Empirical Formulae of Electrical and Thermal Conductivities of Elemental Metals at Room Temperature Ranges

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We propose empirical formulae of the electrical conductivity $\sigma$ and thermal conductivity $\lambda$ for elemental metals such as Na, Cu, or Fe at room temperature ranges. Assuming the relaxation time $\tau = h/k_B T$ for all metals, we propose $\sigma = e^2 n_{\text{atom}} \tau / (m G)$ ($m =$ electron mass; $n_{\text{atom}} =$ number density of atoms in each metal). If we adopt that a single free parameter $G$ is the sum of outer electron numbers in electron configuration such as $G = 1$ for Cu(4s), $G = 1 + 2 = 3$ for In(5s24p1) and $G = 5$ for Nb(41)(3d44s1), the ‘absolute values’ of $\sigma$ and a similar one for $\lambda$ agree with experiments within $\sim 20\%$ for the majority of metals even including semimetals.

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Proposed Formulae.— In this paper we treat only elemental metals such as Na, Cu, Fe, etc. without impurity and at 1 atm in the room temperature range. Conventional formulae [1–3] for the electrical conductivity $\sigma$ and thermal conductivity $\lambda$ in the free electron model are $\sigma = \tau n_e/m^* e^2$ and $\lambda = \tau n_e/m^* \pi^2 k_B^2 T/3$, respectively. Here $\tau$ is the relaxation time of electrons at the Fermi energy $E_F$, $m^*$ is the effective electron mass and $n_e$ is the electron number density of metals, satisfying $n_e = Z n_{\text{atom}}$, where $n_{\text{atom}} =$ metal density/atom weight [m$^{-3}$]. In order to derive ‘the absolute values’ of $\sigma$ and $\lambda$ one needs to know $\tau$, $Z$ and $m^*$, all of which are poorly known for many metals, especially $\tau$ (all not from the observations).

For example, we note that $\tau \sim h/k_B T$ was claimed for $T \gg \Theta$ [4,5] and Abrikosov [6] extends to use it also for $T \approx \Theta$ as in eq. (4.18) (see foot note therein). Here $\Theta$ is the Debye temperature. The accuracy of the ‘tilde’ signs they used is, however, not clear, but also whether it can be used other than monovalent metals is not clearly stated. Pippard [5] holds a high opinion of the 1937-Bardeen [4] calculation for monovalent metals (deformed potential C) on the absolute $\sigma$ value of Na and K, while Ziman [6] expressed that it is not very accurate, probably because of a factor of two to three between difference experiments of $\sigma_{\text{obs}}$ and the Bardeen theory for Rb, Cs, Cu, Ag, and Au, where $\sigma \propto (E_F/C)^2$. A concise derivation of the relaxation time $\tau \equiv 1/W$ is in Kittel’s 8th edition, Appendix J [3] with a slightly modified description from its 7th edition, which still needs the values of $C, m^*/m$ and $c_s$ (the sound speed). Here again no statements were made on non-monovalent metals. Laschoft and Mermin, on the other hand, in foot note 7 of Chap. 1 [1] cast doubt even computations on individual particle collisions.

In this paper we give these absolute values which are in good accord with the observations by adopting assumptions below. We assume for ‘all’ elemental metals

$$\tau = h/k_B T, \quad (1)$$

and introduce a non-dimensional parameter $G$ in place of the conventional $m^*/(m Z)$ appearing in the Drude formula. We then propose

$$\left( \frac{\sigma}{\lambda} \right) = \frac{e^2 n_{\text{atom}} \tau}{m G} \left( \frac{\pi^2 k_B^2 T}{3 e^2} \right). \quad (2)$$

Here $\sigma$ is in $\Omega / m^{-1}$ and $\lambda$ in $W m^{-1} K^{-1}$ unit, $h = h/2\pi$ ($h$ is the Planck constant), and $k_B$ is the Boltzmann constant.

These two equations, eqs. (1) and (2) ‘combined’, do not seem to have been proposed in the past. Certainly, there have been attempts to relate $\sigma$ to electronic configuration as early as 1956, but combination of parameters, such as $G$ and $n_{\text{atom}}$, are unlike the present one, namely effectively unsuccessful, otherwise usual textbooks could have presented in short sentences as in our abstract.

Note that eq. (2) gives $\sigma \propto 1/T$ due to $\tau \propto 1/T$ and temperature ‘independent’-$\lambda$ both being consistent with observations in the room temperature range (‘independent’ means as compared to $\sigma \propto 1/T$ variation). Since $n_{\text{atom}}$ for each metal (from density and atomic weight) and $T$ can be given, the only non-dimensional parameter is $G$. Even if $\tau$ is different from eq. (1), unknown departure factor from it can be included in $G$ (e.g. $m^*/m$ or deformed potential in a non-dimensional constant). Thus assuming $\tau = h/k_B T$, we first empirically determine the parameter $G_{\text{obs}}$ using observed $\sigma_{\text{obs}}$ for each metal. Then we assign $G$ (guessed)-values to be the sum of the outer electron numbers in electron configuration which are ‘close’ to $G_{\text{obs}}$.

Comparison with Experiments.— Fig. 1(a) presents $G_{\text{obs}}$ plotted against ‘group’ number for each ‘period’ in the periodic table. Here $G_{\text{obs}}$ is defined as

$$G_{\text{obs}} \equiv \frac{\sigma_1}{\sigma_{\text{obs}}} \quad \text{and} \quad \sigma_1 \equiv \sigma(G = 1) = e^2 n_{\text{atom}} \frac{h}{k_B T}. \quad (3)$$

Then $G_{\text{obs}}$ can be given for each metal from $\sigma_{\text{obs}}, n_{\text{atom}}$ and temperature $T$ used in the observations. Observed values ($\sigma_{\text{obs}}$ and $\lambda_{\text{obs}}$) for 48 metals are taken from Kittel [3], adding $\lambda(Ca)=201Wm^{-1}K^{-1}$ from the table of Phys. Soc. Japan 10 (PSJ-table). We adopt $T_{\text{obs}}=295K$ from the Kittel’s tabulation for $\sigma_{\text{obs}}$. This
terms in the outer electronic configuration matches
tels periodic table (K-P-table; in the back cover of the
will be quantized! Further we find that in the Kitt-
tif expressed in unit of $1 = 1$ and $Z$
$\sigma$
that eq. (2) for the electrical conductivity
Secondly, which is the basis of the periodic table, may be respon-
sitions for some metals are slightly shifted to avoid overlapp
(FIG. 1(b-upper). These 7 elements in free atomic form
agrees with the observations without further parameters
scales. Thick marks in (a) and (b-upper are
$G$
$\tau$
Gives $\tau = 2.59 \times 10^{-14}s$ from eq. (11), which is very close to
$\tau_{\text{obs}}$ from the observed $\sigma_{\text{obs}}$ such as $\tau_{\text{obs}}(\text{Na})=2.9 \times 10^{-14}s$
and $\tau_{\text{obs}}(\text{Cu})=2.5 \times 10^{-14}s$, using eq. (2) for $G = 1$.
First, we find similar trends of $G_{\text{obs}}$ among periods of 4
($K^{19} \sim \text{Ga}^{31}$), 5 ($\text{Rb}^{37} \sim \text{Sb}^{51}$) and 6 ($\text{Cs}^{55} \sim \text{Bi}^{83}$, inclusive
of $\text{La}^{57}$). This suggests that electron configuration, which is the basis of the periodic table, may be responsible [see e.g. early attempts in figs. 12-13 of ref. 8].
Secondly, $G_{\text{obs}} \approx 1$ is found for $\text{Na}^{11}$, $K^{19}$, $\text{Rb}^{37}$, $\text{Cs}^{55}$ and noble metals of $\text{Cu}^{29}$, $\text{Ag}^{47}$ and $\text{Au}^{79}$. This indicates that eq. (12) for the electrical conductivity $\sigma$ with $G = 1$
agrees with the observations without further parameters
(Fig.1(b-upper)). These 7 elements in free atomic form
are in ns$^1$ outermost electron, where n is the principal quantum number of 3 $\sim 6$. Though one might say that
$Z = 1$ and $m^* = m$ hold as expected, $\tau$ should be specified as we propose.
Third, many metals appear concentrated in $G_{\text{obs}} = 1$
$3, 5$ and $10 \sim 13$, which suggests discreteness of $1/\sigma_{\text{obs}}$
if expressed in unit of $1/\sigma_1$, namely $G$(guessed) may well be quantized! Further we find that in the Kitt-
tels periodic table (K-P-table; in the back cover of the
text), not necessarily in other authors’ tables, sum of
numbers in the outer electronic configuration matches
the observed $G_{\text{obs}}$ quite well. In fact we find that besides $G \approx 1$ (from $G_{\text{obs}} \approx 1$) for $s^1$-electron atoms,
$G = 3$ (from $G_{\text{obs}} \approx 3$) for 3-outer-electron atoms as
in $\text{In}^{49}(5s^25p^1)$, and $G = 5$ for 5-outer-electron atoms as
in $\text{Nb}^{41}(4d^25s^1)$. Other examples besides $G = 1, 3$
and 5 are $\text{Mg}^{12}(3s^2 \rightarrow G = 2)$, $\text{Cr}^{24}(3d^54s^1 \rightarrow G = 6)$,
$\text{Zn}^{30}(4s^2 \rightarrow G = 2)$, $\text{Te}^{43}(4d^55s^2 \rightarrow G = 7$; not $4d^65s^1$),
and $\text{Pb}^{82}(6s^26p^2 \rightarrow G = 4)$. These estimated $G$-values are shown in Fig. (a) in the top and bottom. While the K-P-table actually lists as $3d^{10}4s^2$,
we ignore $3d^{10}$, as we ignore the same $nd^{10}(n = 3 \sim 5)$ in
$\text{Cu, Ag, Au}$, and $\text{Cd}^{49}(5s^2 \rightarrow G=2) ;$ adding $10$ to $G$
is far beyond the observation, though $nd^{10}$ may be
important for the electronic structure. In the case of $\text{Cu}$,
we know that the state density from $d^{10}$-orbits is confined
below the Fermi energy and hence no contribution
(see Fig. 7.12 of ref. 2). Adding further $\text{Al}^{13}(G=1,$
only $2p^2$ is used, since $G_{\text{obs}}=1.2$), $\text{Sr}^{38} \text{Ta}^{73}$
$\text{W}^{74}(G=2, 6s^2)$, $\text{Re}^{75}$, $\text{Ir}^{77}(G=2, 6s^2)$, and $\text{Tl}^{81}$, altogether 22 metals
in the K-P-table show that if one uses these $G$-
values, eq. (2) holds quite well with the scatter rms of
$|G - G_{\text{obs}}|/G_{\text{obs}} = |\sigma_{\text{obs}} - \sigma|/\sigma = 23\%$.
For the remaining 26 metals, we need to inspect in detail,
primarily because the periodic table itself is rather complicated. There seem two ways of guessing $G$. In the first
method, given the observed $G_{\text{obs}}$, we force to choose
configurations counted from the highest term until the
sum of electron numbers becomes closest to $G_{\text{obs}},$ that is
we round off $G_{\text{obs}}$ to integer such that $|G - G_{\text{obs}}| \leq 0.5,$
namely $G \equiv (G_{\text{obs}})$round. Naturally $G/G_{\text{obs}}$ becomes
almost unity as seen in Fig. (b) below. Though there seems no reason to reject this first method, we ‘feel un-
easy’ because $\text{Ag, K}^{19}$ and $\text{Ca}^{20}$, presumably simpler
than other metals, depart more from unity than other more complicated metals, but also more importantly
because many metals show much smaller deviations from unity than the relative differences of ‘non-identical experi-
mental $\sigma$-values’ between the K-P-table and PSJ-table
(±7% for 38 metals).
We adopt then an alternative second method in this
paper as shown below. We add deeper ‘electron configu-
rations’ (hereafter E-config) for some elements than the
K-P-table; examples are $\text{Li}^3$(from $2s^1$ to $1s^22s^1$, leading
to $G = 3$), $\text{Y}^{23}(3d^44s^2 \rightarrow 3p^63d^44s^2 \rightarrow G = 11)$,
and $\text{Bi}^{83}(6s^26p^3 \rightarrow 5s^25p^65d^{10}6s^26p^3 \rightarrow 23)$. Here the
added part is underlined. The last one Bi, a typical semimetal, may be noteworthy, because by including
enough deep levels, it can be treated in the same way
as others, and Bi gives $\sigma \approx \sigma_{\text{obs}}$ using $G_{\text{obs}} = 23.8$ (full
E-config of Bi$^{83}$ is $\{[\text{Pd}^{16}]4f^{14}\}5s^25p^65d^{10}6s^26p^3$).
We could have assigned $G = 21$ by excluding the first $5s^2$,
indicating non unique $G$-values for a large $G_{\text{obs}}$. Another
semimetal $\text{Sb}^{51}(G=10)$ discussed later can be treated similarly. Adding $\text{Y}^{39}(G=11)$, $\text{Zr}^{40}(G=12)$, $\text{La}^{57}(G=11)$,
and $\text{Hf}^{72}(G=10$ from $5p^65d^26s^2)$, altogether 7 metals fall
in this category.
Though it is possible to treat Sc, Ti and iron group simi-
larly, we introduce two rules below to obtain ‘much bet-

ter' agreements with the observations. We first introduce what we call \((10−x)\)-rule. We examine \(\text{Fe}^{26}\) listed as \(3d^94s^2\) in the K-P-table, \(\text{Co}^{27}(3d^74s^2)\) and \(\text{Ni}^{28}(3d^84s^2)\), giving tentative values of \(G_{\text{tent}} = 8, 9\) and 10, respectively. However if we introduce one rule that if \(G_{\text{tent}} > 5\) is encountered in d-orbit where the saturation is 10, we use \(G = 10 − G_{\text{tent}}\) as a subset of d-orbit. Then \(G/G_{\text{obs}}\) becomes closer to unity. Namely, \(G_{\text{obs}} = (6.1, 3.8, 4.7)\) and new \(G = (2+4, 2+3, 2+2)\) are obtained for \(\text{Fe}, \text{Co}, \) and \(\text{Ni},\) respectively, where the first numeral 2's come from \(s^2\). The result is \(G/G_{\text{obs}} = \sigma_{\text{obs}}/\sigma = (6/6.1, 5/3.8, 4/4.7) = (0.98, 1.3, 0.85)\). On the other hand for \(G_{\text{tent}}\) we would have obtained \(G_{\text{tent}}/G_{\text{obs}} = (1.6, 2.9, 2.6)\), which we regard unsatisfactory. We applied this rule altogether to 6 elements in 8th – 10th group, including \(\text{Ru}^{44}, \text{Rh}^{45},\) and \(\text{Os}^{76}\).

A rule of this kind is seen in atomic spectroscopy \([11,12]\), where \(d^x\) and \(d^{10−x}\) give the same LS coupling terms such as \(1^S,1^D,1^G\), together with similar rules like \(p^{6−x}\) and \(f^{14−x}\). Also when the cohesive energy of many metals was estimated, a similar kind of rule has been utilized \([13]\), which is broadly consistent with an extensive calculation \([14]\). The only strong reason however that we use \((10−x)\)-rule is because it gives better agreements with the observations.

Finally we introduce what we call \((1/2)\)-rule. When the \(G_{\text{obs}}\)-value in a metal corresponds just inside of semi-closed shells of \(g=2, 6\) or 10 (statistical weight), we take one half of these values to the last of the sum of E-config. This is a sort of extended \((10−x)\)-rule. Underlying presumption is that though these 2, 6 and 10 electrons are closely packed, there might be weak breaks just in the middle of these, namely 1, 3 and 5. As a first example, \(\text{Pd}^{46}(4d^{10})\) shows \(G_{\text{obs}} = 5.2\) for \(\sigma\), hence instead of adopting \(G = 10\), we adopt \(G = 5\) from \(10/2\). We applied the \('1/2\'-rule' also for \(\text{Ca}^{20}(4s^2, G=1, G_{\text{obs}}=0.6)\), and \(\text{Sn}^{50}\). For 6 metals we combine the addition of deeper terms to the K-P-table and the \('1/2\'-rule'; \(\text{Sc}^{21}\)(2p3s23p23d14s2 → \(G = 14\)), \(\text{Ti}^{22}\)(2p3s23p26d14s2 → \(G = 15\)) and \(\text{Br}^{56}\)(5p66s2 → \(G = 5\)). Here added terms are underlined, and in 6 in \(2p\)-orbits (Sc and Ti) or \(5p\)-orbits (Ba) is replaced by \(6/2 = 3\). Also \(\text{Be}^{4}(G=3), \text{Ga}^{31}(G=8)\) and \(\text{Sb}^{51}(G=10)\) fall in this group. Again it is noteworthy that though \(\text{Sb}\) is a semimetal, it is treated in the same way as the usual metal; namely \(G_{\text{obs}} = 10\) for \(\text{Sb}^{51}\), almost identical to \(G_{\text{obs}} = 10.0\), comes from an addition of 5 from K-P-table (\(5s^55p^3\)), and \(5/10\) (1/2-rule for \(3p^{10}\)) from full E-config of \(\text{Kr}^{36p^{10}5s^55p^3}\). Further, the semimetal \(\text{As}^{33}\) (\(\text{Ar}^{18}3d^{10}4s^24p^3\)), not included so far, shows \(G_{\text{obs}} = 11.2\) from \(1/\sigma_{\text{obs}} = 333n\Omega m\) \([10]\) so that \(G = 10\) (1/2-rule for \(3d^{10}\)) may be appropriate. Although use of the \('1/2\'-rule' is due primarily to better fit the observations, we want to stress that without this rule \(|G − G_{\text{obs}}|/G_{\text{obs}}\) would become much larger than in other metals in the same group where these rules are not needed (see Fig. \(2\)).

Figure \(1\)(b)-upper shows, excluding problematic \(\text{Mn}^{25}\), \(\text{Mo}^{42}, \text{Pt}^{78},\) and \(\text{Hg}^{80}\), an rms scatter of \(\pm 20\%\) (\(\pm 14\%\)) for \(G = (G_{\text{obs}})\)round in Fig. \(1\)(b)-lower), which is larger than the observation error of \((\text{rms})_{\text{obs}} = \pm 7\%\) mentioned before. This suggests that the scatter in Fig. \(1\)(b)-upper stems largely from yet-unknown causes.

For the thermal conductivity \(\lambda\), we also show \(G_{\text{obs}}−\lambda = \lambda_{/}\sigma_{\text{obs}}\) (Fig. \(1\)(a)) and \(\lambda/\sigma_{\text{obs}}\) (Fig. \(1\)(b)-upper) from eq. \(2\) with the same \(G\) used for \(\sigma\) in thick marks [\(\lambda_{/\sigma_{\text{obs}}} = \lambda(\sigma = 1)\)]. We plotted only metals showing large departure from the Wiedemann-Franz law \([1–3]\) \(|(C_{\text{WF}} − 1)| ≥ 0.2\). Here \(C_{\text{WF}} \equiv \lambda/(\sigma T L_{\sigma})\), where \(L_{\sigma} \equiv \pi^2 k_B^2/3e^2\). We find no appreciable differences from \(G_{\text{obs}} = \sigma_{1}/\sigma_{\text{obs}}\) even for those metals of large \(|C_{\text{WF}}|−1\).

Figure \(2\) which is supplementary to Fig. \(1\) shows that the position of estimated \(G\)'s in E-config. For example, E-config of \(\text{Fe}^{26}\) is \(\{\text{Ar}^{18}\}3d^44s^2\) and we adopted \(G = 2 + 4 = 6\) (comes from \(10 − 6\) in \(d^6\)) added from outer ones, where \(4\) is within the 3d-orbit. Hence for \(\text{Fe}\) we plotted at 3d. Fig. \(2\) shows rather systematic behavior, particularly among 4-6 periods (starting from \(\text{K, Rb and Cs}\)). This indicates that our choice of \(G\), though adopted only to match the observations, appears to be rooted from some physical basis. In fact we notice that groups 3–4 (Sc\(^{31}, \text{Ti}^{32}, \text{Y}^{39}, \text{Zr}^{40}, \text{La}^{57}\)) which stem deeper configurations than other met-
als, are all have configurations where electrons are filled in the outer orbits before inner orbits become filled up or closed; e.g. Sc$^{21} = \{\text{Be}^4\}2p^63s^23p^63d^14s^2$ instead of $\{\text{Be}^4\}2p^63s^23p^63d^3$, while the 3d-orbit only saturates at Cu$^{29}$ as 3d$^{10}$. This is of course typical characteristics of the earlier transition elements. It might suggest some unsteadiness of so to speak heavier upper floors than e.g. noble metals, and as a consequence involvement of deeper orbits.

In addition to 48 metals plus As$^{33}$ already discussed, we show $G_{\text{obs}}$-values for rare earth metals in Fig. 2 and find $\sigma/\sigma_{\text{obs}} \approx 1$, mainly because $G_{\text{obs}} \geq 10$ (except Yb$^{70}$) such that it is easier to find $G/G_{\text{obs}} \approx 1$ (the lowest orbits are in 4d, 4f and 5p). A conclusion from Fig. 2 is that our choice of $G$-values shows rather systematic distribution among E-config for various metals, supporting the choice, if not prove, besides giving nearly correct values of $\sigma_{\text{obs}}$.

Concluding Remarks. – In our view, the reason why Cr($1/\sigma_{\text{obs}} =129n\Omega \text{m} =12.9 \times 10^{-6}\Omega \text{cm}$ at $T_{\text{obs}}=295K$ ) is more resistive than Cu ($17n\Omega \text{m}, 4s^1, G=1$), in fact by 7.6, is simply due to large $G$(Cr, 3d$^54s^1)=6, i.e. a larger number of equally contributing orbits (or bands), since $n_{\text{atom}}$(Cr)$=8.3$ is similar to $n_{\text{atom}}$(Cu)$=8.5$ ($10^{28}\text{m}^{-3}$ unit).

We find in this paper that eq.(2) for $\sigma$ and $\lambda$ using $\tau = \hbar/k_BT$ [eq. (1)] agrees well with the observations for the majority of elemental metals, inclusive of semimetals, at room temperature ranges. Here we adopt that $G$ is the sum of outer electron numbers in the electron configuration as listed in the back cover of Kittel’s text with some modifications (e.g. 3d$^{10}$4s is replaced by 4s in Cu).

Certainly one needs theoretical reasoning particularly on $\tau$ and we wish to know the value of $Z \equiv n_e/n_{\text{atom}}$, which is not needed in this paper. We emphasize again that $\tau_{\text{calc}}/\tau_{\text{obs}} = \sigma_{\text{calc}}/\sigma_{\text{obs}}$ is very close to unity for alkali and noble metals where $G = 1$ is adopted ($T=295K$); the ratios are e.g. 0.88(Na), 0.99(Rb), 1.24(Cs), 1.05(Cu), and 0.95(Au). The extreme simplicity of $\tau$ [eq.(1)] and good agreements with the experiments suggest that there might be an ‘extremely’ simple physical explanation for this, which we will discuss in the next paper along with the value of $Z$, for which we will find $Z = 1$ for $\sigma$ in majority of elemental metals.

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