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Thermopower, Hall tensor, and relaxation time approximation for elemental zinc

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The constant relaxation time approximation is investigated through the calculation of the thermopower, anisotropy of the conductivity, and Hall tensor of elemental zinc. It is shown that this approximation is reliable at high enough temperature ($\gtrsim$150 K). Moreover, when a magnetic field is applied to the system, the relaxation time is shown to fulfill a sum rule due to Onsager reciprocity relations. This reduces the range of possible approximations for the relaxation time in Hall tensor calculations. The way in which the basic equations of transport theory have to be used to get better numerical efficiency is also discussed.

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I. INTRODUCTION

Recently, thermopower calculations have been performed on quite complicated systems,[1–5] including noncubic crystal structures. The basic approach is the same for all of these calculations. The system response to the applied fields, $\vec{E}$ and $\vec{\nabla}T$, is investigated within the semiclassical framework of Boltzmann transport theory,

$$\vec{v}^{\,n}_{\vec{k}} \cdot \vec{\nabla} T \frac{\partial f^n_{\vec{k}}}{\partial T} - \frac{e}{\hbar}(\vec{E} + \vec{v}^{\,n}_{\vec{k}} \times \vec{B}) \cdot \frac{\partial f^n_{\vec{k}}}{\partial \vec{k}} = \sum_{n'\vec{k}'} (f^{n'}_{\vec{k}'} - f^n_{\vec{k}}) W_{nn'}(\vec{k},\vec{k}').$$

In this equation f is the one particle phase-space distribution function, $W_{nn'}(\vec{k},\vec{k}')$ is the transition probability from state $n\vec{k}$ to state $n'\vec{k}'$, and $\vec{v}^{\,n}_{\vec{k}}$ is the electron velocity. It is calculated as the derivative of the energy bands $\varepsilon^n_{\vec{k}}$ obtained from a standard density functional theory calculation, $\vec{v}^{\,n}_{\vec{k}} = (1/\hbar)\vec{\nabla}\varepsilon^n_{\vec{k}}$. In a Fermi liquid picture this means that the Kohn-Sham system is chosen as the reference noninteracting fermionic system.

In the absence of a magnetic field and in the relaxation time approximation, when we look for a solution of the Boltzmann equation linear in fields, $f^n_{\vec{k}} = f_0(\varepsilon^n_{\vec{k}}) + e\vec{E}\cdot\vec{\Lambda}^n_{\vec{k}}(\partial f_0/\partial\varepsilon)$, the electrical and heat current densities, $\vec{j}$ and $\vec{j}_Q$, can be found in closed form. Here $\vec{\Lambda}^n_{\vec{k}}$ is the electron mean free path.[6] With the relaxation time $\bar{\bar{\tau}}_n(\vec{k})$ defined by

$$\sum_{n'\vec{k}'} (\Lambda^{n'}_{\vec{k}'} - \Lambda^n_{\vec{k}}) W_{nn'}(\vec{k},\vec{k}') = -\bar{\bar{\tau}}^{\,-1}_n(\vec{k})\Lambda^n_{\vec{k}}, \tag{1}$$

the currents $\vec{j}$ and $\vec{j}_Q$ have the form

$$\vec{j} = \bar{\bar{L}}_{11}\vec{E} + \bar{\bar{L}}_{12}\left(-\frac{\vec{\nabla}T}{T}\right), \tag{2}$$

$$\vec{j}_Q = \bar{\bar{L}}_{21}\vec{E} + \bar{\bar{L}}_{22}\left(-\frac{\vec{\nabla}T}{T}\right), \tag{3}$$

where $\bar{\bar{L}}_{ij}$ are the Onsager coefficients which are expressed in terms of the system transport function $\bar{\bar{\sigma}}(\varepsilon)$,

$$\bar{\bar{L}}_{ij} = \int d\varepsilon \left(\frac{\varepsilon-\mu}{-e}\right)^{i+j-2} \frac{\partial f_0}{\partial \mu}\bar{\bar{\sigma}}(\varepsilon), \tag{4}$$

$$\bar{\bar{\sigma}}(\varepsilon) = \frac{e^2}{(2\pi)^3}\sum_n \int\int_{\varepsilon^n_{\vec{k}}=\varepsilon} \frac{dS}{|\vec{\nabla}\varepsilon^n_{\vec{k}}|}\vec{\Lambda}^n_{\vec{k}} \otimes \vec{v}^{\,n}_{\vec{k}}. \tag{5}$$

In these equations $-e$ is the electron charge, μ the chemical potential, and f_0 the Fermi-Dirac function.

The results[1–5] for real systems obtained from Eqs. (4) and (5) using electron energies from band structure calculations only differ by the numerical methods used to calculate electron velocities and the way in which integrations over surfaces of constant energies are performed. All these calculations use the relaxation time approximation and since they are performed in the context of the design of new complex thermoelectric materials this relaxation time is not even calculated. Rather simplifying assumption are made, like a constant mean free path approximation when the kinetic theory can be used, the Mott approximation in cases where there are localized d states around E_F, or simply a constant relaxation time approximation when nothing can be said about the scattering mechanisms. This is equivalent to assume that the system reaches the Fermi-Dirac distribution following a Poissonian process. Of course, more elaborate procedures where scattering mechanisms are actually calculated are possible,[7] but approximations are useful because they strongly reduce the computational time for complex structures and therefore make theoretical design of new thermoelectric materials possible.[8] Also, they are almost necessary since the materials considered for thermoelectric applications often have a complicated microstructure, as revealed by microprobe, with dispersed secondary phases which are not easy to describe. In the following it will be shown that even the simplest of these approximations, namely the constant relaxation time, gives reliable results at high enough temperature for the thermoelectric and Hall tensors of zinc. Zinc is a good test case as it is a well defined simple system which however has a noncubic crystal structure and is numerically nontrivial because of the topology of the Fermi surface.

The outline of the paper is the following. In Sec. II we present the calculation of the thermopower and anisotropy of the conductivity of zinc. The results for the Hall tensor are presented in Sec. III. The numerical procedure we use is

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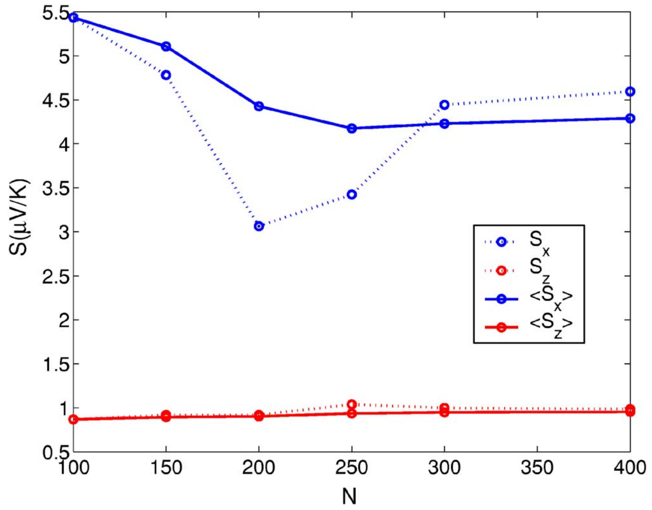

FIG. 1. (Color online) Convergence of the thermoelectric tensor at $T=300$ K. N is the number of thousands of points used to sample the first Brillouin zone. $\langle S\rangle$ is the cumulated average of the thermopower. The upper curves refer to a basal component of the thermoelectric tensor and the lower ones to the z component.

stable and appropriate for automatic calculations. In the last section the relaxation time approximation is discussed, and we show that it is constrained by Onsager reciprocity relations to fulfill a sum rule when a magnetic field is present as in the case of Hall measurements.

II. CALCULATION OF THERMOPOWER AND ANISOTROPY OF CONDUCTIVITY

The thermopower and the anisotropy of conductivity have been calculated using the following k-independent relaxation time,

$$\bar{\bar{\tau}} = \begin{pmatrix} \tau_{xx} & 0 & 0 \\ 0 & \tau_{xx} & 0 \\ 0 & 0 & \tau_{zz} \end{pmatrix}, \tag{6}$$

where z is the c axis and xy are in the basal plane.

Using the electronic structure obtained from a linearized augmented plane waves[9] calculation we obtain for the thermopower the convergence curve shown in Fig. 1. A spectral collocation method has been used to calculate the electron velocities[4] and the surface integral of Eq. (5) is obtained using the tetrahedron method.[10,11] We see that the convergence is much more difficult to obtain for the basal component than for the z component. This is due to the electron velocities, which are normal to the Fermi surface, and vary more slowly along the z axis than in the basal plane (see Ref. 12). It is clear from Fig. 1 that the convergence is already good with 200 000 points in the first Brillouin zone. $\bar{\bar{S}}$ is however not obtained directly from Eq. (4) and

$$\bar{\bar{S}} = \frac{1}{T}\bar{\bar{L}}_{11}^{-1}\bar{\bar{L}}_{12} \tag{7}$$

because $\bar{\bar{L}}_{12}$ is the integral of a quantity which is not positive definite, which makes its evaluation quite difficult and the convergence of the thermopower very slow. Instead we use the identity $(\varepsilon-\mu)(\partial f_0/\partial\mu)=T(\partial f_0/\partial T)$ and obtain

$$\bar{\bar{L}}_{12} = \frac{T}{-e}\frac{d}{dT}\int d\varepsilon f_0(\varepsilon)\bar{\bar{\sigma}}(\epsilon). \tag{8}$$

The quantity integrated is now positive definite. The convergence is therefore much better than with Eq. (4).

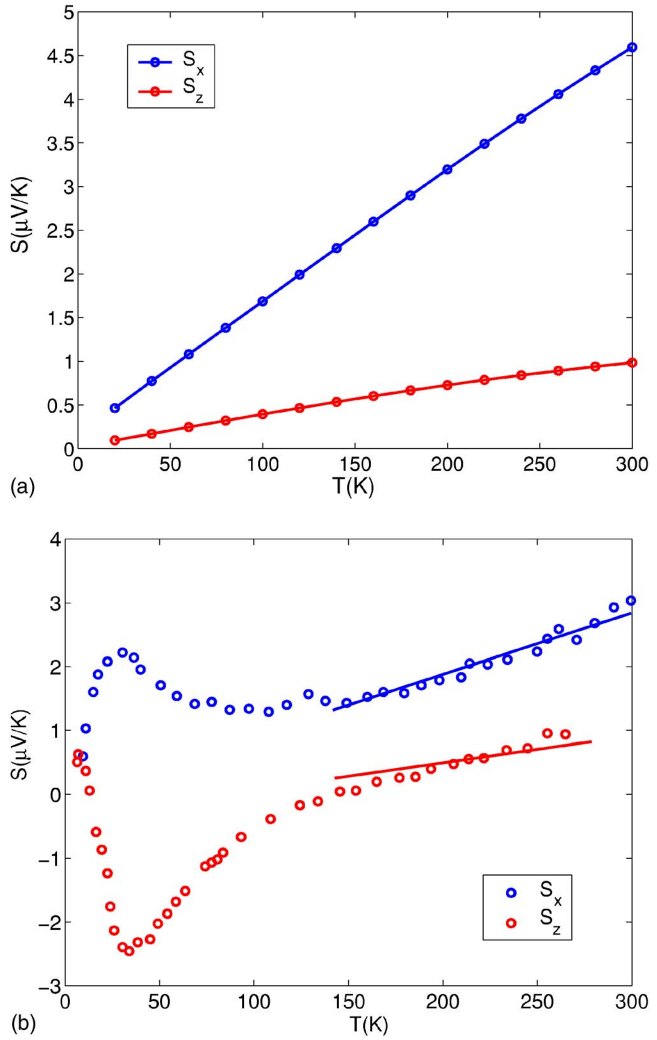

FIG. 2. (Color online) (a) Theoretical and (b) experimental (Ref. 13) thermopower of zinc. In both cases the lower curve refers to the z component of the thermopower and the upper one to a basal component.

In Fig. 2 we compare the calculation of the thermopower as a function of temperature with the experimental measurements. At low temperature the two curves are very different. Indeed at these temperatures the constant relaxation time is no longer satisfactory,[14] the electron-phonon enhancement should be considered, and the phonon-drag contribution should be added to the diffusion thermopower of Eq. (7). In particular, since the phonon drag is not included in our calculation, the hump around 40 K does not appear in the theoretical curve. However, as the temperature increases the phonon-phonon interactions increase and bring the phonon system back to equilibrium. The phonon-drag contribution to

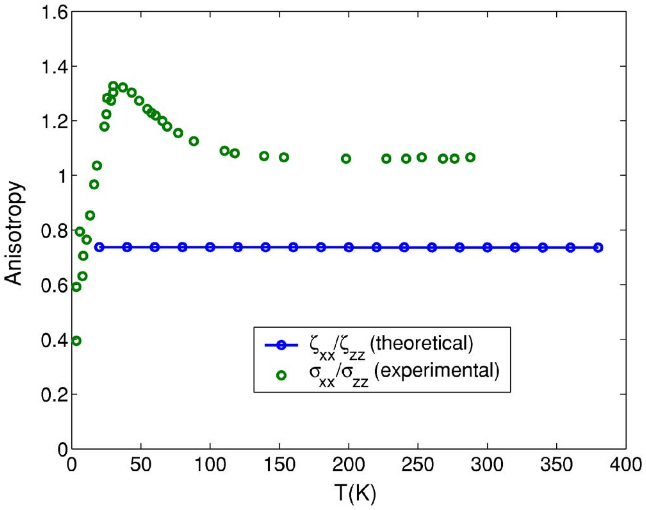

FIG. 3. (Color online) ζ_{xx}/ζ_{zz} factor and the anisotropy of the conductivity of zinc (from Ref. 15).

the thermopower therefore decreases (exponentially) to zero. Consequently, it is only in the high temperature region that we should compare our calculations with experiments. Figures 2(a) and 2(b) show that the agreement is indeed rather good for $T \gtrsim 150$ K.

For the anisotropy of the conductivity, we have

$$\alpha_\sigma = \frac{\sigma_{xx}}{\sigma_{zz}} = \frac{\tau_{xx}}{\tau_{zz}} \frac{\int d\varepsilon \frac{\partial f_0}{\partial \mu} \sum_{nk} \{\vec{v}_x^n(\vec{k}) \vec{v}_x^n(\vec{k})\} \delta(\varepsilon - \varepsilon_{\vec{k}}^n)}{\int d\varepsilon \frac{\partial f_0}{\partial \mu} \sum_{nk} \{\vec{v}_z^n(\vec{k}) \vec{v}_z^n(\vec{k})\} \delta(\varepsilon - \varepsilon_{\vec{k}}^n)} \tag{9}$$

$$\equiv \frac{\tau_{xx}}{\tau_{zz}} \frac{\zeta_{xx}}{\zeta_{zz}}. \tag{10}$$

Therefore, if we compare the experimental value of the anisotropy of conductivity, $\alpha_\sigma|_{\text{expt}}$, to the calculated value of the ratio ζ_{xx}/ζ_{zz}, which is independent of the relaxation time, we can obtain a value for τ_{xx}/τ_{zz}. $\alpha_\sigma|_{\text{expt}}$ is represented in Fig. 3 by the curve in green and ζ_{xx}/ζ_{zz} by the curve in blue. Above 100 K, τ_{xx}/τ_{zz} is therefore constant with a value around $\tau_{xx}/\tau_{zz} \sim 1.42$.

It now appears that the very small anisotropy of the conductivity of zinc, $\alpha_\sigma|_{\text{expt}} \sim 1.04$, comes from a compensation between the anisotropy of the Fermi surface, expressed through $\zeta_{xx}/\zeta_{zz} < 1$, and the anisotropy of the relaxation time $\tau_{xx}/\tau_{zz} > 1$. This is consistent with the two orthogonal plane waves model calculation of Chan and Huntington[16] and the pseudopotential results of Tomlinson,[14] where the anisotropy of the relaxation time was calculated for a phonon mechanism.

At temperature below 100 K the calculation is no longer satisfactory because, as already stated for the thermopower, the relaxation time can no longer be assumed to be $\vec{k}$ independent,[14] and, possibly, also because of the phonon-drag effect.

III. HALL EFFECT CALCULATIONS

When a magnetic field is applied to the system the conductivity can still be written as in Eq. (4) with a transport function which has the form of Eq. (5). The vector mean free path is now obviously different. Substituting $f_{\vec{k}}^n = f_0(\varepsilon_{\vec{k}}^n) + e\vec{E} \cdot \vec{\Lambda}_{\vec{k}}^n (\partial f_0 / \partial \varepsilon)$ in the Boltzmann equation with a magnetic field different from zero and $\vec{\nabla} T = 0$, we find the following expression for $\vec{\Lambda}_{\vec{k}}^n$:

$$\vec{\Lambda}_{\vec{k}}^n = \Lambda_{\vec{k}}^{n,i} \vec{e}_i, \tag{11}$$

$$\Lambda_{\vec{k}}^{n,i} = \frac{\tau_s^i}{\hbar} \partial_j(\varepsilon_{\vec{k}}^n) g^{js} + \frac{e}{\hbar^2} \tau_s^j (\vec{e}_1, \vec{e}_2, \vec{e}_3) \partial_t(\varepsilon_{\vec{k}}^n) \times B_u \partial_l(\Lambda_{\vec{k}}^{n,s}) g^{to} g^{uj} g^{kl} \varepsilon_{ojk}. \tag{12}$$

The Einstein summation convention has been used.

In these equations $\{\vec{e}_i\}$ are unit vectors collinear to the vectors that span the reciprocal cell used for the calculation of energy bands. $g_{ij} = \vec{e}_i \cdot \vec{e}_j$ is the metric tensor and ε_{ijk} the Levi-Civita symbol. B_i and $\Lambda_{\vec{k}}^{n,i}$ are respectively the i components of the magnetic field $\vec{B}$ and $\vec{\Lambda}_{\vec{k}}^n$ vectors.

Using Eq. (12), which is valid in any coordinate system, the vector mean free path can again be evaluated numerically using the spectral collocation method introduced in Ref. 4. This approach uses a Fourier interpolation of electron energies obtained from band structure calculation. From this a matrix representation of the ∂_i operators is found,[17] and therefore Eq. (12) can be solved iteratively for the electron mean free path, or by direct inversion in the general case. The full magnetic field dependent conductivity tensor could therefore be calculated from Eqs. (4), (5), and (12). To obtain the Hall tensor, terms up to first order in the magnetic field are however sufficient.

The conventional definition of the Hall coefficient as the proportionality constant between the Hall electric field and $j_x B_z$ is not the most convenient for numerical calculations in nonorthogonal systems. Instead we propose to use the Onsager reciprocity relations from the beginning. We then obtain an expression which is valid in any coordinate system. Moreover, it is independent of the microscopic model of scattering and therefore allows us to discuss the relaxation time approximation (see the next section).

First we decompose the conductivity and resistivity tensor into symmetric and antisymmetric parts to define the $\vec{s}(\vec{B})$ and $\vec{r}(\vec{B})$ vectors:

$$\vec{j} = \bar{\bar{\rho}}_s(\vec{B})\vec{E} + \bar{\bar{\rho}}_a(\vec{B})\vec{E} = \bar{\bar{\rho}}_s(\vec{B})\vec{E} + \vec{s}(\vec{B}) \times \vec{E}, \tag{13}$$

$$\vec{E} = \bar{\bar{\sigma}}_s(\vec{B})\vec{j} + \bar{\bar{\sigma}}_a(\vec{B})\vec{j} = \bar{\bar{\sigma}}_s(\vec{B})\vec{j} + \vec{r}(\vec{B}) \times \vec{j}. \tag{14}$$

Now Onsager reciprocity relations tell us that the symmetric part is an even function of the magnetic field and the antisymmetric part an odd function. Therefore, to first order in $\vec{B}$, we get

$$\vec{j} = \bar{\bar{\rho}}_s(0)\vec{E} + \bar{\bar{\mathcal{A}}}_S\vec{E} + O(B^2) = \bar{\bar{\rho}}_s(0)\vec{E} + (\bar{\bar{S}}\vec{B}) \times \vec{E} + O(B^2), \tag{15}$$

$$\vec{E} = \bar{\bar{\sigma}}_s(0)\vec{j} + \bar{\bar{\mathcal{A}}}_R\vec{j} + O(B^2) = \bar{\bar{\sigma}}_s(0)\vec{j} + (\bar{\bar{R}}\vec{B}) \times \vec{j} + O(B^2). \tag{16}$$

These are the defining equations for the tensor $\bar{\bar{S}}$ and the Hall tensor $\bar{\bar{R}}$ which are independent of the magnetic field. $\bar{\bar{\mathcal{A}}}_S$ and $\bar{\bar{\mathcal{A}}}_R$ are respectively first order approximations of tensors $\bar{\bar{\sigma}}_a(\vec{B})$ and $\bar{\bar{\rho}}_a(\vec{B})$.

From the above equations we get finally

$$\bar{\bar{\mathcal{A}}}_R = -\bar{\bar{\sigma}}_s(0)^{-1}\bar{\bar{\mathcal{A}}}_S\bar{\bar{\sigma}}_s(0)^{-1}. \tag{17}$$

Since $\bar{\bar{\mathcal{A}}}_R$ is the antisymmetric tensor associated with the vector $\bar{\bar{R}}\vec{B}$ its knowledge, for fixed $\vec{B}$, is sufficient to find the Hall tensor $\bar{\bar{R}}$.

This procedure for the calculation of the Hall tensor is numerically very convenient since it involves only symmetric and antisymmetric parts of the conductivity tensor $\bar{\bar{\sigma}}(\vec{B})$ and is thus very stable. Note also that because $\bar{\bar{\mathcal{A}}}_S$ is the linear approximation to $\bar{\bar{\sigma}}_a(\vec{B})$, Eq. (12) has to be solved for the mean free path with only one iteration. For a cubic system, this approach is of course equivalent to the Ziman formula.[18]

The Hall tensor of zinc has been calculated in this way. It has two independent coefficients since zinc has a hexagonal structure. R_1, the coefficient with the $\vec{B}$ field along the x axis, and R_2, the coefficient when $\vec{B}$ is along the z axis. These coefficients are independent of the relaxation time which is assumed to be constant and now also isotropic. As demonstrated in the next section, this is needed to fulfill the Onsager reciprocity relations when a magnetic field is applied to the system.

Figure 4 shows the convergence curve for the cumulated average of R_1 and R_2 as functions of the inverse number of points, $\mathcal{N}$, used to sample the first Brillouin zone. Taking the $\mathcal{N} \to \infty$ limit to obtain the values of the coefficients, we find

$$R_1 = -0.39 \times 10^{-10}\ \text{m}^3/\text{C}, \quad R_2 = 1.5 \times 10^{-10}\ \text{m}^3/\text{C}.$$

These calculated values should be compared to experimental ones,[19]

$$R_1 = -0.28 \times 10^{-10}\ \text{m}^3/\text{C}, \quad R_2 = 1.4 \times 10^{-10}\ \text{m}^3/\text{C}.$$

The agreement is therefore rather good. This shows that the crude approximation of a constant isotropic relaxation time allows us to calculate the Hall tensor at 300 K with a good accuracy without any adjustable parameters. The small discrepancies with experiments may be due to this approximation, but also to the extrapolating procedure $\mathcal{N} \to \infty$.

IV. THE RELAXATION TIME APPROXIMATION

The symmetry of microscopic equations over the past and future may constrain the relaxation of the system toward equilibrium. The compatibility of the approximations used for the relaxation time with these constraints must therefore be checked.

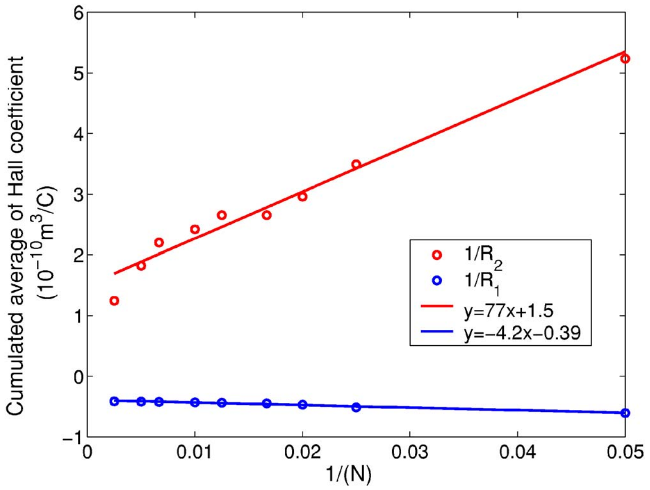

FIG. 4. (Color online) Convergence curves for the Hall tensor. N is the number of thousands of points used to sample the first Brillouin zone. R_2 is clearly positive and R_1 negative.

When electric field and temperature gradient are applied to the system the invariance of the microscopic equations under time inversion, which is expressed through Onsager reciprocity relations, only implies that second rank tensors like conductivity have to be symmetric. Formula (6) for $\bar{\bar{\tau}}$ is therefore perfectly allowed.

The situation is different when a magnetic field is applied on the system. Symmetric and antisymmetric tensors have a defined parity. They are respectively even and odd functions of the magnetic field. For the $\bar{\bar{\mathcal{A}}}_S$ tensor defined in the preceding section, this gives

$$(\mathcal{A}_S)_{ij} + (\mathcal{A}_S)_{ji} = 0$$
$$\Leftrightarrow \int d^3k \varepsilon_{\alpha\beta\gamma} v_\beta B_\gamma \partial_\alpha(\tau_{sp} v_p)(\tau_{is} v_j + \tau_{js} v_i)\frac{\partial f_0}{\partial \varepsilon} = 0. \tag{18}$$

This can be seen as a sum rule the relaxation time $\tau_{ij}(\vec{k})$ must fulfill.

In the case of a k dependent scalar approximation, $\tau_{ij}(\vec{k}) = \delta_{ij}\tau(\vec{k})$, integrating by part the term proportional to v_i, the above sum rule becomes

$$\int d^3k \partial_\alpha\left(\varepsilon_{\alpha\beta\gamma} v_\beta B_\gamma \frac{\partial f_0}{\partial \varepsilon}\right)\tau^2 v_j v_i = 0. \tag{19}$$

Since $\varepsilon_{\alpha\beta\gamma}\partial_\alpha v_\beta = 0$ the integral is zero. Equation (18) is therefore fulfilled for any function $\tau(\vec{k})$.

On the other end if the relaxation time is considered as a k independent tensor, in the coordinate system where $\bar{\bar{\sigma}}_s$ is diagonal we have $\tau_{ij}=\tau_{ii}\delta_{ij}$. As before, integrating by part the term proportional to v_i, formula (18) becomes

$$(\tau_{ii}^2-\tau_{jj}^2)\int d^3k\varepsilon_{\alpha\beta\gamma}v_\beta B_\gamma v_j(\partial_\alpha v_i)\frac{\partial f_0}{\partial\varepsilon}=0. \quad (20)$$

Because the integral is in general different from zero, we get

$$\tau_{ii}^2=\tau_{jj}^2, \quad \forall\ i,j=1,2,3. \quad (21)$$

We can therefore conclude that *whenever a magnetic field is applied on the system, a constant relaxation time must also be isotropic*. This allows the use of a tensorial relaxation time for the calculation of the conductivity and Seebeck coefficient, since no magnetic field is present, but implies a scalar constant relaxation time for the Hall tensor calculations. These are two different approximations for the solution of the Boltzmann equation. In each case one must choose the most general one compatible with space and time symmetries. This has not always been realized by previous authors.[20]

V. CONCLUSION

To conclude, the thermopower, the anisotropy of conductivity, and the Hall tensor have been calculated for elemental zinc. It has been shown that Eqs. (8) and (17) allow us to do this in a numerically efficient way.

These calculations show that at high enough temperature a constant tensorial relaxation time allows us to calculate quite accurately transport properties such as the thermopower when $\vec{E}$ and $\vec{\nabla}T$ are applied with no magnetic field. The small anisotropy of the conductivity of zinc then appears as a consequence of a compensation between the anisotropy of the relaxation and the one of the Fermi surface.

When a $\vec{B}$ field is applied with no temperature gradient this anisotropic relaxation time no longer fulfills Onsager reciprocity relations. If it is assumed to be k independent then it must also be isotropic. We have shown that this crude approximation is however sufficient to calculate the Hall tensor successfully.

These good results for zinc add some credit to the use of simple relaxation times in the thermopower and Hall calculation of complex materials.

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