Supplementary information for: First Principles explanation of the positive Seebeck coefficient of lithium

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METHODOLOGIES

The LOVA formalism, developed by Allen[1] since the 1970s for the case of electron transport, centers around a scattering operator description of the diffusive propagation of electrons in a phonon bath (eventually with impurity or other scattering added). The main quantity is a spectral function for transport, $\alpha_{tr}^2 F$, analogous to the Eliashberg spectral function and expressed as:

$$
\begin{aligned}
\alpha_{tr}^2 F(s, s', \alpha, \beta, \epsilon, \epsilon', \omega) &= \frac{1}{2N(\epsilon_F)} \sum_{\mathbf{kk'}} |g_{\mathbf{k}j\mathbf{k'}j'}^{\mathbf{q}\nu}|^2 \\
&\times \left[F_\alpha(\mathbf{k}) - sF_\alpha(\mathbf{k'}) \right] \times \left[F_\beta(\mathbf{k}) - s'F_\beta(\mathbf{k'}) \right] \\
&\times \delta(\epsilon_{\mathbf{k}} - \epsilon)\delta(\epsilon_{\mathbf{k'}} - \epsilon')\delta(\omega_{\mathbf{q}} - \omega)
\end{aligned}
\tag{1}
$$

where

$$
g_{\mathbf{k}j\mathbf{k'}j'}^{\mathbf{q}\nu} = \frac{\vec{\eta}_{\mathbf{q}\nu}}{\sqrt{2M\omega_{\mathbf{q}\nu}}} \langle \psi_{kj} | \delta V^{\mathbf{q}\nu} | \psi_{k'j'} \rangle
\tag{2}
$$

is the electron-phonon coupling (EPC) matrix between electrons in bands j at $\mathbf{k}$ and j' at $\mathbf{k'}$, through phonon mode ν at point $\mathbf{q}$. $\mathbf{k'} - \mathbf{k} = \mathbf{q} + \mathbf{g}$ with $\mathbf{g}$ a reciprocal lattice vector. M is the atomic mass, and $\vec{\eta}_{\mathbf{q}\nu}$ are the phonon eigenvectors. The transport spectral function $\alpha_{tr}^2 F$ is analogous to the Eliashberg spectral function for superconductivity, but weighted by contributions from electron velocities.

The scattering operators are calculated as:

$$
\begin{aligned}
(Q_{nn'})_{\alpha\beta} &= \frac{2\pi V_{cell} N(\epsilon_F)}{\hbar k_B T} \int d\epsilon d\epsilon' d\omega \sum_{s,s'=\pm 1} f(\epsilon) \left[1 - f(\epsilon') \right] \\
&\times \{ [N(\omega) + 1] \delta(\epsilon - \epsilon' - \hbar\omega) + N(\omega)\delta(\epsilon - \epsilon' + \hbar\omega) \} \\
&\times \alpha_{tr}^2 F(s, s', \alpha, \beta, \epsilon, \epsilon', \omega) J(s, s', n, n', \epsilon, \epsilon')
\end{aligned}
\tag{3}
$$

where ϵ, ϵ' are electron energies relative to the Fermi level ϵ_F, ω is a phonon frequency, V_{cell} is the unit cell volume, f and N are the Fermi-Dirac and Bose-Einstein distributions at temperature T, respectively.

For the sign of S a crucial quantity is the joint function $J(s, s', n, n', \epsilon, \epsilon')$ in Eq. (3):

$$
\frac{1}{4} \left[\frac{\zeta_n(\epsilon)}{N(\epsilon)v(\epsilon)} + s\frac{\zeta_n(\epsilon')}{N(\epsilon')v(\epsilon')} \right] \left[\frac{\zeta_{n'}(\epsilon)}{N(\epsilon)v(\epsilon)} + s'\frac{\zeta_{n'}(\epsilon')}{N(\epsilon')v(\epsilon')} \right]
$$

composed of energy polynomials $\zeta_n(\epsilon)$, with $\zeta_0 = 1$ and $\zeta_1 = \sqrt{3}\epsilon/\pi k_B T$.

PHONON DISPERSION

The calculated phonon band structures of Li and Na are shown in Fig. 1, which are in good agreement with previous theoretical results. [2–4] The slight overestimation relative to the experimental data can be attributed to the typical underestimation of the lattice constant from LDA.
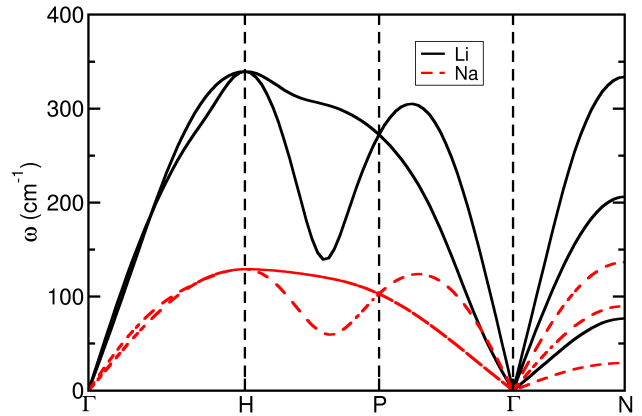

FIG. 1. (Color online) Phonon dispersion curves of bcc Li (black solid line) and Na (red dahsed line).

ELECTRICAL RESISTIVITY

Fig. 2 shows the resistivity of Li within the full VA formalism. The agreement with experimental values is quite good, in particular considering the LOVA is only valid in principle up to a temperature a bit higher than the Debye temperature (see the analysis in Savrasov and Savrasov[5]) - in practice agreement almost always extends much further.

SEEBECK COEFFICIENT OF POTASSIUM

For further justification of the variational approach, we also calculated the Seebeck coefficient of K, as shown in Fig. 3. Above 150 K, we obtain very good agreement
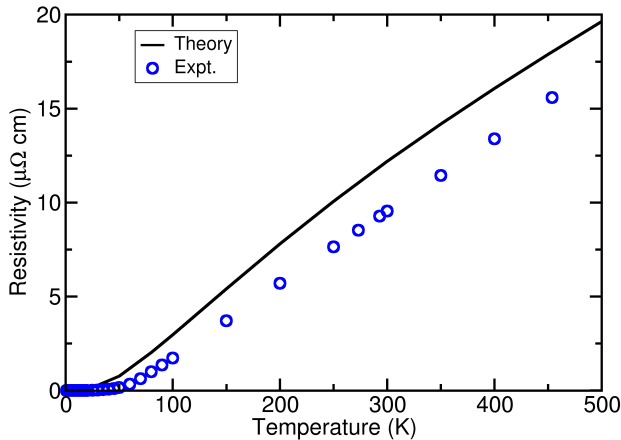
FIG. 2. (Color online) Electrical resistivity of Li, as a function of temperature. Black solid line is the VA calculated ρ of bcc Li. Discrete points are experimental data from Chi.[6]
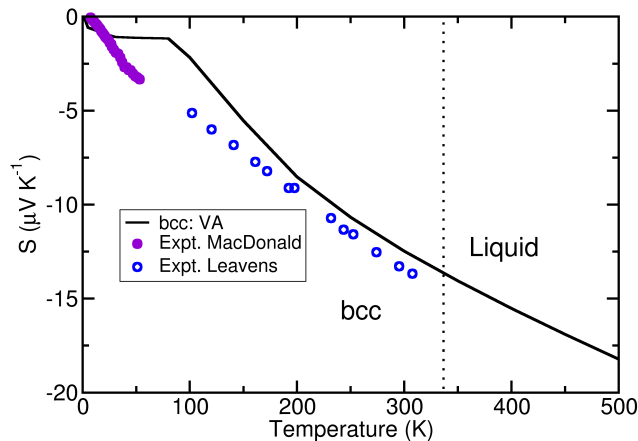

FIG. 3. (Color online) Seebeck coefficient of K, as a function of temperature. Black solid line is the VA calculated S of bcc K using the variational approach (extended beyond the experimental melting point). Discrete points are experimental data from MacDonald [7] and Leavens.[8]

with measured data. Note that the convergence of our calculation with respect to the **k**- and **q**-grid ($24 \times 24 \times 24$ **k**-grid and $6 \times 6 \times 6$ **q**-grid, the same as Na) depends on the temperature. Low-temperature calculation requires finer energy resolution, so denser grids are necessary.

ANALYSIS OF THE SIGN OF S

There are four summations in $Q_{nn'}$ (shown in Eq. (3)), including integrations $\int d\epsilon$, $\int d\epsilon'$, $\int d\omega$, and the summation $\sum_{s,s'=\pm 1}$. The integral $\int d\epsilon'$ can be eliminated, considering the energy conservation in the phonon absorption ($\epsilon' = \epsilon + \hbar\omega$) and emission ($\epsilon' = \epsilon - \hbar\omega$) processes. The integrand is the product of three terms, viz., the positively defined transport spectral function $\alpha_{tr}^2 F$, the joint energy polynomial J, and the factors that are relevant to the electron and phonon occupations, which are also positive.

The two occupation factors for absorption $f(\epsilon)\left[1 - f(\epsilon')\right]N(\omega)$ and emission $f(\epsilon)\left[1 - f(\epsilon')\right]\left[N(\omega) + 1\right]$, appearing in Eq. (3), depend sensitively on the relative magnitudes of $k_B T$ and phonon frequency, as illustrated in Fig. 4. Four representative cases are present, (a) low temperature, low phonon frequency; (b) low temperature, high phonon frequency; (c) high temperature, low phonon frequency; and (d) high temperature, high phonon frequency. The absorption and emission curves are symmetric about the Fermi level, and the maxima occur at $-\omega/2$ and $\omega/2$, respectively. When $\hbar\omega \gg k_B T$, the magnitudes of these two factors become negligible (as in Fig. 4(b)). Thus the participating phonons in the transport that have significant contribution should not exceed the thermal energy. Also recall that ϵ and ϵ' in Eq. (3) are measured from the Fermi energy, so they are negative if the energy is below ϵ_F.
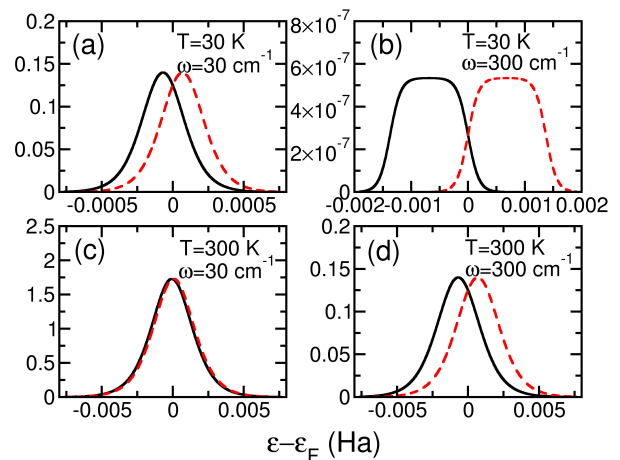

FIG. 4. (Color online) $f(\epsilon)\left[1 - f(\epsilon')\right]N(\omega)$ with $\epsilon' = \epsilon + \hbar\omega$ (absorption, solid black lines) and $f(\epsilon)\left[1 - f(\epsilon')\right]\left[N(\omega) + 1\right]$ with $\epsilon' = \epsilon - \hbar\omega$ (emission, dashed red lines) as a function of energy ϵ, with (a) low T low ω; (b) low T high ω; (c) high T low ω; (d) high T high ω.

Since ϵ and ϵ' are separated by the phonon energy, and only relatively low-frequency phonons (compare to the energy span of $\sim \epsilon_F \pm 8k_B T$, which is adopted in Fig.

4(a), (c), and (d)) are considered due to the occupation factors. The densites of states $N(\epsilon)$ and $N(\epsilon')$ are close to each other for metals. As a consequence, only the J terms with $s = 1$ and $s' = 1$ have major contributions, while the other three combinations yield small numbers due to rough cancellation. J_{11} is quadratic and can only be positive, which leads to positive Q_{11}: the sign of S is the same as the sign of Q_{01}.
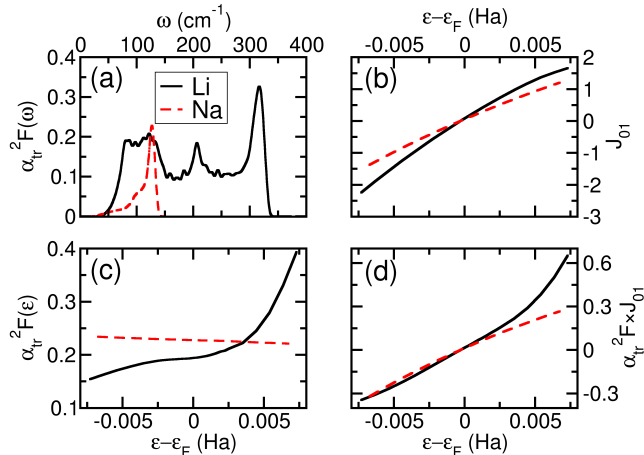

FIG. 5. (Color online) For Li (solid black line) and Na (dashed red line) at 300 K, with $s = s' = 1$, $\omega = 127$ cm^{-1}, $\epsilon = \epsilon_F$ and $\epsilon' = \epsilon + \hbar\omega$. (a) the transport spectral function $\alpha_{tr}^2 F$ as a function of phonon frequency; (b) the joint energy polynomial J_{01} as a function of energy ϵ; (c) $\alpha_{tr}^2 F$ as a function of ϵ; (d) the product of $\alpha_{tr}^2 F$ and J_{01} as a function of ϵ.

Because $\alpha_{tr}^2 F(\omega)$ (Fig. 5(a)) and the phonon population factor are positive, and J remains the same sign with the variation of ω, no change of sign in Q_{01} will result from the integral over ω. As the occupation factors of phonon absorption and emission are symmetric about

ϵ_F, the sign of Q_{01} comes from the sign of the integral over ϵ, which is determined by the energy dependence of $\alpha_{tr}^2 F \times J_{01}$. This energy dependence varies with the change of phonon frequency, but without loss of generality, we show the energy dependencies of J_{01}, $\alpha_{tr}^2 F$, and $\alpha_{tr}^2 F \times J_{01}$ for Li and Na, respectively in Fig. 5(b), (c), and (d), with $\omega = 127$ cm^{-1}. This frequency corresponds to the peak in $\alpha_{tr}^2 F(\omega)$ for Na (Fig. 5(a)), and a significant contribution is also present in Li. As can be seen from Fig. 5(b), J_{01} alone favors negative sign of S (larger magnitudes for $\epsilon < \epsilon_F$ than $\epsilon > \epsilon_F$) for both Li and Na, mainly because $N(\epsilon)$ increases with ϵ (Fig. 3(a) of the main article). Although $v(\epsilon)$ (note that the definition is different in RTA, e.g., in Fig. 3(b) of the main article) decreases with ϵ in Li (increasing in Na), the variation with energy is much weaker than $N(\epsilon)$. On the other hand, distinct differences appear in the energy dependence of $\alpha_{tr}^2 F(\epsilon)$ between Li and Na, i.e., significantly increasing in Li while weakly decreasing in Na. As a consequence $\alpha_{tr}^2 F \times J_{01}$ favors positive S in Li, and negative in Na.

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