The Hardy's corrections to the Maradudin's lattice part of the total heat current operator are shown to yield no corrections to the hopping thermoelectric coefficients of amorphous solids and glasses in the lowest (minus-first) order of the electron phonon coupling constant. But even after including the magnetic field \( \mathcal{H} \equiv (0, 0, a_z) \), the lowest non-zero (zeroth order) contributions to the Peltier and Seebeck tensors are shown to be diagonal, yielding thus no contribution to the Nernst and Ettingshaussen coefficients. Therefore, the Hardy corrections, which might yield the next (first) order contributions to these coefficients, appear to be crucial for treating the thermomagnetic phenomena in amorphous and glassy materials.

1. INTRODUCTION

The sign of the Peltier (or Seebeck) coefficient in amorphous semiconductors and glasses is usually (along with the sign of the Hall constant) the main criterion for regarding these materials to be of n- or p-type. Unfortunately, there is no unique correlation between signs of the Peltier and Hall constants [1]. Therefore, the detailed theory of these phenomena is needed.

In a recent work [2] it was shown that (in the lowest order in the electron phonon coupling constant) the sign of the Peltier and Seebeck coefficients is determined predominantly by the asymmetry of the mobility gap around the chemical potential. This is in accordance with the usual conception but the implicit assumption is avoided that the electrons which take part in the transport conserve their energy [1] (which is clearly invalid for the hopping case).

Nevertheless, all the treatment suffers yet from the well-known non-uniqueness of the microscopic heat current operator. In [2] the total energy current operator has been used in the form

\[
\mathcal{J}_a^H = \int dr \sum_i \frac{i}{\hbar} [H, h(r)]
\]

where \( H \) is the total Hamiltonian and \( h(r) \) is its density. When switching off the electron phonon coupling constant \( g \), (1) is a simple sum of the electronic and lattice terms. No problems arise in the former but difficulties in defining the density \( h_{ph}(r) \) of the lattice Hamiltonian cause the latter term to be problematic even when \( g \neq 0 \).
Non-uniqueness of the heat current operator...

the form of $h_{ph}$ which yields the Maradudin’s expression [3] for the lattice part of (1). HARDY [4] argues that (when $g = 0$ but the same applies even when $g \neq 0$) the exact form of (1) should contain yet an additional term

$$\Delta \mathcal{H}_a = \frac{1}{2} \sum \left\{ \frac{p_a(l)}{M(l)}, \sum_{\beta} \frac{p_{\beta}(l)^2}{2 M(l)} + V(l) \right\} +$$

$$+ \frac{1}{2} \sum_{l, l'} \left\{ u_a(l) - u_a(l'), \frac{i}{\hbar} \left[ V(l'), \sum_{\beta} \frac{p_{\beta}(l)^2}{2 M(l)} \right] \right\},$$

which is due to an alternative definition of $h_{ph}(r)$. Here

$$p_a(l) = -i \sum_k \sqrt{\left( \frac{\hbar \omega_k}{2 MN} \right)} M(l) v^{(k)}_a(l) \left[ b_k - b_k^+ \right],$$

$$u_a(l) = \sum_k \sqrt{\left( \frac{\hbar}{2 MN \omega_k} \right)} v^{(k)}_a(l) \left[ b_k + b_k^+ \right],$$

$$\alpha = 1, 2, 3; \quad l = 1, 2, \ldots, N$$

are the momentum and displacement operators of the $l$-th atom with the mass $M(l)$ and the real amplitudes $v^{(k)}_a(l)$ are chosen to obey

$$\sum_{\beta, l'} \left[ \Phi_{a \beta}(l, l') - \delta_{a \beta} \delta_{ll'} \omega_k^2 M(l) \right] v^{(k)}_a(l') = 0,$$

$$\sum_{a, l} M(l) v^{(k)}_a(l) v^{(k')}_a(l) = NM \delta_{kk'},$$

($M$ being e.g. the mean atomic mass). In addition to it,

$$V(l) = \frac{1}{2} \sum_{a, \beta, l'} \Phi_{a \beta}(l, l') u_a(l) u_{\beta}(l')$$

is that part of the total lattice potential energy which is ascribed to the atom $l$ (see (7) below).

Interpreting e.g. the first term on the right hand side of (2) as a diffusion term (which is essential for gases for example) and reminding the structure of the second term, it is trustworthy to regard the Hardy’s corrections to be essential only near or above the melting point [3]. Nevertheless, the exact proof is lacking. Moreover, $\Delta \mathcal{H}_a$ contains the odd powers of the phonon creation and annihilation operators $b_k^+$ and $b_k$. Consequently, when disturbing the equilibrium by e.g. the external d.c. electric field, (2) yields (in $\langle \Delta \mathcal{H}_a \rangle$) terms proportional to the first and higher odd powers of the electron-phonon coupling constant $g$, while the Maradudin’s-like term (1) leads (in $\langle \mathcal{H} \rangle$) to the second and higher even powers of $g$, as long as the electron-phonon interaction hamiltonian is linear in (3b). Therefore, to make the discussion in [2] and thus the usual conception meaningful for non-zero temperatures and small electron-phonon coupling, it is necessary to show that the linear term