# The Thomson Challenge

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**29 January 2011**

The analysis of thermoelectric circuits made by Thomson (Lord Kelvin) in the 19th C was of historical importance in showing the wider applicability of thermodynamics. We would now arrive at the Thomson relations between Seebeck and Peltier coefficients from the Onsager-Casimir arguments valid in the linear phenomenological range where we can expect various transport phenomena, such as Ohm's Law and Fourier's Law to be valid.

Observing that the Seebeck coefficient was not generally constant with temperature, Kelvin introduced the Thomson coefficient $\tau$ with units of $J/KC = V/K$ into the analysis. To start with he was concerned only with the difference between two materials, arms of the thermoelectric circuit with their junctions at different temperatures $\tau^{\alpha\beta}$. Writing before the discovery of the electron, his colleague Tait formed the hypothesis that this would be a linear function of absolute temperature $\tau^{\alpha\beta} = c_{\alpha\beta}T$. Whereas most thermoelectric phenomena are a matter of the difference between the properties of the two arms, it was recognised that the Thomson coefficient for a single material $\tau^{\alpha}$ was an observable capable of measurement as an absolute value. The key to such challenging experiments is to reverse the applied current, reversing the linear Thomson effect but leaving the quadratic Ohmic heating unchanged.

Such experiments have established values of the Thomson coefficient with considerable detail and accuracy for more than fifty years. But their interpretation remains a problem in view of the discrepancies with any simple theory of electron heat capacity and the startling divergence in different groups of the Periodic Table. The challenge as I see it is for modern quantum dynamics to explain these wide divergences and offer a possibility of calculating the Thomson coefficient in new materials such as semiconductors.

The original and naïve thermoelectric theory supposes that the electric current carries heat or more precisely thermal energy with it to be released (or further absorbed) at the junctions between materials where the heat capacity of the current changes, the Peltier effect. This heat transport is distinct from the patent flow of heat according to Fourier's Law. If the electrical heat capacity varies with temperature along an arm, then we look for patent heat as a source or sink, the origin of the Thomson coefficient. Thus a naïve quasi-equilibrium view holds the Peltier coefficient to be like a latent heat and the Thomson coefficient to be a heat capacity.

This naïve view is misleading. That we have a transport and non-equilibrium problem is clear from the measured values in hexagonal lattices, such as magnesium and zinc, where the Thomson coefficient varies with the direction of electric current, axial or perpendicular – just as the thermal conductivity in graphite varies with the direction of heat flow.

Although data for the Thomson coefficient can be found directly, it is more commonly processed into an integral, originally called the absolute thermoelectric power but now more accurately I think called the entropy of transport of a material

$$S^{\alpha}(T)=\int_{0}^{T}\frac{\tau^{\alpha}}{T}dT \qquad (1)$$

This is justified by the observation that the Thomson coefficient, like conventional heat capacities, goes to zero with absolute temperature (conducting materials become superconductors) and the Third Law applies. The analogy with specific heat capacities is evident. This would certainly be true if Tait's hypothesis is valid for the individual components. In that case we would simply have $S^{\alpha}(T)=\tau^{\alpha}$. In any case, the Thomson relations can then be written as $\Sigma^{\alpha\beta}=S^{\beta}-S^{\alpha}$ for the Seebeck coefficient (the slope of the open-circuit *emf*against junction temperature) and $\Pi^{\alpha\beta}(T)=T\Sigma^{\alpha\beta}$ for the Peltier coefficient at a junction.

Figure 1 is taken from the Russian data handbook, perhaps the most comprehensive source of data, and shows the entropy of transport for several pure materials. Values indeed go to zero. Since electrons close to zero display superconductivity and act as bosons in Cooper pars rather than fermions this consistency with the Third Law is gratifying but not surprising. Above some 100 $K$ the curves are straight lines, consistent with Tait; it is their slope that is the challenge varying from negative (expected per coulomb of negatively charged electrons) to positive. Below this region the transition is satisfactorily explained by phonon drag, scattering of the electron current by the phonon energy driven by the temperature gradient in the lattice. What are we to make of the major region where, in alkali metals, lithium alone is anomalous and in-group 11; copper, silver and gold are anomalous despite sharing a face-centred lattice with group 10, nickel, palladium and platinum?

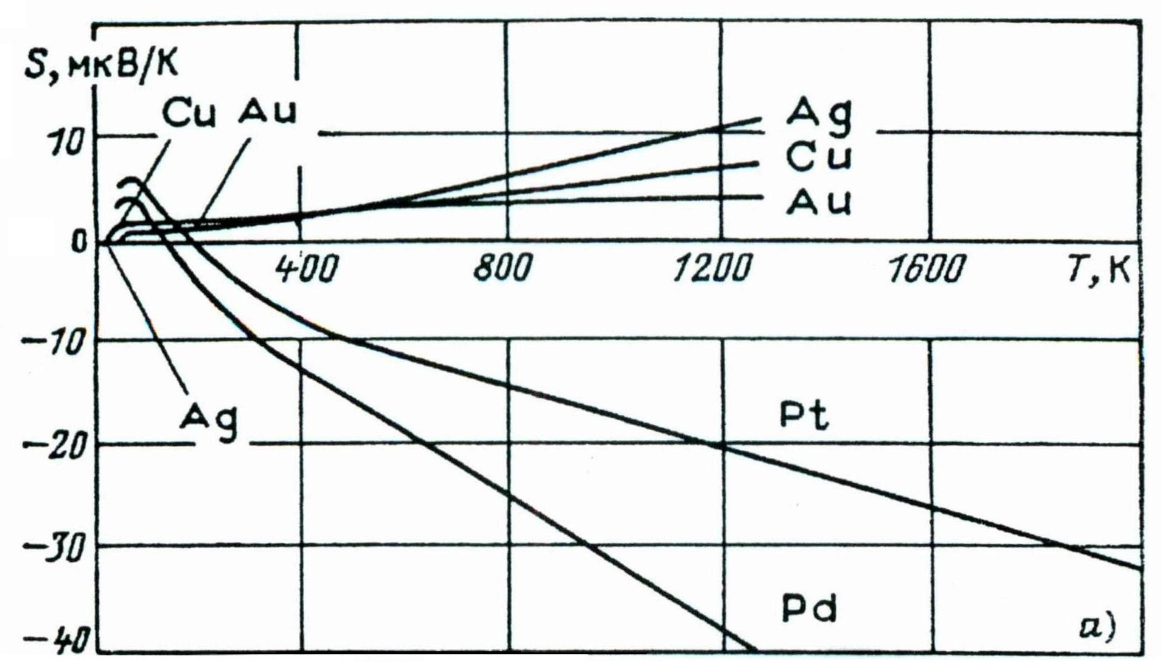

**Figure 1. Entropy of Transport of some Elements**
Source: Grigoryev and Meilihov (1991).

### Electron heat capacity, Free-electron Gas and the Fermi energy

The anomalous behaviour of Group 11, having positive Thomson coefficient, is not the only difficulty. In Group 10 the values are *more* negative than expected from standard results for electron heat capacities per coulomb. Briefly I mention the naïve argument based on the free-electron gas model and its prediction of a heat capacity, since this is the starting point for the conventional account of the anomaly through Bragg scattering. In the free-electron gas, the conducting electrons are taken to move in a uniform electric field smeared from the positive ions, in the absence of an applied external field that would impose only a small perturbation. Thus the electric field is taken to be zero and no potential energy is involved. These conducting electrons are represented as travelling plane waves, orthogonally in rectangular axes but as the quantum cells are filled in momentum space, these waves travel in all directions.

At zero temperature the system will be expected to minimise its energy content and as all electrons are taken to have the same potential energy, this means minimising the kinetic energy content. The Pauli exclusion principle prevents all electrons occupying a zero energy state and so at zero temperature the electrons pack into a sphere in momentum space or wave vector space, the outer electrons on the Fermi surface having the Fermi energy given by $E_F = \frac{h^2}{8m_e}\left(\frac{3}{\pi}n\right)^{\frac{2}{3}}$ in terms of the density of conducting electrons $n$. If we knew how many conducting electrons per ion are present, the Fermi energy would be readily calculated although this simple picture of a sphere is modified later. A useful consequence of this model is the prediction that the heat capacity of electrons at all normal temperatures is proportional to the absolute temperature as $c_{ev} = \frac{\pi^2}{2}\frac{k}{e}T/T_F$ J/KC with $e$ the electronic charge and $T_F = E_F/k$, typically many kilokelvin. The heat capacity goes to zero at absolute zero, allowing the definition of an entropy, and is seen to satisfy Tait's hypothesis for the Thomson coefficient. We might hope then that the electron heat capacity predicts the Thomson coefficient. But Table 1 shows that in neither Group 10 nor 11 is there any agreement.

Table 1. Electron heat capacities **at 300** $K$

| Element | Density $Mg/m^3$ | Cell vol $nm^3$ | Conducting electrons per ion * | Fermi energy $fJ$ | Fermi temperature $kK$ | Electron heat capacity ** $\mu J/KC$ | Thomson Coefficient *** $\mu J/KC$ |
|---|---|---|---|---|---|---|---|
| Group 10 | | | | | | | |
| Ni | 8.8 | 0.042 | 0.58 | 0.88 | 64 | -2.00 | -16.5 |
| Pd | 12.2 | 0.057 | 0.48 | 0.82 | 68 | -1.88 | -16.6 |
| Pt | 19.8 | 0.058 | 1(0.46) | 0.81 | 67 | -1.90 | -12.0 |
| Group 11 | | | | | | | |
| Cu | 8.93 | 0.058 | 1 | 1.06 | 77 | -1.66 | 1.33 |
| Ag | 10.49 | 0.066 | 0.99 | 0.878 | 64 | -2.00 | 1.28 |
| Au | 19.32 | 0.065 | 0.57 | 0.885 | 58 | -2.21 | 1.62 |

*Group 10 values from Reale (1971). Values in Group 11 from densities quoted on the internet, for which I cannot assess the validity.

** Using $c_{ev} = \frac{\pi^2}{2}\frac{k}{e}T/T_F$ *** Data from MacDonald, 1962.

**Bragg scattering and the reciprocal lattice.**

Our problem is a transport problem where a current of electrons flows through the lattice[1]. The applied electric field is taken to perturb the Fermi sphere but slightly although I have difficulty in reconciling this with the free electron model, which would seem to lead to continued acceleration; the resulting scattering is hardly compatible with electrons being free.

Electron-electron scattering might be represented classically in the free-electron gas model but electron-ion scattering calls for a different approach. We should first deal with a simplistic objection. If, as in Group 11, it is an above average electron that enters an adjacent cell at higher temperature, is it not replacing an above average electron moved on to the next cell? Surely the heat required is only the small difference? But this overlooks the relative time scales. The drift speed of electrons in a heavy current, say 10 $MA/m^2$ in copper is some $m/s$. The *rms* mean speed of the electrons is some $km/s$ with correspondingly shorter relaxation time. Before the next electron leaves, the system has lost all memory of the previous entrant.

The standard approach (Ziman, MacDonald) is to introduce Bragg scattering between the lattice planes and a subsequent modification of the Fermi surface, no longer a sphere. These, and other authors, claim that a transport integral "over the Fermi surface" would yield the desired values.

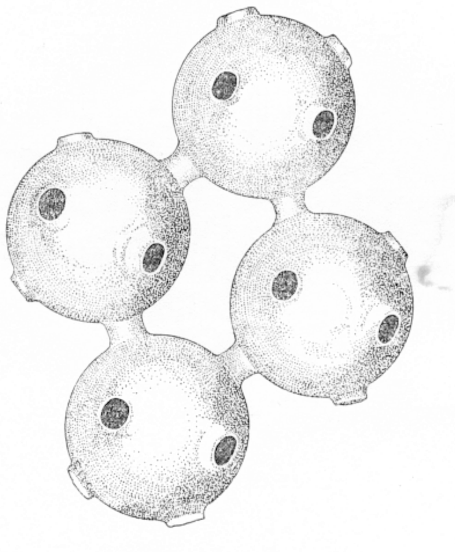

Fig. 136. Fermi surface of copper.

**Figure 2. The Fermi surface of copper (after Ziman 1970).**
[Ziman repeats the First Zone as a Wigner-Seitz cell. The eight principal diagonals thus provide 'mouseholes' to adjacent cells.]

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[1] I suspect that in rectangular lattices there might be an off-axis variation of the Thomson coefficient but there would be great difficulty in preparing specimens.

This requires knowledge of the Fermi surface and much has been learnt in the last fifty years. The figure shows Ziman's representation of copper in the first Brillouin zone, showing the distortion expected in the direction of the principal diagonals of the face-centred lattice. Ziman remarks that here is a source of higher energy electrons in Group 11. But where is the comparable source of low energy electrons in Group 10? It is said that reactions in the Fermi 'sphere' take place only close to the surface, because thermal interactions are only a fraction of an eV, our transport process may well involve electrons drawn from deeper inside.

It will be recollected that the simple cubic lattice cell of side $d$ leads to a reciprocal vector of wave number $2\pi / d$ in the six rectangular directions corresponding to the six sides of the original cube and hence to a cubic first Brillouin zone. The spacing is then the Bragg vector of length $2\pi / d$ and from an origin midway, any electron with wave vector reaching the zone surfaces satisfies the Bragg condition and should be reflected and thus trapped. These planes can be described as the six-set $\{\pm 1, 0, 0\}$. The next set of scattering planes corresponds to the 12 edges of the cube $\{\pm 1, \pm 1, 0\}$ forming a twelve—sided figure of rhombic faces. The next set corresponds to the eight diagonals of the cube $\{\pm 1, \pm 1, \pm 1\}$ forming an eight-sided figure with equilateral faces. The reciprocal lattice cube fits snugly inside both octagon and dodecahedron thus forming the first zone.

For our face-centred cubic lattice we have double the scattering planes in the first and second sets and thus the first zone is the octagon with faces cut off by the enlarged cube to become hexagons connected by six squares, Figure 3.

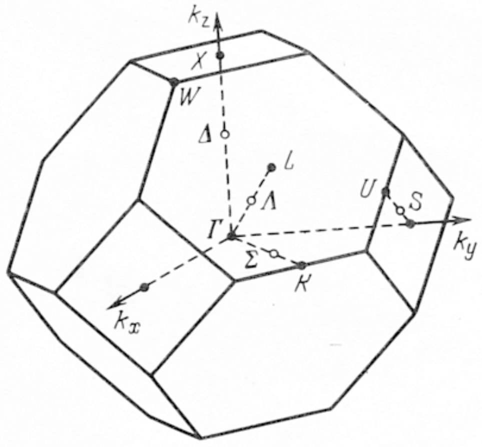

Fig. 1.1. Brillouin zone of a face-centered cubic lattice.

**Figure 3 (after Ziman 1970).**

*The ratio of the length of the normal vector to the square over the normal vector to the hexagon is as* $2 / \sqrt{3}$.

I summarise the conventional representation of Bragg scattering in the reciprocal lattice. A simple quantum argument employs a one-dimensional potential well. The two travelling waves of the free-electron gas (in opposite directions) can be replaced by two standing waves each of wavelength double the well-to-well spacing. One lies principally in the well, with low potential energy an anti-node at the well centre while the other lies principally out side the well, at higher potential energy and with node at the well centre. [2]

At zero temperature the system will seek to minimise the total and not just the system kinetic energy and thus the higher kinetic energy standing wave can appear in the Fermi surface if it corresponds to the low potential energy. Strictly the standing wave has zero expected momentum but we can represent it in wave-vector space through the root mean square value and correctly indicate its kinetic energy. The Fermi surface is sucked out towards these standing waves, as in Figure 2, and the rest of the sphere correspondingly shrunk. We expect a smooth transition to the Bragg values (harmonic interference) so the wormholes narrow towards the Bragg plane as in Figure 2. In a simple theory, from the symmetry of the zones, a scattered electron continues to be scattered and is thus trapped, allowing us to think of Bragg scattering as a filter on the current. This replaces the original travelling waves with half the number of quantum states calling for an increase in the sphere elsewhere.

This is a one-dimensional argument and, I suggest, does not fully represent our situation. I note that nothing has been said as to the efficiency of Bragg scattering. Does it not depend on the density of scattering centres in the scattering plane? Thus in the rectangular directions the scattering planes are twice as close due to the face-centred nuclei, but the distance between the centres is still the cell side and we might expect Bragg events at half the reciprocal vector, restoring the cube shape to the first Brillouin zone. Referring back to Figure 2 it might be thought surprising that the Fermi surface is perturbed in the diagonal directions but not in the rectangular directions where the Bragg vector is only 16% larger. . Perhaps this is because Bragg scattering has already occurred in this direction inside the Fermi surface. We can put actual numbers to this in k-space using free-electron gas theory and values of Table 1 for conduction electron per atom and thus four stoms in the FCC cell of side d, Table 2.

**Table 2. Semi-Bragg and Fermi Wave Numbers in units of $2\pi / d$.**

<table>
<tr><td colspan="2">First zone principal diagonal</td><td colspan="2">First zone rectangular axis</td><td colspan="2">Crypto zone rectangular axis</td></tr>
<tr><td colspan="2">$\sqrt{3} = 0.87$</td><td colspan="2">1</td><td colspan="2">0.5</td></tr>
<tr><td>**Ni**</td><td>**Pd**</td><td>**Pt**</td><td>**Cu**</td><td>**Ag**</td><td>**Au**</td></tr>
<tr><td>0.50</td><td>0.54</td><td>0.54</td><td>0.62</td><td>0.62</td><td>0.51</td></tr>
</table>

If we can refer to the possibility of scattering between alternate loaners leading to a crypto-Brillouin inner zone (‘zeroth’ zone?) the original Fermi sphere lies partly inside and partly outside the crypto zone.

Specialists in diffraction will be able to elucidate these aspects. Our position is that Bragg scattering cannot explain the differences between Groups 10 and 11 and the Brillouin zones however useful they might be in representing the phenomena. What will be needed is a fundamental quantum mechanic transport calculations, taking cognisance of relativistic effects deep in the heavy nuclei.

## The Challenge

We see that Group 10 and Group 11 are equally anomalous seen from the free-electron gas perspective. How can we improve our qualitative understanding of the

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[2] Compare the theorem in celestial mechanics where a satellite in stable circular orbit where total energy is an invariant.

differences between the groups so that we might successfully calculate the Thomson coefficient? Alternatively, if a transport calculation of the Thomson coefficient is possible, how can this be interpreted to explain the differences? Will this explain the anomalous values of lithium? If outward distortion of the Fermi surface provides above average energy electrons in Group 11,where do the below average energies in Group 10 come from?

As subsidiary questions, does the efficiency of Bragg scattering play a role in the availability of lower than average energy electrons in Gp 10? How should we represent the Brillouin zones? Is the transport confined to electrons close to the Fermi skin or drawn more deeply from within the Fermi sphere?

The Magdalene Prize in Thermodynamics will be awarded to the author(s) of the best paper on this topic submitted to the Editors of the Journal of Non-equilibrium Thermodynamics in accordance with the rules attached. The hope is that these advances will make it possible to calculate, with understanding, the Thomson coefficient in other, and potentially better, thermoelectric materials.

I am grateful to Professor Lawson, Dr Bartok Partay and Mr Alexander Büll.

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