


Efficient thermoelectricity in Sr₂Nb₂O₇ with energy-dependent relaxation timesGiulio Casu , Andrea Bosin , and Vincenzo Fiorentini *

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We evaluate theoretically the thermoelectric efficiency of the layered perovskite Sr₂Nb₂O₇ via calculations of the electronic structure and transport coefficients within density-functional theory and Bloch-Boltzmann relaxation-time transport theory. The predicted figure-of-merit tensor ZT , computed with energy-, chemical potential-, and temperature-dependent relaxation times, has one component increasing monotonically from around 0.4 at room temperature to 2.4 at 1250 K at an optimal carrier density of around $2 \times 10^{20} \text{ cm}^{-3}$, while the other components are small. The Seebeck coefficient is about 250 to 300 $\mu\text{V/K}$ at optimal doping and reaches 800 $\mu\text{V/K}$ at lower doping. We provide a PYTHON code implementing various approximations to the energy-dependent relaxation-time transport, which can be used to address different systems with an appropriate choice of material parameters.

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I. INTRODUCTION

Thermoelectricity as an energy source has been the focus of much research effort recently. Materials are assessed as candidate thermoelectrics based on their figure of merit,

$$ZT = \frac{\sigma S^2}{\kappa_e + \kappa_L} T,$$

with σ the electrical conductivity, S the Seebeck coefficient, T the temperature, and κ_e and κ_L the electronic and lattice thermal conductivities. Recently, we analyzed theoretically a few materials [1,2], in particular [2] the layered perovskite La₂Ti₂O₇ (LTO), finding interesting figure-of-merit results. In this paper, we study the layered perovskite Sr₂Nb₂O₇ (SNO), which is fairly close to LTO in terms of its low thermal conductivity and has a well-established growth procedure. The predicted figure of merit of SNO is very good, monotonically increasing from 0.3 at room temperature to 2.4 at 1250 K.

We also examine several approximations to the definition and use of relaxation times in the transport coefficient calculations in the Bloch-Boltzmann approximation [3], extending our approach in Ref. [2]. We provide and discuss a PYTHON code [4] that performs the calculations using data generated by the *ab initio* VASP [5] code and using the BOLTZTRAP2 (BT2) [6] code as a library.

II. METHOD AND AUXILIARY RESULTS

A. General

The ingredients of ZT are the electronic transport coefficients that can be obtained from the electronic structure (electrical and electronic-thermal conductivity, Seebeck thermopower) and the lattice thermal conductivity. For the latter, we adopt the experimental data of Ref. [7]: About 1 W/K/m, temperature independent, along the b axis and 1.8 W/K/m,

roughly isotropic and temperature independent, in the a, c plane. This assumption is justified by the fact that, based on our previous analysis of the thermal conductivity (Ref. [2], Sec. II C) in the analogous material La₂Ti₂O₇, the low thermal conductivity of SNO is probably intrinsic to the material and not defect originated.

For the electronic transport coefficients we use the *ab initio* density-functional band structure to calculate the coefficients as a function of the temperature and doping in the relaxation-time approximation to the linearized Boltzmann transport equation, known as Bloch-Boltzmann theory [3,6]. We explore several approximations to the energy- and temperature-dependent relaxation time (Secs. II C and II D). Based on preliminary calculations and the behavior of LTO, we choose to concentrate on n -type doping.

B. *Ab initio* calculations

Ab initio density-functional structure optimization and band-structure calculations are performed with the generalized gradient approximation [8] and the projector augmented wave (PAW) method [9] using the VASP code [5] with the Sr_sv, Nb_pv, and O_s PAW data sets and using the maximum of all suggested maximum cutoffs, 283 eV (increased as usual by 30% for calculations involving stress). The structure of the orthorhombic phase of SNO (Fig. 1) has space group $Cmc2_1$ up to 1615 K, above which it becomes $Cmcm$ (we neglect the minor incommensurate modulation [10] below 490 K, as it preserves closely the layered structure and the space group). We optimize the structure following quantum forces (threshold 0.01 eV/Å) and stress (threshold 0.5 kbar). The computed lattice constants are $a = 4.00 \text{ Å}$, $b = 27.30 \text{ Å}$, and $c = 5.82 \text{ Å}$, which are 1.5%, 2.1%, and 2.4% from the experimental values [7] 3.933, 26.726, and 5.683 Å, as expected due to the density functional we use. Electronic states are calculated on a $(24 \times 8 \times 16)$ k -point grid.

The conduction band minimum is at Γ , while the valence band maximum is at $X = (\pi/a, 0, 0)$; the minimum gap is

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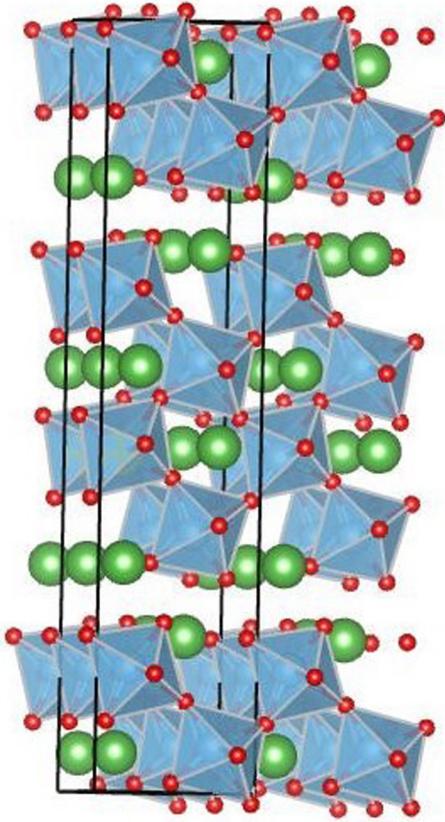


FIG. 1. Sketch of the structure of SNO. The a axis points into the page, the b axis vertically, and the c axis from left to right. The primitive cell is outlined.

2.5 eV (underestimated, as expected, in comparison to the roughly 4 eV experimentally [11,12]), so the n -type coefficients are essentially unaffected by valence states at any temperature. A closeup view of the conduction bands in the vicinity of the Γ point is shown in the left and center panels in Fig. 2; the right panel shows the density of states weighted by the Fermi-Dirac function (i.e., the energy-dependent carrier density), which clearly comes from the first four conduction bands at typical temperatures. [The density of states is recalculated by our code (Sec. IV) from the interpolated band structure on a $120 \times 40 \times 80$ k grid.]

C. Transport coefficients and relaxation time

To compute the transport coefficients accounting for the energy-dependent relaxation times we built a new code [4] (see Sec. IV) using parts of the BT2 [6] transport code as libraries. Via BT2, the *ab initio* bands (assumed to be rigid, i.e., not changing with doping or temperature) are interpolated as explained in Ref. [6] over a k grid much finer than the *ab initio* one. For the calculations reported below, the grid contains 60 times more points than the *ab initio* grid, so it is approximately equivalent to a $(94 \times 32 \times 62)$ grid.

As discussed in Refs. [1,2] in the constant-relaxation-time (CRT) approach the constant $\tau = \tau_0$ will factor out of the integrals determining the Onsager coefficients. In this case, the BT2 code returns the reduced coefficients $\bar{\sigma}_0 = \sigma/\tau_0$ and $\bar{\kappa}_{e,0} = \kappa_e/\tau_0$, determined by the band structure, temperature,

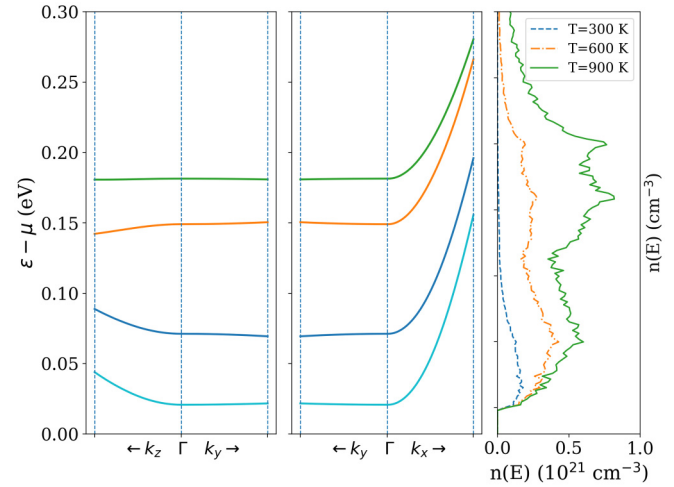


FIG. 2. Left and center: Conduction bands of SNO along the three reciprocal lattice directions, starting at their minimum at Γ . Right: Energy-dependent carrier density, i.e., the Fermi distribution times the density of states, for $T = 300, 600,$ and 900 K. The chemical potential is 15 meV below the conduction edge.

and doping but independent of τ_0 . ZT is then calculated from the reduced transport coefficients under some hypothesis for the relaxation time τ_0 . This is generally a poor approximation because a constant τ_0 is uncertain and largely arbitrary, and it cannot account for various relevant physical effects, such as Fermi distribution tails and phonon occupation changes, among others.

To improve over the constant-time approximation, we adopt a model relaxation time which depends on the temperature T , chemical potential μ , and carrier energy E . τ enters the kernel of the Fermi integrals (see Eq. (9) in Ref. [3]) which provide the building blocks of the Onsager transport coefficients. The relaxation time is

$$\tau(T, E, \mu) = 1/P_{\text{imp}} + 1/P_{\text{ac}} + 1/P_{\text{polar}},$$

where the rates P of impurity, acoustic-phonon, and polar-phonon scattering are given in Refs. [1,14,15] and, for convenience, in the Supplemental Material [16]. Piezoelectric scattering is neglected because the relevant matrix element [14] vanishes by symmetry [17,18]. Also, as in LTO, spontaneous polarization points along the c axis, so by symmetry it will not affect transport along a ; as it turns out, thermoelectric transport in SNO is sufficiently interesting only along the a axis.

The behavior of $\tau(E, T)$ in SNO is sketched vs E and T in Fig. 3. Clearly the LO polar phonon scattering dominates, and its downward jump across the LO phonon energy is at a very low energy, the most relevant region for transport (the detailed parameter values involved are discussed below). We mention in passing that it is now becoming possible [19] to compute *ab initio* the full k and energy dependence of the τ components related to electron-phonon scattering. This approach is, however, hugely more complex than ours, is still in its infancy in the field of thermoelectricity, and is therefore beyond our present scope.

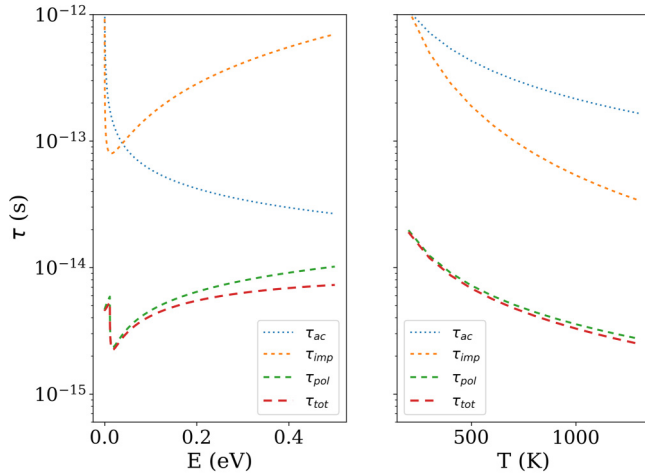


FIG. 3. Relaxation time $\tau(T, E)$ vs E ($T = 700$ K) and T ($E = 54$ meV above the conduction edge). μ is fixed at 0.

D. Approximations and parameters for τ

With the τ model just discussed, here we calculate the transport coefficients ZT using two approximations. The best one is the NCRT (nonconstant relaxation time), which uses the full energy-dependent time in the calculation of the Fermi integrals, including its chemical-potential dependence (specifically τ multiplies the kernel σ in the integral of Eq. 9 in Ref. [6]). The ART (average-relaxation-time) approximation uses instead the T - and μ -dependent, energy-averaged [20]

$$\tau_{\text{ART}}(T, \mu) = \frac{2 \int_0^\infty E \tau(T, E, \mu) D(E) \left(-\frac{\partial f(T, E, \mu)}{\partial E} \right) dE}{3 \int_0^\infty D(E) f(T, E, \mu) dE}$$

[$D(E)$ is the density of states, and f the Fermi-Dirac distribution] to compute ZT vs T from the reduced transport coefficients, as in Eq. 3 in Ref. [2]. The relaxation time, computed off-line and only once for each T and μ , still accounts for the T dependence of μ , Fermi function, etc., also improving slightly over Ref. [2], which used a parabolic band density of states.

The NCRT is typically relatively inexpensive (depending on the system and control parameters, up to at most a few hours on a laptop with a few gigabytes of memory usage, but typically much less than that). The ART is even lighter and is useful for exploratory work, providing in our experience a good guide to the full results (see the discussion below). Of course, CRT results can be compared by recalculating the reduced coefficients with BT2 and using a constant time (which we choose to be $\tau_0 = 5$ fs) to obtain ZT . All three codes are provided in the Supplemental Material [16] as well as online and discussed in Sec. IV.

The model τ requires several parameters. Some are imported from experiment or previous calculations: dielectric constants $\epsilon_\infty = 4.7$ and $\epsilon_{\text{lattice}} = 33.5$ [13,21], average sound velocity $v = 4438$ m/s [7], and dominant LO-phonon frequency $\hbar\omega_{\text{LO}} = 11.4$ meV [22]. Some others are computed directly: effective conduction mass $m_c^* = 0.3m_e$, deformation potential $D = 10$ eV, and density = 4930 kg/m³. The mass is obtained from a polynomial fit to the conduction band vs k (we use the a component of the mass tensor, since the

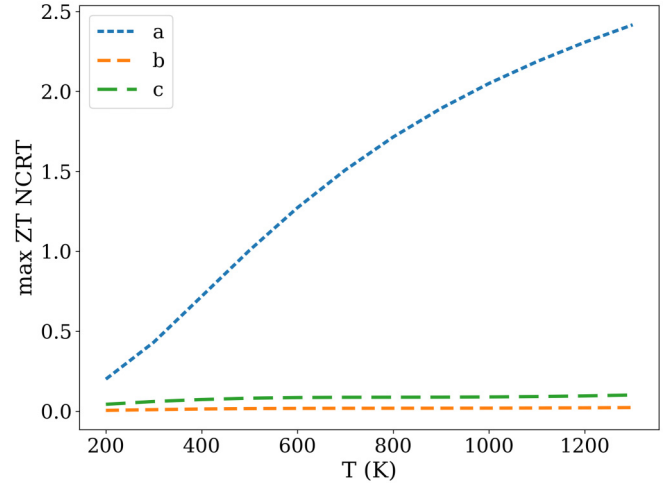


FIG. 4. Components of the ZT tensor at optimal doping (off-diagonal components are 0).

transport along the other directions is negligible anyway); the deformation potential is a numerical derivative of the conduction edge energy vs the strain. We note that the lowest LO phonon with a polarization in STO is much lower than in LTO, which enhances the polar scattering at low energy. We use only one phonon replica in the polar scattering rate.

III. RESULTS

In Fig. 4 we show the diagonal components of the ZT tensor at optimal doping (i.e., the maximum value as a function of the doping; as shown below, in this case the optimal doping changes little with temperature) obtained with our best approximation NCRT. The b and c components are small and of no relevance for the thermoelectricity, so we disregard them henceforth. The a component of ZT is instead large and therefore of practical interest, especially in the 500–1000 K range, where it is between about 1 and 2.

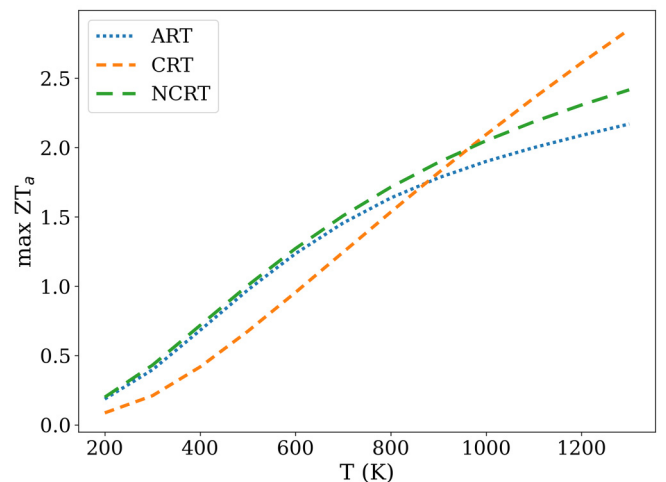


FIG. 5. ZT vs T (a component) for the different relaxation time treatments. In the CRT, $\tau_0 = 10$ fs.

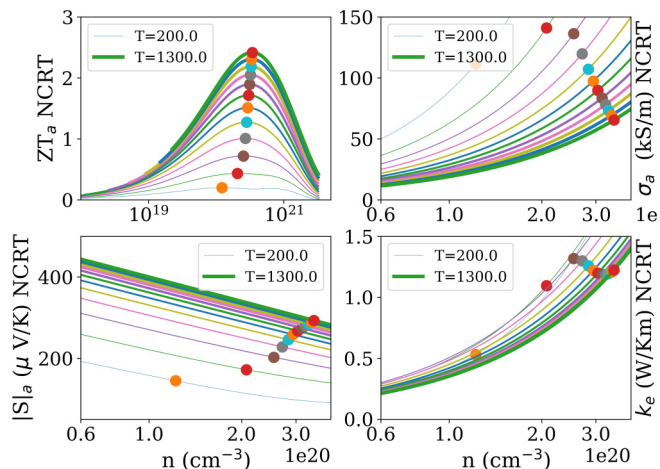


FIG. 6. ZT , Seebeck coefficient, conductivity, and electronic thermal conductivity vs doping at different T 's in the NCRT approach. T increases from 200 to 1300 K in steps of 100 K, indicated by increasing line thickness. Circles indicate the values at optimal doping, i.e., where ZT is maximal at that T .

In Fig. 5 we show ZT (a component) vs T at optimal doping for the three methods discussed above. Clearly, there are no dramatic deviations between the ART and the NCRT. The CRT result, aside from its direct dependence on τ_0 (which in this case was chosen sensibly after the fact), deviates most from the others due to its lack of temperature dependence.

Next, in Fig. 6 we report the ZT , Seebeck coefficient, electrical conductivity, and electronic thermal conductivity vs the doping as obtained by the NCRT, for T between 200 and 1300 K. The different curves for increasing T have increasing line thicknesses. The circles indicate the values at optimal doping, i.e., the doping at which ZT is maximal, which is between 1 and $3 \times 10^{20} \text{ cm}^{-3}$. Of course, it is easy to read off the graph any of the quantities at a fixed doping; for example, $ZT \simeq 1$ at $5 \times 10^{19} \text{ cm}^{-3}$ and 900 K. Similarly, the T behavior can be inferred by following the positions of the circles, and it is similar to that of LTO [2].

This prediction of ZT vs doping is also, implicitly, a prediction of the optimal doping needed to achieve the maximum ZT . We are in no position to evaluate the dopability of SNO, so it remains to be seen whether the optimal doping, or anything close to it, can be achieved experimentally. Also, we recall in passing that the conductivities are determined solely by electrons living in the perfect-crystal bands and subject to scattering from (mostly polar) phonons and charged impurities as embodied in $\tau(T, E, \mu)$, but no scattering is accounted for from disorder, dislocations, neutral impurities, traps, etc.; these could affect transport in ways we cannot quantify.

In this context, we note that the material may be useful even if not highly dopable, for applications requiring just a high thermoelectric power: $|S|$ is indeed larger at low doping, about $750\text{--}800 \mu\text{V/K}$ at 10^{18} cm^{-3} .

In Fig. 7 we report $(X_{\text{ART}} - X_{\text{NCRT}})/X_{\text{NCRT}}$, the relative deviation between the ART and the NCRT methods for quantity X . It appears that the ART is within about $\pm 5\%$ to 10% of the full result for ZT in the optimal doping region. The

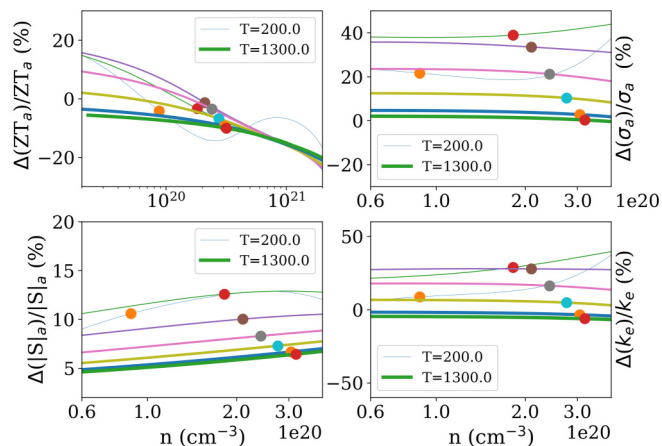


FIG. 7. Percentage deviations of the various quantities calculated with the ART from those calculated with the NCRT in Fig. 6. Circles as in Fig. 6.

conductivities are overestimated (by 0 to roughly 40%) using the ART, although the difference is largely compensated in the ZT ratio. Interestingly, this figure also reveals the extent to which the treatment of τ affects the Seebeck coefficient. S does depend on τ in the NCRT, whereas by construction it does not in the ART. The NCRT description appears to reduce S (in absolute value) by about 5% to 10% in this material. Note that, of course, none of the above findings need be generally applicable to other systems.

We close with an estimate of a directional average of ZT , potentially useful for polycrystalline material. In Fig. 8 we report three averages: The trace of ZT , the harmonic average [25] of the components of ZT , and ZT calculated from the harmonic averages of the conductivities and the trace of the Seebeck coefficient. The latter is probably the appropriate choice, but in any event the results are, as expected, much less exciting due to the small c and b components and the dominance of low conductivities in the averages. This suggests that the scope for SNO in thermoelectricity is as a monocrystal, not quite as a polycrystal. This may not

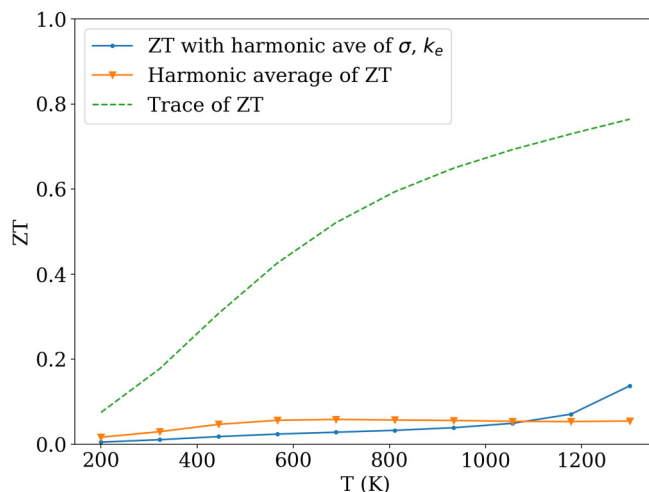


FIG. 8. Three types of directional averages of ZT .

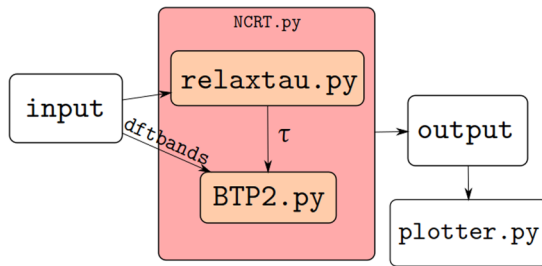


FIG. 9. Flux diagram of the code for the NCRT.

be entirely disheartening, because the structural and growth properties [23] of SNO render it unlikely to be produced in the form of nanometer-sized polycrystals, multimicron-sized crystallites as in sintered powder ceramics being likely [24]). Decently sized monocrystals are indeed fairly common and should be the ultimate goal of growth experiments.

IV. THE CODE AND HOW TO USE IT

Our code [4] is written in PYTHON (tested up to version 3.7) and is a free and open source. We provide its current snapshot in the Supplemental Material [16], with the VASPRUN.XML and INPUT files used for the present material. The code comes in three stand-alone versions implementing the approximations CRT, ART, and NCRT discussed above.

In the CRT and ART, the reduced coefficients calculated by BT2 [6] are used to compute ZT either with the constant τ_0 or, in the case of ART, with an energy-averaged τ , computed separately. If the NCRT is used, the code follows BT2 [6] up to the calculation of energies $\varepsilon_b(\mathbf{k})$ on the fine grid, at which point it computes the relaxation time $\tau(\varepsilon)$ on the same energy grid and multiplies the integrand of the Fermi integrals by τ . After that, it goes back to the BT2 sequence and eventually outputs the full coefficients. The current version works for n -type doping; extension to p -type doping may be implemented, in which case the code will be updated at [4].

The multiprocessing PYTHON library is used for τ and the Fermi integrals (currently only for ART.PY). The output is saved in JSON format, and the data structure is based on NUMPY multidimensional arrays: For example, the figure of merit ZT is a three-dimensional array, the dimensions being a Cartesian component (with no magnetic field, ZT has only diagonal elements), the temperature T , and the chemical potential μ .

The operative structure comprises three folders: SCRIPT, INPUT, and DATA. The folder SCRIPT contains the code in the three versions CRT.PY, ART.PY, and NCRT.PY (Fig. 9). Also, it hosts the utilities TAU.PY, which computes the relaxation times vs T and E for plotting and external use, and

PLOTTER.PY, which plots a number of quantities of interest, as well as the custom libraries FUNZVAR.PY and RELAXTAU.PY. The latter contains the τ model and can be edited to include, for example, additional scattering mechanisms.

The folder INPUT must contain two (optionally, three) files. The file VASPRUN.XML contains the *ab initio* calculation results, including the band structure, obtained with VASP (for information on using other DFT codes refer to the BT2 forum [26]). The file INPUT contains control parameters (among which are the mesh multiplier from Sec. II C and the ranges of temperature, chemical potential, energy, etc.) and material parameters (dielectric permittivities, effective masses, deformation potentials, sound velocities, LO-phonon energies) that enter the relaxation-time model, as well as the lattice thermal conductivity tensor. The latter can alternatively be read from the third optional file LATTCOND.

The chosen script (or scripts) plus TAU.PY are run in SCRIPTS. The output, dumped in DATA, is then analyzed using PLOTTER.PY, which reads and deserializes JSON data to NUMPY arrays and plots the quantities of interest (and can of course be adapted to fit individual requirements). The package is stand-alone and its disk occupation is minor, so it can be placed anywhere, for example, in a local directory for the material under study. More information is given in the package's README.pdf file [4] and in the Supplemental Material [16].

As already mentioned, the NCRT is fairly inexpensive computationally, depending on the system and control parameters. For the present material, it costs a couple of hours with about 1 Gbyte memory usage for production-level parameters. We will implement multiprocessing in the NCRT also shortly, which will speed up the proceedings accordingly. The ART, on the other hand, will run in minutes, being lighter by its very nature as well as its use of parallelism.

V. SUMMARY

We predicted a monotonic ZT of between 0.4 and 2.2 at between 300 and 1200 K under n doping in the layered perovskite $\text{Sr}_2\text{Nb}_2\text{O}_7$ via calculations of the electronic structure and transport coefficients. The optimal carrier density is in the low- 10^{20} cm^{-3} range. At optimal density the Seebeck thermopower coefficient is between 220 and 320 $\mu\text{V}/\text{K}$, but it can reach 800 $\mu\text{V}/\text{K}$ at lower doping. The largest ZT is along the a crystal axis; other components are one to two orders of magnitude smaller. Much of the potential of this material is due to its low and almost T -independent lattice thermal conductivity. We explored the use of constant or energy- and temperature-dependent relaxation times. Averaged-time or full calculations are rather comparable in the present case, though of course this need not be the case in general. To help improve the treatment of relaxation time for other materials, we provide a code [4] implementing our approach.

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- $$\frac{3}{x_h} = \frac{1}{x_1} + \frac{1}{x_2} + \frac{1}{x_3}.$$
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