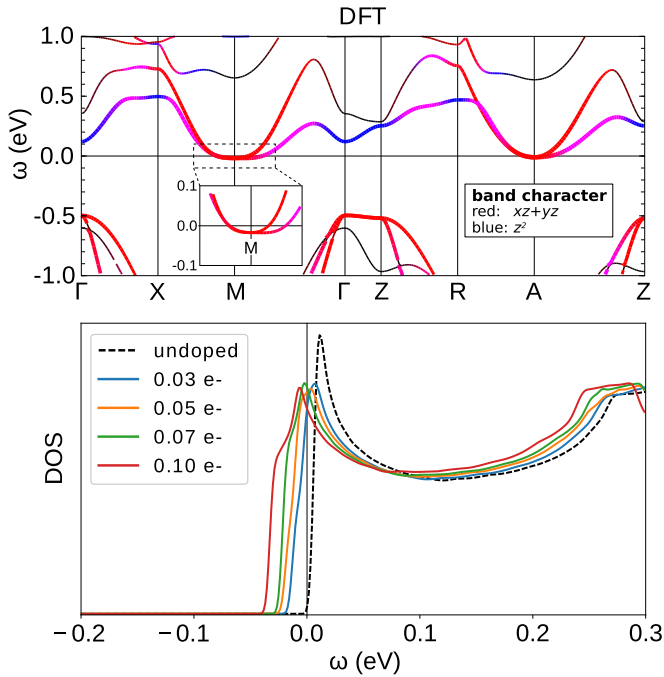


FIG. 2. Top: Spin-polarized (antiferromagnetic) DFT band structure at 5% electron doping on the Γ -X-M- Γ -Z-R-A-Z \mathbf{k} path. The band character of the xz/yz orbitals is shown by red lines, and that of the z^2 orbitals by blue lines. Inset: Low-energy region around the M point. The prima WIEN2k add-on [50] was used to create this panel. Bottom: Evolution of the total antiferromagnetic DFT DOS for 3%, 5%, 7%, and 10% electron doping (colored lines). Additionally, the undoped DFT DOS (dashed black line) is shown, shifted such that the onset of the unoccupied states is at the Fermi energy ($\omega = 0$ eV).

and is still in good agreement at doping levels of 5% and 7%. On the other hand, a paramagnetic (PM) DFT + DMFT calculation (blue squares) of S_{av} yields only $-40 \mu\text{V K}^{-1}$ at 5% doping. The large discrepancy at 5% between the PM and the AFM result suggests that the magnetic ground state is an essential ingredient to describe the thermoelectric properties of LaMnAsO at the lower doping levels.

The experimental data show a strong change of S to only $-30 \mu\text{V K}^{-1}$ when doping is increased from 7% to 10%. A similar behavior has been observed for SmMnAsO $_{1-\delta}$ samples [16]. In this compound the Seebeck coefficient is $S = -280 \mu\text{V K}^{-1}$ for an oxygen deficiency of $\delta = 0.17$ at room temperature, but upon a further increase to $\delta = 0.2$ it jumps to only $-40 \mu\text{V K}^{-1}$. In SmMnAsO $_{1-\delta}$ this change in S , which is also accompanied by a strong increase in the conductivity, is connected to the transition to the PM state. Although the Néel temperature in the case of F -doped LaMnAsO has not been measured, the conductivity does change abruptly by two orders of magnitude, from 7% to 10% doping [18]. Furthermore, experiments demonstrated that the AFM phase can be destroyed under H doping of about 8%–14% [51]. At 10% doping our calculation in the PM phase is in accordance with the experimental value, which can be seen as a further hint that the suppression of S_{av} from 7% to 10% doping is probably connected to the AFM-PM transition. However, in this work we do not intend to investigate the phase transition from an AFM to a PM state within DFT + DMFT. It is

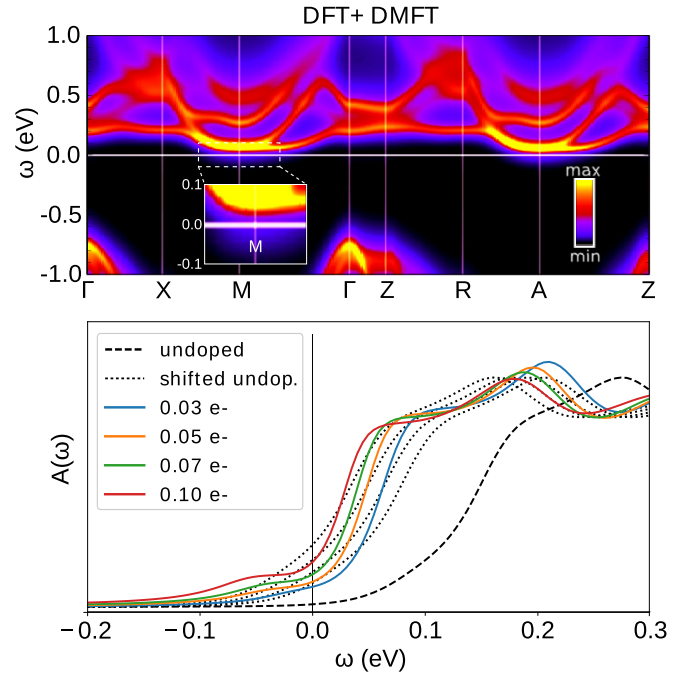


FIG. 3. Top: Antiferromagnetic correlated spectral function $A(\mathbf{k}, \omega)$ at 5% electron doping on the Γ -X-M- Γ -Z-R-A-Z \mathbf{k} path. Inset: Low-energy region around the M point. Bottom: Evolution of momentum-integrated DFT + DMFT spectral functions for 3%, 5%, 7%, and 10% electron doping (colored lines). The undoped spectral function (dashed black line) is shown for comparison, and a simple energy shift of it, adjusted to fillings corresponding to the four doping levels, is indicated by the dotted black lines.

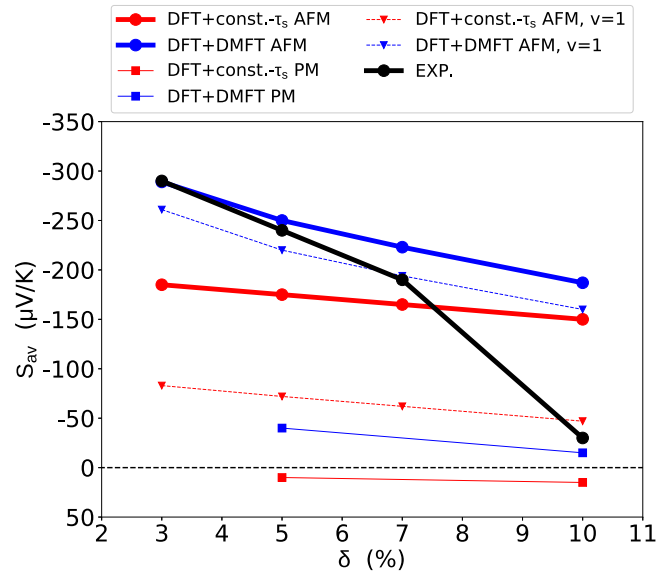


FIG. 4. Averaged Seebeck coefficient S_{av} as a function of electron doping level δ calculated with the spin-polarized (antiferromagnetic) DFT + const.- τ_s (red circles), DFT + DMFT in the antiferromagnetic phase (blue circles), nonmagnetic DFT + const.- τ_s (red squares), and DFT + DMFT in the paramagnetic phase (blue squares) and compared to experimental results from Ref. [18] (black circles). The evaluation of S_{av} with $v(\mathbf{k}) = 1$ [Eq. (8)] in the antiferromagnetic phase is shown by blue and red triangles. Lines are a guide for the eye.

well known that DMFT is not too reliable in predicting the absolute value of magnetic transition temperatures [24,52,53], as well as the transition as a function of the doping, which has been discussed, for example, in the context of high- T_C cuprate superconductors [54,55].

The doping dependence of S_{av} (see Fig. 4) shows that the DFT + const.- τ_s approximation cannot provide an accurate description over the full range of doping levels. For example, at 3% doping $|S_{av}|$ is smaller by more than $100 \mu\text{V K}^{-1}$ than the DFT + DMFT value and the experimental data. From the evaluation of $S_{av}^{y=||}$ (red and blue triangles) we see that the fundamental difference in the interpretation of S_{av} within DFT + DMFT and DFT + const.- τ_s , as discussed above at 5% doping, applies to the whole studied doping range. We, finally, point out that, in contrast to the PM DFT + DMFT, the nonmagnetic DFT + const.- τ_s calculations result even in a positive Seebeck coefficient of $10 \mu\text{V K}^{-1}$ at 5% doping and $15 \mu\text{V K}^{-1}$ at 10% doping (red squares).

For thermoelectric applications not only is S crucial, but more so the power factor $S^2\sigma$ (numerator of ZT). The calculated out-of-plane conductivity σ^{zz} of electron-doped LaMnAsO is a factor of about 50 lower in our DFT + DMFT calculations than the in-plane conductivity σ^{xx} . This is a consequence of the quasi-two-dimensional nature of LaMnAsO [24]. The crystal symmetries demand $\sigma^{xx} = \sigma^{yy}$ and $S^{xx} = S^{yy}$, and thus the averaged Seebeck coefficient is mainly determined by its in-plane value, $S_{av} \approx S^{xx}$ [Eq. (5)]. However, we find that the quasi-two-dimensional nature is not pronounced in the direction-dependent Seebeck coefficient itself. For all studied doping levels in the AFM phase $|S^{zz}|$ is less than $40 \mu\text{V K}^{-1}$ smaller than $|S^{xx}|$. Putting everything together, the in-plane direction offers a slightly higher Seebeck coefficient and exhibits a substantially higher conductivity than the out-of-plane direction. Therefore, we predict that a possible single-crystalline LaMnAsO $_{1-\delta}$ F $_{\delta}$ sample should show the highest power factor ($S^2\sigma$) if thermoelectricity is harvested in the in-plane direction.

V. CONCLUSION

We have studied the electronic influences on the Seebeck coefficient of electron-doped LaMnAsO within the framework of fully charge self-consistent DFT + DMFT calculations. To model experimentally synthesized LaMnAsO $_{1-\delta}$ F $_{\delta}$ we used the virtual crystal approximation at electron doping levels of $\delta = 3\%$, 5% , 7% , and 10% . In DFT the doping pushes the bottom of the flat xz/yz bands below the Fermi energy. On the contrary, the incorporation of electronic correlations within DMFT shows that doping leads to an incoherent weight at and below the chemical potential, whereas the renormalization of the unoccupied states results in strongly pronounced spectral features located directly above it. Both DFT and DFT + DMFT calculations predict negative Seebeck coefficients, however, with completely opposing underlying mechanisms. While the DFT + const.- τ_s approximation points towards a picture where the asymmetry in the velocities is pivotal, DFT + DMFT traces the Seebeck coefficient almost exclusively back to the asymmetry of the correlated spectral function. Therefore, our calculations demonstrate that the interpretation of the Seebeck coefficient in materials with

strong electronic correlations and nonnegligible incoherent spectral weight requires us to go beyond the constant scattering time approximation. Considering finite-lifetime effects within the DFT + DMFT framework yields a higher Seebeck coefficient in electron-doped LaMnAsO than what would be anticipated from DFT and, also, is in much better agreement with experimental data. The emergence of an incoherent spectral weight under doping is unique to correlated systems and could potentially offer new routes in the engineering of thermoelectric materials.

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APPENDIX: VIRTUAL CRYSTAL APPROXIMATION

A simple way of incorporating the effect of doping within band-structure methods is the virtual crystal approximation. Computationally, the VCA is efficient, because calculations can be carried out at the same cost as for the corresponding undoped structure. However, the VCA neglects charge localization and assumes that there is a virtual atom at all sites which interpolates between the original atom and the dopant. This picture is only adequate for atoms with similar radii and the same number of core electrons. Another possibility for taking doping effects into account is the construction of supercells, where the doped atoms are directly replaced by the dopant in a larger unit cell. Supercells assume a long-range order of the dopants in the crystal matrix. Using this approach within DFT + DMFT is certainly feasible at high enough doping levels, but it would be demanding for the lower doping levels used in this work due to the size of supercells needed.

To assess the applicability of the VCA to LaMnAsO $_{1-\delta}$ F $_{\delta}$ we compare our WIEN2k calculations to supercell calculations carried out with VASP 5.4.1 [56–59] with the projector augmented wave method [60,61] and pseudopotentials v. 54 [62]. The plane-wave energy cutoff is set to 400 eV. Like in the WIEN2k calculations, the PBE density functional and the same crystal structure parameters are used. The full Brillouin zone of the supercell is sampled with a $10 \times 10 \times 12$ Γ -centered Monkhorst-Pack \mathbf{k} grid [63], whereas for the WIEN2k calculation 10000 \mathbf{k} points in the Brillouin zone of the initial cell, which is nine times smaller in real space, are used. To be consistent with the experiment, we replaced the O atoms with F atoms in a $3 \times 3 \times 1$ supercell, which corresponds to a doping level of 11.1% (see inset in Fig. 5). In WIEN2k the VCA is employed by adjusting the atomic number of the O atoms to $Z = 8.11$. We note that the choice of WIEN2k for the VCA calculation and VASP for supercells is intrinsic to the differences in these two DFT codes. In the full-electron code WIEN2k large supercell calculations are demanding. On the other hand, VASP is a pseudopotential code, which makes it cumbersome to use the VCA.

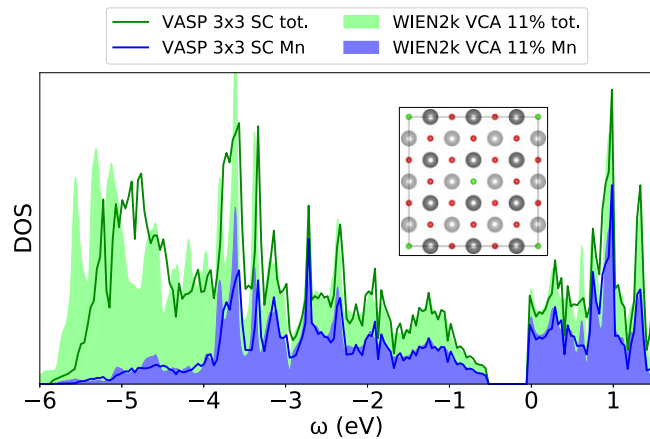


FIG. 5. Comparison of the WIEN2k VCA DOS in the antiferromagnetic state at 11% electron doping (filled areas) with the VASP DOS for a $3 \times 3 \times 1$ supercell (lines), i.e., a 11.11% substitution of O with F. The total DOS is shown in green, and the projected Mn-3d DOS in blue. Inset: Prepared with VESTA [64]. Top view of the La-O layer; the positions of the F atoms (green) substituting the O atoms (red) are indicated. La atoms sitting below the O plane are lighter in color than those above.

The agreement of the VCA with the supercell calculations (Fig. 5) is especially good in the energy region with no or only weak hybridization of the La-O and Mn-As layers, which is roughly between -3.5 and 1.5 eV. Note that the Mn-3d projected densities of state are in even better agreement than the total DOS. The former is the more important quantity, as only the Mn-3d orbitals are treated within DMFT. Of course, in energy regions exhibiting dopant states one cannot expect a good agreement between the VCA and the supercell calculation. This is visible from -6.0 eV to about -3.5 eV, where the DOS is mainly determined by O states, i.e., the properties of the La-O layer.

Supercell calculations with a different arrangement of the dopants in the unit cell did not substantially change the DOS. We also compared the VCA to a supercell calculation for the non-spin-polarized state and found an agreement on the same level as for the spin-polarized calculations (not shown). Furthermore, calculations for the undoped compound gave perfect agreement between WIEN2k and VASP. As we are mainly interested in spectral properties in the vicinity of the Fermi energy, which are to a great extent determined by the Mn-As layer, the comparison presented in Fig. 5 highlights the fact that VCA is an eligible approximation for the doping levels considered in this study.

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