

## Specific heat of metals not due to hypothesized valence electrons

### Thermic radiation due to trembling solid rods of the crystal lattice; influence of lattice nodes minor

**Free valence electrons don't exist in metals, therefore they cannot be the carriers of temperature oscillation, they cannot be agents of bonding and electrical conduction**

#### Introduction and abstract

*Hyperphysics* textbooks mystery:

*One of the great mysteries in physics in the early part of the 20th century was why electrons didn't appear to contribute to **specific heat**. How could they contribute to electrical conduction and heat conduction and not to specific heat?*

Quantum mechanics explains metallic bonding due to dynamic equilibrium of electrostatic distant forces between positively charged atomic ions and negatively charged electrons, where the latter oscillate very fast because they are thought of as the main contributors of heat. Besides that this bonding model cannot explain stability of the lattice, the free electron gas model of Drude has been proved that this model greatly overestimates heat capacities: recall that free electron gas model predicts heat capacities as

$$C = (2/3) N k_{obo}$$

Where  $k_{obo}$  = Boltzmann constant and  $N$  = number of electrons.

We show that the later introduced Fermi-valence electrons with Fermi-energies cannot resolve the problem.

Comparisons of measured specific heats *per volume* indicate that

- Heat capacity depends predominantly on crystal structure.
- Concerning the crystal structure, heat capacity depends predominantly on lattice spacing. Data show that heat capacity is mainly due to trembling of lattice bars; heat capacities of lattice bars depend on effective bar lengths.
- Lattice bars cannot be thought of as distant forces or *virtual bars*. Solid lattice bars consist of hydrogen building blocks.
- Volume of lattice nodes determine effective lengths of rods. Generally, the influence of different masses in the lattice nodes is minor. But when the mass number ratio for two elements considered is great, effective lengths cannot be neglected. Example Co ( $A = 59$ ) and Be ( $A = 9$ ).
- Heat capacities of lattice rods depend also on the elasticity of their fixing in the nodes. Influence unknown.

- Magnitudes of strength modules (shear, bulk, elasticity modulus) decide on structures of bonding links: Bonds can be made up of one single hydrogen (H), two H's in series or parallel.
- Alleged valence electrons cannot be the agents for bonding and heat capacity.
- A significant empirical indication that the free electron cloud in metal conductors does not exist is the measurement of the molar specific heat. According to the empirical Dulong-Petit rule the specific heat is about 6 cal/(K mol), which is the specific heat of the crystal lattice. If there would be an electron gas inside the lattice, the specific heat of the metal should be 9 cal/(K mol) because the specific heat of the electron gas is 3 cal/(K mol)! This is well known [jaworski] and refutes the electron gas concept.

## Metals possess a solid lattice

### Hydrogen is the construction material of lattice rods

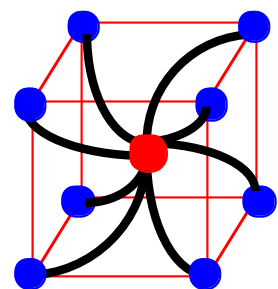
According to the prevailing quantum theory metallic bonding is interplay of the valence electrons and the ion cores of the lattice atoms. The bonding model explains metals as a lattice of ion cores held together by electrons! This is an untenable explanation. Electrons cannot hold together the ion cores that are repelling each other!

Here I propose an atomic model according to William Prout (1815): each chemical element is made out of hydrogen atoms. The so-called mass numbers  $A$  represent the number of the constituting hydrogen atoms. Bonding is due to magnetic coupling because each hydrogen atom is a magnet. Conjecture: Hydrogen itself is composed of 4 elementary ring magnets that are charged  $+ - + -$ .

There are 3 varieties of H-bonds:  
 single hydrogen,  
 2 hydrogen atoms in series — —  
 or 2 hydrogen bonds parallel ||.

If we conjecture that the contribution to heat capacity is mainly due to vibrating (solid) lattice rods, we must compare heat capacities per volume:  $J/cm^3K$  and not per grams  $J/gK$ , which is not meaningful.

Temperature of metal lattices due to oscillations of bars (= solid bonds).  
 In reality, oscillations are small ones!  
 Small displacements of nodes.



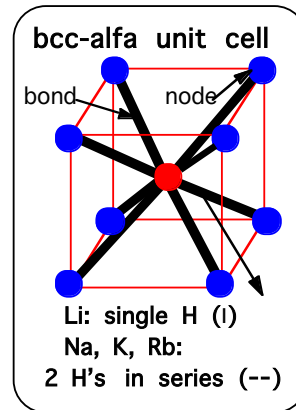
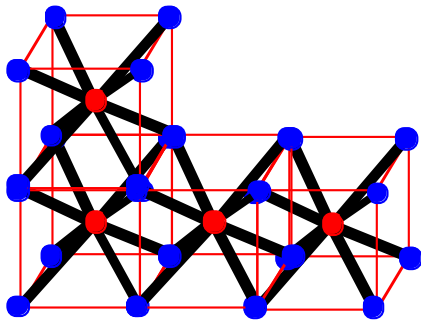
### The real **solid** fundamental building block of metals

The alternative to QM's valence electrons and their role as bonding agents are metal lattices that possess **solid bars** made out of hydrogen. These bonds can be single or double H-bonds. Even two H's in series are possible. Then one must decide which atomic cores are joined by bars. For example, the fcc structures are very stable. Atomic cores are connected by bars such that the resulting basic building block is a octahedron, one of the platonic bodies.

Two different lattice types with bcc unit cells:

■  **$\beta$ -bcc for transition metals: diagonals and edges of the unit cube are lattice bars, building block of the lattice is a bipyramid**

■  **$\alpha$ -bcc for alkali metals and Ba: only diagonals of the unit cube are lattice bars.**



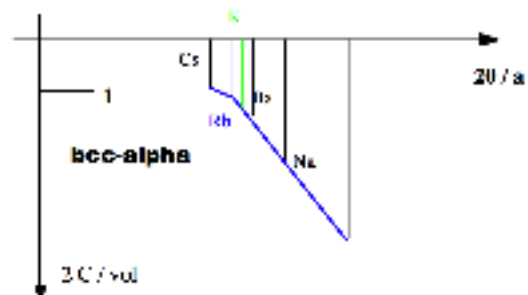
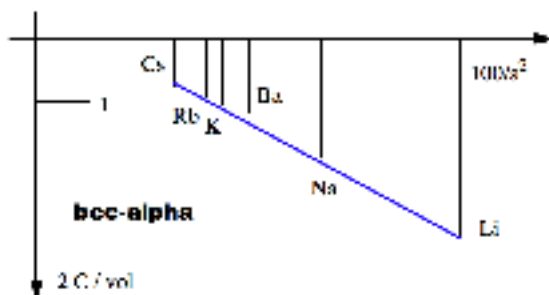
**Grid-nodal system of metallic bonding  
Lattice type of alkali metals and Ba**

In the first row of the table below the supposed hydrogen bonding is mentioned. Bonding, lattice spacing, rigidity and specific heats are compared.

Criterion for heat capacity is heat capacity per volume ( $\text{cm}^3$ ).

Shear modulus is the coefficient of elasticity for a shearing or torsion force, it expresses rigidity.

| bcc. unit cell<br>bars: cube diagonals      | single<br>bond  | 2 H's in series<br>-- |                 |                  |                   |                   |
|---|-----------------|-----------------------|-----------------|------------------|-------------------|-------------------|
| Element                                     | <sup>7</sup> Li | <sup>23</sup> Na      | <sup>39</sup> K | <sup>85</sup> Rb | <sup>133</sup> Cs | <sup>138</sup> Ba |
| a   | 3.51            | 4.29                  | 5.33            | 5.56             | 6.14              | 5.03              |
| d: density $\text{g}/\text{cm}^3$           | 0.535           | 0.968                 | 0.856           | 1.532            | 1.879             | 3.51              |
| $d \times C = \text{J}/\text{cm}^3\text{K}$ | 1.91            | 1.16                  | 0.648           | 0.558            | 0.455             | 0.72              |
| $10 \times 1/a$                             | 2.9             | 2.3                   | 1.9             | 1.8              | 1.6               | 2                 |
| $10^2 \times 1/a^2$                         | 8.1             | 5.4                   | 3.5             | 3.2              | 2.6               | 4                 |
| shear modulus [GPa]                         | 4.3             | 3.3                   | 1.3             | 0.9c             | N/A               | 4.9               |



**Interpretation of data: specific heat per volume depends on  $1/L^2$ , where L is the effective bar length of the lattice.**

## Beams necessitate simplification

Heat is expressible as  $mv^2$  of particles of a gas, for instance. Here the parts of the bars vibrate.

The mass of the beam is thought of to be concentrated in the middle of the beam and the beam itself is a flat spring (spring constant  $k$ ). At room temperature the beam is performing only small vibrations.

Then the frequency squared is  $\omega^2 = k/m$ ,

For a narrower range we set  $k = \text{const}$ .

For  $m = L A \rho$  ( $A \dots$  area,  $\rho \dots$  density)  $\rightarrow \omega^2 \sim 1/L$

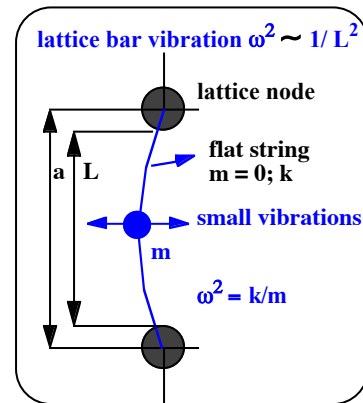
Because the frequency squared is proportional to temperature, specific heat would then depend on  $1/L$ . But the  $1/L^2$  dependency is better. Why?

In reality, spring force depends on  $k = 1/L$ , then  $\omega^2 \sim 1/L^2$

Effective bar lengths, supporting modes, elasticity and so on are unknown...

But: The greater the bar length the less energy is needed to set in vibration the bar.

Temperature is due to bar and nodes vibration, not due to vibrating electrons...



Compare bcc structures with 2 H's in series as bars from Na to Cs: the decrease of volume heat capacity  $d \times C$  is accompanied by an increase of the mean bond lengths from 3.9 to 5.59 Å. One would expect that the energy input for heating the metal increases with more matter in the lattice nodes, but volume heat capacity  $d \times C$  decreases from 1.16 to 0.455.

That decrease is mainly due to the increase of lattice spacing!

Therefore the influence of lattice spacing is overwhelming: Heat means trembling of the lattice bars, the lattice nodes don't oscillate remarkably!

Regarding the sequence

Na  $\rightarrow$  K  $\rightarrow$  Rb  $\rightarrow$  Cs, the decrease of  $1/a^2$  is

|     |     |     |     |
|-----|-----|-----|-----|
| 5.4 | 3.5 | 3.2 | 2.6 |
|-----|-----|-----|-----|

and volume heat capacities decrease:

|             |              |              |              |
|-------------|--------------|--------------|--------------|
| <b>1.16</b> | <b>0.648</b> | <b>0.558</b> | <b>0.455</b> |
|-------------|--------------|--------------|--------------|

$1/a^2$  instead of  $1/L^2$  is used because the effective length  $L$  is not known.

But for the atomic numbers  $A$  there are the following jumps:

137  $\rightarrow$  39  $\rightarrow$  85  $\rightarrow$  133.

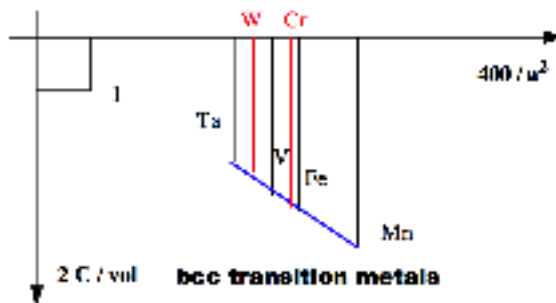
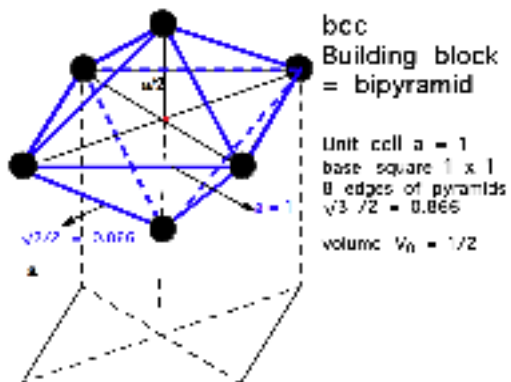
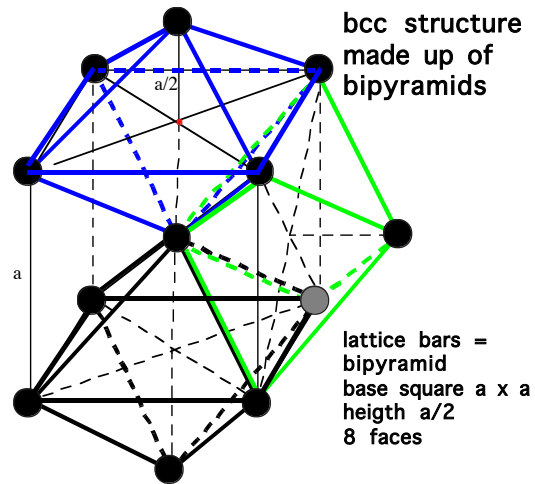
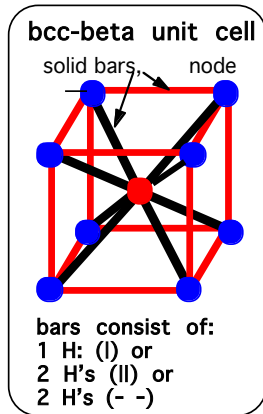
Again, matter contents of nodes play a minor role for specific heats...

Obviously, temperature is mainly due to vibrations of solid lattice bars. But there is an influence of big atomic numbers on specific heats: Big atomic numbers are the cause that the corresponding lattice nodal joints reduce the bond lengths. Therefore the effective bond lengths are shorter than the lattice constant  $a$ !

Below there are examples.

## $\beta$ -bcc unit cell:

diagonals and edges of the unit cube are lattice bars,  
building block of the lattice is a bipyramid



## $\beta$ -bcc transition metals

|  |       |         |       |       |      |      |       |       |
|--|-------|---------|-------|-------|------|------|-------|-------|
| Hydrogen links                           |       |         |       |       |      |      |       | --    |
| Element                                  | Mo    | W       | Fe    | Cr    | V    | Nb   | Ta    | Mn    |
| Most abundant isotopes                   | 98,96 | 184,186 | 56,54 | 52,53 | 51   | 93   | 181   | 55    |
| $a$ [Å]                                  | 3.15  | 3.16    | 2.87  | 2.91  | 3.03 | 3.3  | 3.3   | 8.91  |
| $10^3 \times 1/a^2$                      | 1.01  | 1       | 1.21  | 1.18  | 1.09 | 0.92 | 0.92  | 1.49  |
| Specif heat /vol. [ J/cm <sup>3</sup> K] | 2.58  | 2.54    | 3.53  | 3.2   | 3.04 | 2.27 | 1.91  | 3.56? |
| Young's modulus E [GPa]                  | 329   | 411     | 211   | 279   | 128  | 105  | 186   | 198   |
| Rigidity G [GPa]                         | 118   | 161     | 64e   | 115   | 47   | 38   | 69    | N/A   |
| Density g/cm <sup>3</sup>                | 10.28 | 19,25   | 7.872 | 7,14  | 6,11 | 8,57 | 16,65 | 7,44  |
| Specific heat [ J/(kgK)]                 | 251   | 132     | 449   | 448   | 498  | 265  | 140   | 479   |
| Valency #                                | 6     | 6       | 3     | 6     | 5    | 5    | 5     | 4     |

## $\beta$ -bcc transition metals:

Increasing bond lengths shows a decrease of specific heat for bcc (and fcc) metals.

The graph can be interpreted that lattice bar lengths are the determining factor for specific heat. Further, on the other hand, that oscillations of lattice nodes — irrelevant of their mass content — can be neglected.

**Fcc structure**

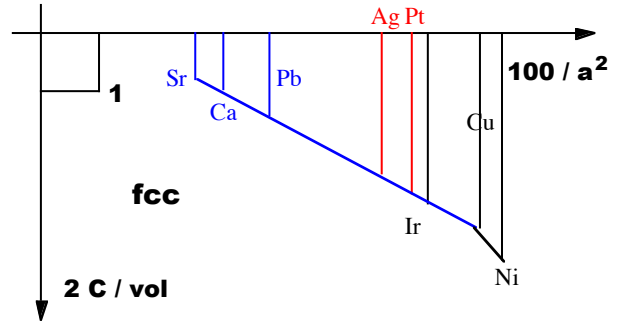
| Bonds                    |             |             |             |             |             |             |             |             |             | --          |             |             |
|--------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| element                  | Ir          | Rh          | Ni          | Cu          | Pt          | Pd          | Au          | Ag          | Al          | Pb          | Ca          | Sr          |
| Mass # A                 | 193         | 103         | 60          | 63          | 195         | 106.        | 197         | 107.        | 27          | 208         | 40          | 88          |
| dens g/cm <sup>3</sup>   | 22.6        | 12.5        | 8.9         | 8.92        | 21.1        | 12.         | 19.3        | 10.5        | 2.7         | 11.3        | 1.55        | 2.63        |
| J/kgK                    | 0,13        | 0,24        | 0.44        | 0.38        | 0.13        | 0.24        | 0.13        | 0.23        | 0.90        | 0.13        | 0.63        | 0.30        |
| <b>J/cm<sup>3</sup>K</b> | <b>2.97</b> | <b>2.99</b> | <b>3.92</b> | <b>3.42</b> | <b>2.8</b>  | <b>2.89</b> | <b>2.49</b> | <b>2.47</b> | <b>2.44</b> | <b>1.44</b> | <b>0.98</b> | <b>0.79</b> |
| 10/a <sup>2</sup>        | <b>0.68</b> | <b>0.69</b> | <b>0.81</b> | <b>0.77</b> | <b>0.65</b> | <b>0.66</b> | <b>0.6</b>  | <b>0.6</b>  | <b>0.61</b> | <b>0.4</b>  | <b>0.32</b> | <b>0.27</b> |
| Lattice a [Å]            | <b>3.84</b> | <b>3.8</b>  | <b>3.52</b> | <b>3.61</b> | <b>3.92</b> | <b>3.89</b> | <b>4.08</b> | <b>4.08</b> | <b>4.05</b> | <b>5.0</b>  | <b>5.6</b>  | <b>6.08</b> |
| Shear m. Gpa             | 210         | 150         | 76          | 48          | 61          | 44          | 27          | 30          | 26          | 5.6         | 7.4         | 6.1         |

— Comment:

Imagine the lattice of Ag, Au and Al as an elastic 3D-mattress. Both lattice spacing and lattice structure of Ag, Au and Al are roughly the same. The sole difference between the mattresses concerns the lattice nodes. But vibrations of nodes due to temperature is minor. Therefore all thermodynamic properties of Ag and Au have roughly the same value!

The other fcc metals are not shown in the graph because their bond lengths are near by.

Because of their great shear moduli, Ir and Rh must have two H's parallel as bonds.



Heat means the intensity of lattice bar structure vibration, the vibrations of the lattice points is minor.

It is interesting to compare Pd with Pb: Densities don't differ remarkably but heat capacities do. Obviously, we must pay attention to the different unit cell spacing's: 3.9 vs. 5 Å. Much more work must be done to set the smaller Pd-bonds into vibrations than longer ones of Pb! The contribution of lattice nodes is minor, heating up a metal volume means bring the lattice bars into oscillation... The graph shows a linear dependence of heat capacity on lattice spacing.

• Additional comparisons

All physical properties of **Ir and Pt** are roughly equal, except G, E, and B moduli. (See the article on metallic bonding.) For example Young's modulus E for Ir is roughly 3 times greater than for Pt. The bonding of Ir must be stronger. It is assumed that Ir possesses a double H bond, whereas Pt possesses only a single H bond. The specific heat is equal..

|              | Crystal | Young mod. GPa | bonds | Spec. h/vol J/cm <sup>3</sup> K | Atomic weight | Proton # | dens. ρ = g/cm <sup>3</sup> | Valency z | n = z×ρ/A | lattice a [Å] |
|--------------|---------|----------------|-------|---------------------------------|---------------|----------|-----------------------------|-----------|-----------|---------------|
| <b>Ir</b>    | fcc     | 528            |       | 2.97                            | 192.2         | 77       | 22.5                        | z=6       | 0.7       | 3.84          |
| <b>Pt</b>    | fcc     | 168            |       | 2.8                             | 195.1         | 78       | 21.5                        | z=6       | 0.66      | 3.92          |
| <b>Ir/Pt</b> | 1       | 3.14           | 2     | 1.06                            | 0.98          | 0.99     | 1.05                        | 1         | 1.06      | 0.98          |

### Rh compared to Pd

|                          |             |             |
|--------------------------|-------------|-------------|
| bonds                    |             |             |
| element                  | Rh-103      | Pd-106      |
| <b>J/cm<sup>3</sup>K</b> | <b>2.99</b> | <b>2.89</b> |
| Lattice a [Å]            | <b>3.8</b>  | <b>3.89</b> |
| Shear m. Gpa             | <b>150</b>  | <b>44</b>   |

### double bonds || compared to single bonds |

| bonding                       |      |     |      |      |     |      |      |      |      |
|-------------------------------|------|-----|------|------|-----|------|------|------|------|
| element                       | W    | Ta  | W/   | Mo   | Nb  | Mo/  | Cr   | V    | Cr/  |
| Mass # A                      | 184  | 181 | 1.02 | 96   | 93  | 1.03 | 52   | 51   | 1.02 |
| a [Å] unit cell               | 3.17 | 3.3 | 0.96 | 3.15 | 3.3 | 0.96 | 2.91 | 3.03 | 0.96 |
| Spec heat J/cm <sup>3</sup> K | 2.5  | 2.3 | 1.1  | 2.6  | 2.3 | 1.1  | 3.19 | 3    | 1.1  |

### Comparison bcc/fcc specific heats:

Specific heat of a fcc unit cell is two times the specific heat of a bcc unit cell (rounded).

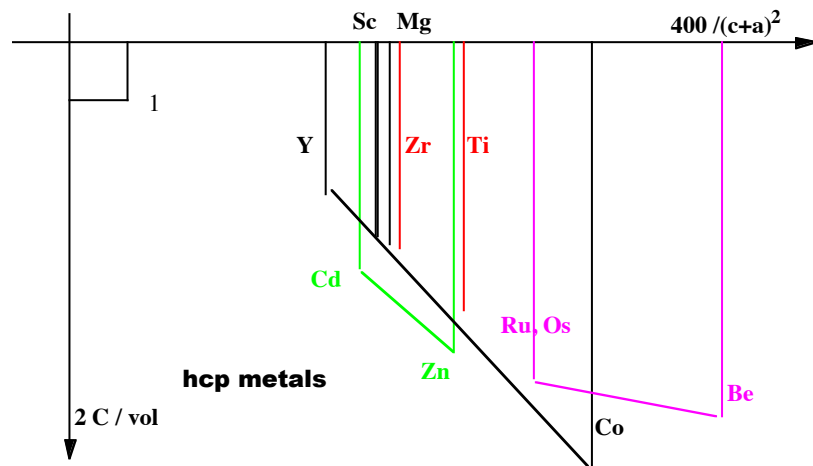
Example: Both, Ba and Pb have a lattice constant of  $\sim 5\text{\AA}$ , specific heat per volume is 0.72 for Ba and 1.44 for Pb. Therefore the specific heats ratio for bcc/fcc =  $\frac{1}{2}$  for equal unit cells.

Notice also that for Pb and Ba because of the great lattice spacing ( $5\text{\AA}$ ) the bare is assumed to consist of two H's in series.

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## hcp metals

| *                       | Be      | Ru      | Os      | Co      | Mg      | Sc       | Y       | Ti      | Zr      | Zn      | Cd       |
|-------------------------|---------|---------|---------|---------|---------|----------|---------|---------|---------|---------|----------|
| Mass #                  | 9       | 102,104 | 192,190 | 59      | 24, 26  | 45       | 89      | 48, 46  | 90, 94  | 64, 66  | 114, 112 |
| bonds                   | I       | II      | II      | --      | --      | --       | --      | --      | --      | --      | --       |
| g/cm <sup>3</sup>       | 1,85    | 12,4    | 22,6    | 8,9     | 1,74    | 2,99     | 4,47    | 4,51    | 6,5     | 7,14    | 8,65     |
| Young GPa               | 287     | 447     | 559     | 209     | 45      | 74       | 64      | 116     | 68      | 108     | 50       |
| G GPa                   | 132     | 173     | 222     | 75      | 17      | 29       | 26      | 44      | 33      | 43      | 19       |
| Melting/10 <sup>3</sup> | 1.29    | 2.33    | 3.03    | 1.5     | 0.65    | 1.54     | 0.82    | 1.67    | 1.86    | 0.42    | 0.32     |
| Spec heat               | 1.82    | 0.238   | 0.13    | 0.421   | 1.02    | 0.567    | 0.298   | 0.52    | 0.278   | 0.388   | 0.23     |
| Therm. exp              | 11.3    | 6.4     | 5,1     | 13      | 8.2     | 10.2     | 10.6    | 8.6     | 5.7     | 30.2    | 30.8     |
| a/c                     | 2.3/3.6 | 2.7/4.3 | 2.7/4.3 | 2.5/4.1 | 3.2/5.2 | 3.31/5.2 | 3.7/5.7 | 2.9/4.7 | 3.2/5.1 | 2.7/5.0 | 2.98/5.6 |
| (1/a+c) <sup>2</sup>    | 2.87    | 2.04    | 2.04    | 2.3     | 1.41    | 1.358    | 1.137   | 1.73    | 1.45    | 1.69    | 1.28     |
| Sp heat/vol             | 3.3     | 2.95    | 2.94    | 3.75    | 1.77    | 1.7      | 1.33    | 2.35    | 1.81    | 2.71    | 1.99     |



**Bonding:** Dimensions of lattice constants  $a$  are large, from 4 to 6 Å. Assumption: They consist of two hydrogen atoms in series. (— —)

Exceptions Be, Ru, Os because of their great stiffness. Be has single H bonds I, Ru, Os possess double bonds II.

Table: Last row: standard of comparison is  $10^3 \times (1/a+c)^2$ , where  $a$  and  $c$  are cunit cell dimensions.

Be: It must be seen with Ru and Os because they have not two bonds in series — — like the other hpc metals but two bonds parallel II. Take account of the small mass number of Be ( $A = 9$ ), for which reason a considerable part of the specific heat per volume is probably due to oscillations of the lattice nodes!

Specific heats of Cd and Zn show a deviation. The cause is their deviating high thermal expansion that is over 3-fold..

### Résumé: dependence of specific heat per volume $C = J/cm^3K$ on crystal structure

| $C=J/cm^3K$ Range | Lattice constant $a$ [Å]m | Shear modulus GPa | bonds | structure |
|-------------------|---------------------------|-------------------|-------|-----------|
| 1.2 — 0.45        | 4.2 — 5.1                 | $\leq 3.3$        | — —   | bbc       |
| 3.57 — 2.27       | 2.2 — 3.6                 | 160 — 38          | II    | bbc       |
| $\leq 1.45$       | $\geq 5.0$                | $\leq 7.5$        | — —   | fcc       |
| 3.4 — 2.9         | 3.8                       | 247 — 108         | II    | fcc       |
| 2.49 — 0.78       | 3.8 — 6.1                 | 30 — 6            | — —   | fcc       |
|                   | 3.5 — 3.6                 | 3.6               | I     | fcc       |



## Contribution of alleged metallic valence electrons to heat capacity fictitious

According to QM, the agents of metallic bonding are valence electrons. Sodium for example possesses valency „1“. Every Na atom delivers one electron (from the outermost shell) in order to produce equivalence of these valence electrons with negative charge and the atomic ions with positive charge. Aluminium, Al, has valency 3, so per Al atom 3 valence electrons produce equilibrium for bonding. Wiki pedia explains

[http://en.wikipedia.org/wiki/Valence\\_band](http://en.wikipedia.org/wiki/Valence_band):

*The valence electrons are bound to individual atoms, as opposed to conduction electrons, which can move freely within the atomic lattice of the material. On a graph of the electronic band structure of a material, the valence band is located below the conduction band, .... In metals, the conduction band has no energy gap separating it from the valence band.*

Comment: According this explanation, because valency of Na is „1“, the outermost electron of Na serves for conduction and bonding....

This concept of valence originates from *chemical bonding* where it identifies the number of chemical bonds or better: chemical combinations of elements.

This concept of valence is irrelevant for metallic bonding, where members of one element form a huge molecule. To apply chemical valence numbers to explain metallic bonding as well as specific heat is a category mistake! Another question is the possibility of stability for the alleged electron sharing between atoms in order to form electrostatic forces between atoms (now ions) and electrons.

Specific heat depends pedominantly on crystal structure.

Some comparisons:

| 3 valence electrons |                     | 4 valence electrons |                     | 5 valence electrons |                          |
|---------------------|---------------------|---------------------|---------------------|---------------------|--------------------------|
| Al                  | fcc                 | Pb                  | fcc                 | Bi                  | base centered monoclinic |
| In                  | centered tetragonal | Sn                  | centered tetragonal |                     |                          |
| Tl                  | hcp                 |                     |                     |                     |                          |
| Co                  | hcp; > 450C°: fcc   | Ti                  | hcp; > 882C°: bcc   |                     |                          |

Regarding the trio Al, Pb, Co versus trio In, Sn, Tl, different numbers (3, 4) of valence electrons cause the same crystal structure?

Same number of valence electrons causes different crystal structures?

Regarding Co, for example, it shows hexagonal structure (hcp), but above 450 C° the structure is fcc! Random intergrowth of the two is common (wikipedia, Cobalt). Ti, is hpc structured, above 882 C° bcc.

Valences for Co and Ti are 3 and 4, respectively.

Valency obviously does not explain metallic bonding in terms of coordination number or crystal structure... for instance the alleged 5 valence electrons don't explain the baase centered momoclimic structure of metallic Bi.

Obviously valence electrons have nothing to do with metallic bonding.

However the use of valence electrons as carriers of heat capacities refutes this unfounded model!

Valency is involved in the formula for the Fermi energy, which attempts to explain heat capacities, see below. If valency is meaningless, Fermi energy and Fermi energy based heat capacities are meaningless.

We refer to hyperphysics, chapter:

## Electron Specific Heat

Using *Fermi-Dirac statistics* (as opposed to *Einstein-Bose* for phonons), a small fraction of the electrons are available to participate in specific heat. This fraction contributes a specific heat:

$$C_{electrons} = \frac{\pi^2 N_A k^2 T}{2E_F} \text{mole}^{-1}$$

$$E_F = (\hbar^2/2m) (3\pi^2 N/V)^{2/3}$$

Electron density:

$$n_e / V = (\text{valency}) \times N_A (\text{Avogadro \#/mol}) \times \text{density } d [\text{g/cm}^3] / A (\text{mass number } [\text{g/mol}])$$

Example Al:  $n_e / V = (3) \times 6.022 \times 10^{23} \times 2.7 / 27 = 1.8066 \times 10^{23} / \text{cm}^3 \rightarrow E_F = 11.7 \text{ eV}$ .

$E_{F_{\text{fermi}}}$  = depends on (valency × density / mass number A)<sup>2/3</sup>

Ba:  $n_e / V = (1) \times 6.022 \times 10^{23} \times 3.51 / 137.33 = 0.154 \times 10^{23} / \text{cm}^3 \dots 1/(n/V)^{2/3} = 3.48, \times 137.33 = 478 \times 3.51 = 1678$

Pb:  $n_e / V = (4) \times 6.022 \times 10^{23} \times 11.34 / 207.2 = 0.131 \times 10^{23} / \text{cm}^3 \dots 1/(n/V)^{2/3} = 2,16 \times 207 = 447, 5070$

Crystal structure and number of grid bonds are not considered...

An introduction to current theory of heat capacities in metals is available at:

Kai Hock, <http://hep.ph.liv.ac.uk/~hock/Teaching/2011-2012/2-electrons-in-metals.pdf>

## Law of Dulong and Petit for electron gas of metals refuted

According to hyperphysics web textbook the Law of Dulong and Petit holds:

*When looked at on a molar basis, the specific heats of copper and lead are quite similar:*

Cu:  $0.386 \text{ J/gmK} \times 63.42 = 24,48$

Pb:  $0.128 \text{ J/gmK} \times 207.24 = 26,53$

Similar, but not equal, therefore there is no law of Dulong and Petit (D+P) for metals.

Concerning carbon C as graphite and as diamond, it is obvious that not molar specific heat but specific heat per volume should be considered:

| Element                          | C graphite  | C diamond    | Be          | B           |
|----------------------------------|-------------|--------------|-------------|-------------|
| d: density g/cm <sup>3</sup>     | 2.26        | 3.52         | 1.85        | 2,46        |
| C = J/gK                         | 0.676       | 0.502        | 1.82        | 1.03        |
| C = J/mol K                      | 8.11        | 6.02         | 16.4        | 9.3         |
| <b>d × c = J/cm<sup>3</sup>K</b> | <b>1.53</b> | <b>1.77</b>  | <b>3.37</b> | <b>2.53</b> |
| Melting C°                       | 3550        | 3550         | 1287        | 2075        |
| Crystal form                     | hcp         | diam., cubic | hcp         | trig.       |
| Lattice Å                        | 2.46/6.7    | 3.57         | 2.3/3.6     | 5           |

D + P law asserts for specific heat per mole:  $C_v = 3k_B N_A$  (mole = 24.94 J/mole where k = Boltzmann constant, T = Temperature in Kelvins,  $N_A$  = Avogadro's number. (For mole I calculated the mean of isotopes, hyperphysics used atomic weights, which is not correct, see below)

The law of D + P is wrong because it does not pay attention to crystal structure.

D + P law holds for gases. For the alleged electron gas it does not work simply because it

does not exist!

Concerning specific heats the molar basis has no rationale. If specific heats are regarded with respect to crystal structure, heat capacity must be related to volume:  $C_{vol} = J/cm^3K$

IN the table above this was done. So we obtain  $C_{vol} = 3.43$  for Cu and  $C_{vol} = 1.45$  for Pb. This difference can be explained: bond length is 36 for Cu but 50 for Pb. Pb lattice is wobbly, therefore to produce vibrations of the lattice goes easier than for Cu. Then consider the low melting point of Pb: 327 Celsius, whereas for Cu: 1085 Celsius!

Pay attention to Be,

### Molar heat capacity for ideal gases

One mole of a gas contains  $6,022 \cdot 10^{23}$  molecules:  $N_A = 6,022 \cdot 10^{23} /mol$  ...denotes Avogadro's number. The ideal gas law states:

$$PV = n RT = N_A kT$$

Where  $n$  = number of moles,  $k$  = Boltzmann constant =  $1,381 \cdot 10^{-23} J/K$  and  $R$  = universal gas constant =  $8,3145 J/mol K$ .

According to the kinetic theory of ideal gases the average translational kinetic energy of any kind of atom or molecule per mole is given by  $E_{kin} = 3R/2$ . This value is in good agreement with empirical heat capacities per mole for monatomic gases, see the table below.

Specific heat capacities of gases at 25° C, 1 bar [Paus]

|                 | $c_p$ J/kgK | $C_p$ J/mol K | $C_v$ J/mol K | $C_p - C_v$ |   |
|-----------------|-------------|---------------|---------------|-------------|---|
| He              | 5233        | 20,93         | 12,61         | 8,32        | $C_p \approx C_v + R$<br>$C_v \approx 3R/2 = 12,47 J/mol K$ |
| Ne              | 103         | 20,79         | 12,48         | 8,31        |   |
| Ar              | 523         | 20,91         | 12,48         | 8,43        |   |
| Kr              | 248         | 20,91         | 12,37         | 8,54        |   |
| Xe              | 160         | 20,98         | 12,64         | 8,34        |   |
| H <sub>2</sub>  | 14300       | 28,83         | 20,45         | 8,38        | $C_p \approx C_v + R$<br>$C_v \approx 5R/2 = 20,79 J/mol K$ |
| Cl <sub>2</sub> | 473         | <u>33,56</u>  | <u>24,84</u>  | 8,72        |   |
| N <sub>2</sub>  | 1041        | 29,15         | 20,81         | 8,34        |   |
| O <sub>2</sub>  | 917         | 29,31         | 21,12         | 8,19        |   |

Comment: Paus calculated for the molar heat capacity:  $C_p J/mol K = c_p J/kgK$  times inertial mass of the element or molecule. For example for Kr:  $248 \cdot 83,8 = 20,78 J/mol K$ . This is a flaw, see above. In order to calculate the molar heat capacity the amount of matter must be used. Kr is mixture of isotopes, for example  $^{84}Kr = 57\%$ ,  $^{86}Kr = 17,3\%$ ,  $^{83}Kr = 11,5\%$ ,... One mole Kr is 84,31.  $248 \cdot 84,31 = 20,91 J/mol K$ ! For the other elements in the table the difference is smaller.

The relationship for ideal gases:  $C_p = C_v + R$  is empirically confirmed for both elements and molecules.

The illustrations show the meaning of the formula. If we supply heat to a gas that can expand at a constant pressure then a part of the heat goes to doing external work, namely to elevate the weight. The other part of the heat goes to raising the temperature of the enclosed gas.

If we keep the volume of the gas constant then the entire amount of heat that we supply goes towards raising the temperature of the gas! This is the reason that the molar heat capacity is greater if the gas was held at a constant pressure than if the gas is forced to remain at a constant volume. Therefore we have a molar heat capacity at constant pressure:  $C_p$  and a molar heat capacity at constant volume  $C_v$  and  $C_p > C_v$ .

For monoatomic gases the molar heat capacities are nearly the same, but there are significant different values for diatomic gases.

How can we interpret this behaviour? Obviously heat is not only stored in the translational and rotational motion but is also stored as potential energy in the elastic bonds of the molecule. For diatomic gases this potential energy is comparatively small, but for metals it is the main part of energy.