

# On the Anomalous Electronic Heat Capacity $\gamma$ -Coefficient

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As is common knowledge, the experimentally measured and theoretically deduced values of the  $\gamma$ -coefficient of the electronic heat capacity of metals exhibit a clear discrepancy. This discrepancy is usually attributed to the neglected effects such as the electron self-interaction and the electron interaction with phonons and the Coulomb potential. Despite the said pointers to the possible cause in the obtaining theoretical and experimental dichotomy, no dedicated effort has been put in order to come up with a theory to explain this. An effort is here made to come-up with an alternative theoretical framework whose endeavour is to proffer a theory that may explain why there is this theoretical and experimental dichotomy by invoking the hypothesis that the temperature of electrons and the lattice may be different. We argue that the different electron and lattice temperatures can – *in-principle* – give an alternative explanation as to the said theoretical and experimental dichotomy in the  $\gamma$ -coefficient of the electronic heat capacity of metals without the need to invoke the effective mass theory as currently obtains.

“Thermodynamics is a funny subject. The first time you go through it, you don’t understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don’t understand it, but by that time you are so used to it, it doesn’t bother you anymore.”

Arnold J. W. Sommerfeld (1868–1951)

## 1 Introduction

The main purpose of the present reading is to provide (propose) an alternative model that seeks to explain the existing discrepancy in the electronic heat capacity  $\gamma$ -coefficients for different metals. That is to say, for temperatures below the Debye ( $\theta_D$ ) and Fermi temperature ( $\theta_F$ ), in terms of the temperature ( $T$ ) of the metal in question, the total molar heat capacity at constant volume  $C_V^T$  of metals is satisfactorily described by the sum of a *linear electronic* ( $C_V^e \propto T$ ) [1, 2] and a *cubic phononic* ( $C_V^l \propto T^3$ ) contribution [3], *i.e.*:

$$C_V^T = \gamma T + AT^3, \quad (1)$$

where  $\gamma = \pi^2 n_* \mathcal{R} / 2\theta_F$  is the said  $\gamma$ -coefficient in question, with  $n_*$  being the number of free electrons per lattice point,  $\mathcal{R} = 8.3144600(50) \text{ Jmol}^{-1}\text{K}^{-1}$  is the ideal gas constant and is such that  $\mathcal{R} = N_A k_B$ , where  $N_A = 6.022140857(74) \times 10^{23}$  is the Avogadro number and  $k_B = 1.38064852(79) \times 10^{-23} \text{ JK}^{-1}$  is the Boltzmann’s constant, and:

$$A = \frac{9\mathcal{R}}{\theta_D^3} \int_0^{x_D} \frac{x^4 e^x dx}{(e^x - 1)^2}, \quad (2)$$

where  $x = \hbar\omega/k_B T$  and  $x_D = \theta_D/T$ ,  $\hbar$  is Planck’s normalized constant and  $\omega$  is the angular frequency of the oscillating lattice points (*i.e.* atom or molecule). In the low temperature

region, *i.e.*  $x \ll 1$ ,  $A$  is such that:

$$A \simeq \frac{12\pi^4 \mathcal{R}}{5\theta_D^3}. \quad (3)$$

For a given metal in question – the coefficients  $\gamma$  and  $A$  are constant coefficients which are determined experimentally.

It was after Albert Einstein’s [4] first great insights into the quantum nature of solids that the cubic term  $C_V^l \propto T^3$ , was successfully explained by Peter Debye [3]. At low temperatures the lattice contribution  $C_V^l \propto T^3$  is significantly smaller than the electronic contribution  $C_V^e \propto T$ , it vanishes faster than the electronic contribution and from this,  $\gamma$  (also known as the *Sommerfeld constant*) can be measured experimentally. As will be seen in the next section, there is a clear marked difference in the theoretical and experimental values of the  $\gamma$ -coefficient and we seek here an answer to as to why this fragment disagreement between theoretical and experiment.

## 2 Problem

Table 1 lists the theoretical  $\gamma_{\text{theo}}$  and experimental  $\gamma_{\text{exp}}$  values of twenty one elements and these values are plotted in Figure 1. One finds that they can fit either a linear, quadratic, a general power law or logarithmic curve to these data points. The marked difference in the theoretical and experimental values of the  $\gamma$ -coefficient is clear. From column 3 of Table 1, the percentage deviations are presented and it can be seen from this that the mean square deviation is as high as 35%, while the mean value of the ratio  $\gamma_{\text{exp}}/\gamma_{\text{theo}}$  (column 5 of Table 1) together with its deviation from this mean value is  $1.30 \pm 0.40$ .

The said marked difference in the theoretical and experimental values of the  $\gamma$ -coefficient as presented in Figure 1

Table 1: Table of 21 elements for the experimental and theoretical values of the electronic heat capacity coefficients. From left to right, the columns represent the element, its corresponding theoretical and experimental  $\gamma$ -coefficient and the percentage  $(1 - \gamma_{\text{exp}}/\gamma_{\text{theo}}) \times 100\%$  deviation of the experimental value from the theoretical one, respectively. The values of  $\gamma_{\text{exp}}$  and  $\gamma_{\text{theo}}$  are adapted from Kittel (2005, 1986) [5, 6] and Tari (2003) [7].

Element	$\gamma_{\text{theo}}$ ( $\text{mJmol}^{-1}\text{K}^{-2}$ )	$\gamma_{\text{exp}}$ ( $\text{mJmol}^{-1}\text{K}^{-2}$ )	% Dev.	$\frac{\gamma_{\text{exp}}}{\gamma_{\text{theo}}}$
Li	1.63	0.75	+54	2.18
Be	0.17	0.50	+190	0.34
Na	1.38	1.09	+20	1.26
Mg	1.30	0.99	+24	1.31
Al	1.35	0.91	+32	1.48
K	2.08	1.67	+20	1.25
Ca	2.90	1.51	+48	1.92
Cu	0.70	0.51	+27	1.38
Zn	0.64	0.75	-18	0.85
Ga	0.60	1.03	-72	0.58
Rb	2.41	1.91	+21	1.26
Sr	3.60	1.79	+50	2.01
Ag	0.65	0.65	+0.15	1.00
Cd	0.69	0.95	-38	0.73
In	1.69	1.23	+27	1.37
Sn	1.78	1.41	+20	1.26
Cs	3.20	2.24	+30	1.43
Ba	2.70	1.94	+28	1.39
Au	0.73	0.64	+12	1.14
Hg	1.79	0.95	+47	1.88
Pb	2.98	1.51	+49	1.97
<b>Mean Square Deviation</b>		$\mapsto$	<b>35</b>	

**Comparison of Experimental and Theoretical Values for the Electronic Heat Capacity Coefficient**

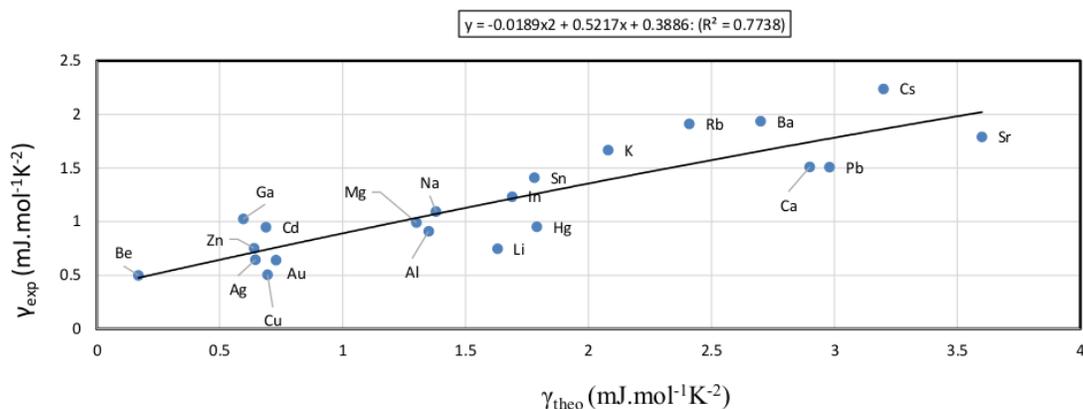


Fig. 1: A comparison graph of the experimental and theoretical values for the electronic heat capacity coefficients for the twenty one elements listed in Table 1. If there was a good agreement between theory and experimental, the values of  $\gamma_{\text{exp}}$  and  $\gamma_{\text{theo}}$  would lay along the line  $\gamma_{\text{exp}} = \gamma_{\text{theo}}$ . This is not the case implying a sure fragment disagreement between theory and experiment.

demonstrates an underlying correlation between these values. Amongst others, a correlation such as this, suggests some correlated physics must be at play – *one way or the other*. Given that electrons do interact with phonons, this correlation must have something to do with the electron-phonon interaction. We are not going to seek a fundamental origin of this correlation but merely suggest that this deviation may (as will be demonstrated) very well be due to a possible inequality in the electron and lattice temperatures.

The general and widely held view (see *e.g.* [5,6,8–10]) as to this discrepancy is that:

1. The interaction of the conduction electrons with the periodic Coulomb potential of the rigid crystal lattice is neglected.
2. The interaction of the conduction electrons with phonons is also neglected. This interaction causes changes in the effective mass of the electron and therefore it affects the electron energy.
3. The interaction of the conduction electrons with themselves is also ignored. For example, a moving electron causes an inertial reaction in the surrounding electron gas.

Since  $\gamma \propto m_e$  (see *e.g.* [5, 6]), to bring about agreement between theory and observation, the mass of the electron is corrected by introducing an effective mass  $m_e^*$  for the electron (*e.g.* [5, 6, 8–10]). Whatever difference there exists between theory and experiment, the effective mass is wholly assumed to shoulder this discrepancy (*e.g.* [5, 6, 8, 9]) as follows:

$$\frac{\gamma_{\text{exp}}}{\gamma_{\text{theo}}} = \frac{m_e^*}{m_e}, \quad (4)$$

where  $m_e = 9.10938356(11) \times 10^{-31}$  kg is the usual elementary mass of the electron.

The effective mass theory (see *e.g.* [5, 11] or any good textbook on the subject) is essentially about the equation of motion of a charged particle (electron in this case) inside the energy band of the crystal. In this theory, the electron is treated as a wave-packet in the typical *de Broglie* wave-particle duality model. That is to say, the electron is assumed to be a wave-packet made up of wavefunctions near a particular wavevector  $\vec{k}$  and this wave-packet has a group velocity  $\vec{v}_g = \partial\omega/\partial\vec{k}$ . All the effects of the environment on the electron are contained in the dispersion relation  $\omega = \omega(k)$ . For an electron whose energy is  $\epsilon$ , the effective mass theory (see *e.g.* [5, 11] or any good textbook on the subject) predicts that:

$$\frac{1}{m_e^*} = \frac{1}{\hbar^2} \frac{\partial^2 \epsilon}{\partial k^2} = \frac{1}{\hbar} \frac{\partial^2 \omega}{\partial k^2} = \frac{1}{\hbar} \frac{\partial v_g}{\partial k}, \quad (5)$$

where  $m_e^*$  is the effective mass of the electron as it moves in the energy band of the crystal. For example, in the case of a free electron where  $\epsilon = \hbar^2 k^2 / 2m_e$ , we have  $m_e^* = m_e$ , *i.e.* the electron has its usual mass  $m_e$ . Inside the crystal structure

where there is no current flow, the valency electrons are free having only thermal energy, they do not have a net drift velocity, but have random fluctuations whose net velocity is zero – hence, the effective mass theory should not be inapplicable to such electrons since measurements of the electronic  $\gamma$ -factor is conducted on such electrons. It is this that has made us to doubtfully question the effective mass theory in accounting for the  $\gamma$ -factor discrepancy.

The effective mass  $m_e^*$  can be larger or smaller than the electron's actual mass  $m_e$  and this depends on whether the states within the electron's energy band are denser (more compressed) or less dense (expanded) compared with those of a free gas [5, 6, 11]. The effective mass also reflects the inertia of the charge carriers. The two (effective mass & the inertia of the charge carriers) are related, because narrower, denser, bands reflect a smaller overlap of neighbouring electron clouds and hence greater difficulty for electrons to travel from one atom to the next.

This communication presents an alternative model whose aim is to explain the discrepancy in theoretical and experimental values of the electronic heat capacity coefficient. As pointed above – currently this is explained by invoking the effective mass theory. As shown in Figure 1, there is a clear trend in the experimental and theoretical values of the electronic heat capacity coefficient. We have not seen any theory that tries to explain this trend, not even *within* the effective mass theory. It is our firm belief that the effective mass theory should fail to explain this trend for the reason pointed above about the electrons inside metals during the measurement of  $\gamma$ , namely that they have a net zero group velocity. This communication makes an endeavour to provide an alternative model by invoking the not so unreasonable idea that electrons and atoms (molecules) in solids are at different temperatures.

### 3 Electron-lattice temperature correction

In our suggested alternative explanation – as to the discrepancy between theory and experiment, we propose to reconsider the issue of the lattice and electron temperatures. That is to say, a solid can be viewed as a homogeneous mixture of the lattice and the valency electrons. Just like any mixture, the different species are not expected to be at the same temperatures. Yes, the mixture will come together to a common temperature  $T$ , which is the temperature that we generally assign to the solid in question. The species with “*more heat*” will transfer this heat to the species with “*less heat*”. In this case of the electron-lattice mixture, we expect the lattice to have “*more heat*” with the valency electrons having “*less heat*”. If  $\Delta Q_l$  is the heat transfer from the lattice and  $\Delta Q_e$  is the heat received by the free electrons, then we must have:

$$\Delta Q_e + \Delta Q_l = 0. \quad (6)$$

So, unlike in the conventional treatment where the lattice and electron temperatures are assumed to be equal, we here as-

sume them to be different. If one accepts this, then what follows is straightforward.

If  $M_e, c_v^e, T_e; M_l, c_v^l, T_l$  is the total mass, specific heat capacity and temperature of the electrons gas and the lattice respectively, and  $T$  is the common temperature of the mixture, then, from (6), we will have:

$$\underbrace{M_e c_v^e (T - T_e)}_{\Delta Q_e} + \underbrace{M_l c_v^l (T - T_l)}_{\Delta Q_l} = 0. \quad (7)$$

Rearranging (7) and making  $T$  the subject, we will have:

$$T = \left( \frac{M_e c_v^e}{M_e c_v^e + M_l c_v^l} \right) T_e + \left( \frac{M_l c_v^l}{M_e c_v^e + M_l c_v^l} \right) T_l. \quad (8)$$

Further – rearrangement of (8), gives:

$$T = \left( 1 + \frac{M_l c_v^l}{M_e c_v^e} \right)^{-1} T_e + \left( 1 + \frac{M_e c_v^e}{M_l c_v^l} \right)^{-1} T_l. \quad (9)$$

We know that:

$$c_v^e = \frac{C_V^e}{N_A m_e} \quad \text{and} \quad c_v^l = \frac{C_V^l}{N_A \mathcal{A}_l}, \quad (10)$$

where  $\mathcal{A}_l$  is the atomic mass of the lattice and  $C_V^e$  and  $C_V^l$  are the electronic and lattice molar heat capacity respectively, and that:

$$\frac{M_l}{M_e} = \frac{\mathcal{A}_l}{n_* m_e}, \quad (11)$$

and substituting (10) and (11) into (9), we will have:

$$T = \left( 1 + \frac{C_V^l}{n_* C_V^e} \right)^{-1} T_e + \left( 1 + \frac{n_* C_V^e}{C_V^l} \right)^{-1} T_l. \quad (12)$$

Now – because of the different temperatures of the electrons and the lattice, the total internal energy  $\mathcal{U}_e$  of the electrons is to be expressed as a function of the electron temperature  $T_e$  *i.e.*  $\mathcal{U}_e = \mathcal{U}_e(T_e)$  and likewise, that of the lattice structure is such that  $\mathcal{U}_l = \mathcal{U}_l(T_l)$ . With the internal energy given in terms of the electron and lattice temperatures respectively, the corresponding electronic and lattice molar heat capacities are:

$$C_V^e = \frac{\partial \mathcal{U}_e(T_e)}{\partial T_e} \quad \text{and} \quad C_V^l = \frac{\partial \mathcal{U}_l(T_l)}{\partial T_l}. \quad (13)$$

The total internal energy  $\mathcal{U}_T$  of the solid is such that:

$$\mathcal{U}_T = \mathcal{U}_e(T_e) + \mathcal{U}_l(T_l). \quad (14)$$

Now, to compute the total molar heat capacity of the solid, one does this by differentiating (14) with respect to the common temperature  $T$  as follows:

$$C_V^T = \frac{\partial \mathcal{U}_T}{\partial T} = \frac{\partial \mathcal{U}_e(T_e)}{\partial T_e} \frac{dT_e}{dT} + \frac{\partial \mathcal{U}_l(T_l)}{\partial T_l} \frac{dT_l}{dT}. \quad (15)$$

Eq. (15) can be re-written as:

$$C_V^T = a_e C_V^e + a_l C_V^l, \quad (16)$$

where  $a_e = dT_e/dT$  and  $a_l = dT_l/dT$ . From (12) and (16), it follows that:

$$a_e^{-1} = \frac{1}{1 + C_V^l/n_* C_V^e} + \frac{1}{\eta} \frac{1}{1 + n_* C_V^e/C_V^l}, \quad (17)$$

where  $\eta = dT_e/dT_l$ . Setting:

$$x = n_* \left( \frac{C_V^e}{C_V^l} \right), \quad (18)$$

it follows that:

$$a_e = \left( \frac{x}{1+x} + \frac{1}{\eta} \frac{1}{1+x} \right)^{-1} = \eta \left( \frac{1+x}{1+\eta x} \right). \quad (19)$$

It is expected that the lattice contribution will always be significantly larger than that of the electrons and this means or directly translates to:  $x \ll 1$ . In addition to the said condition  $x \ll 1$ , if we assume  $|\eta x| < 1$ , then, to first order approximation, we will have:

$$a_e \approx \eta \quad \text{and} \quad a_l \approx 1, \quad (20)$$

hence:

$$C_V^T = \eta C_V^e + C_V^l. \quad (21)$$

Clearly, from (21) above, the obvious identification:

$$\gamma_{\text{exp}} = \eta \gamma_{\text{theo}}, \quad (22)$$

can be made, the meaning of which is that the theoretical and experimental discrepancy in the values of the  $\gamma$ -coefficient can be ascribed to  $\eta$ .

We shall reiterate: one very important thing to note is that the effective mass of the electron applies only in the case of an electron that is in motion with  $v_g \neq 0$  in the crystal structure and this is in the case of an applied potential across the metal. The  $\gamma$ -coefficient is measured not for a metal that has a flow of current in it, but one with no current, thus making is logically inappropriate in this instance to ascribe an effective mass to the electron that is different to its bare mass  $m_e$ . In such a case, it would make sense to ascribe the different values of  $\gamma_{\text{exp}}$  and  $\gamma_{\text{theo}}$  to the difference in the electron and lattice temperatures as suggested herein.

#### 4 General discussion

We herein have provided an alternative model whose endeavour is to explain the existing discrepancy between the experimental and theoretical values of the electronic heat capacity  $\gamma$ -coefficient. We must say that – at a reasonable and satisfactory level, the proposed model does explain the discrepancy in the experimental and theoretical  $\gamma$ -values. The prevalent (current mainstream) view is that this discrepancy comes

about as a result of a variable effective mass of the electron – wherein, the difference between the experimental and theoretical  $\gamma$ -values is wholly shouldered by the effective mass of the electron (see *e.g.* [5–10]). This idea of the effective mass may be logically inappropriate because the effective mass theory applies only in the case of an electron that is in motion with  $v_g \neq 0$  in the crystal structure whereas the  $\gamma$ -coefficient is measured not for a metal that has a flow of current in it, but one with no current. Current flow implies “with  $v_g \neq 0$ ”, and no-current flow implies “with  $v_g = 0$ ”.

In the proposed model, this discrepancy is explained as being due to the different temperatures of the electrons and the lattice. In the mainstream model, the thermodynamic temperature of the electrons and atoms (molecules) of the solid are assumed to be equal. This view may not be correct. It is actually not unreasonable to think that electrons and atoms (molecules) of the solid are at different temperatures as this is common place in *e.g.* the study of molecular clouds in *Astro-physics* and as well as in *Plasma Physics*.

This model does not discard the effective mass model where results of experiments are made to agree with the theoretical value by postulating that the entire discrepancy be shouldered by the resulting effective mass of the electron. What the model does is basically to “tell” us that the different electron and lattice temperatures may have a role to play in the said observed discrepancies, or both models may be at play. This is something that can be investigated in a separate study unit altogether. As to what use this model may hold in the immediate future, we can not say, but we hope it will prove useful in the future as our knowledge horizons broaden and push further than where they lie at present.

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