

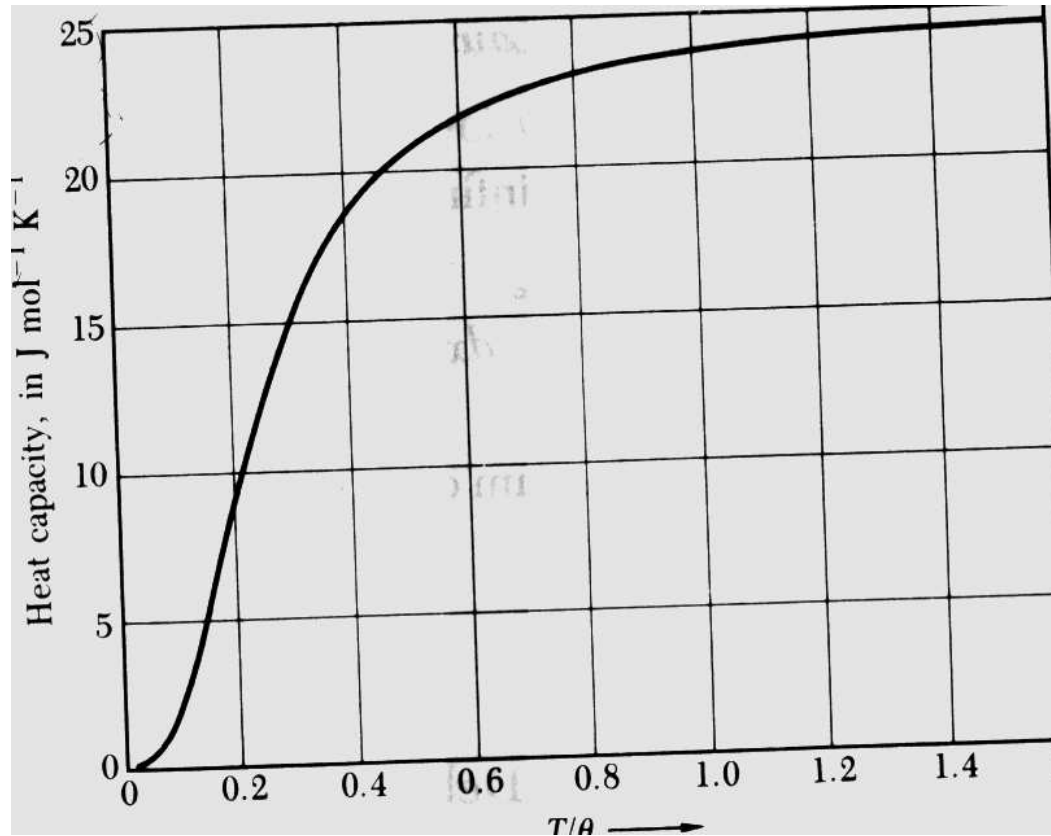


The Need for Quantum Mechanics in Materials Science



Some Experimental Facts Regarding Metals

● Dulong-Petit Law



(Kittel)

- High-Temperature Molar Specific Heat = $3R$
- Atoms - Classical Oscillators



Some Experimental Facts Regarding Metals

- **Wiedemann-Franz Law:** Ratio of thermal (κ) to electrical conductivities (σ) depends linearly on T

$$\kappa/\sigma = (Const)T, \quad (Const) \approx 2.3 \times 10^{-8} \text{ watt-ohm/K}^2$$

EXPERIMENTAL THERMAL CONDUCTIVITIES AND LORENZ NUMBERS OF SELECTED METALS

ELEMENT	273 K		373 K	
	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K ²)	κ (watt/cm-K)	$\kappa/\sigma T$ (watt-ohm/K ²)
Li	0.71	2.22×10^{-8}	0.73	2.43×10^{-8}
Na	1.38	2.12		
K	1.0	2.23		
Rb	0.6	2.42		
Cu	3.85	2.20	3.82	2.29
Ag	4.18	2.31	4.17	2.38
Au	3.1	2.32	3.1	2.36
Be	2.3	2.36	1.7	2.42
Mg	1.5	2.14	1.5	2.25
Nb	0.52	2.90	0.54	2.78
Fe	0.80	2.61	0.73	2.88
Zn	1.13	2.28	1.1	2.30
Cd	1.0	2.49	1.0	
Al	2.38	2.14	2.30	2.19
In	0.88	2.58	0.80	2.60
Tl	0.5	2.75	0.45	2.75
Sn	0.64	2.48	0.60	2.54
Pb	0.38	2.64	0.35	2.53
Bi	0.09	3.53	0.08	3.35
Sb	0.18	2.57	0.17	2.69

(Ashcroft-Mermin)



Some Basics

- Electron charge (e), mass(m), number density(n)
- Newtons' Law $\frac{dp}{dt} = F$ (p –momentum, F –force, t –time)
- Force on a charged particle (q), ($q = -e$ for electron, E, B –electric and magnetic fields)

$$F = q(E + \frac{p}{m} \times B)$$

- Current density $j = -en\frac{p}{m}$
- Conductivities:

$$j = \sigma E \text{ (Electrical),} \quad q = -\kappa \nabla T \text{ (Thermal)}$$



Drudé Theory

- Early 19th century
- Electrons treated as classical particles
- Electrons collide with atoms (and other electrons)
- About 10^{23} electrons (How to do this???)
- What do you expect?



Drudé Model

- How to handle all the electrons?
- Relaxation time approximation:
 τ – time in which an electron will definitely undergo a collision
- Drudé Equation

$$p(t + dt) = \underbrace{\left(1 - \frac{dt}{\tau}\right)}_{\text{prob. no coll.}} (p(t) + F dt)$$

$$\Rightarrow \frac{dp}{dt} = -\frac{p}{\tau} + F$$



Drudé Model

- Over a long time t_l , electrons attain drift velocity and do not accelerate
- Thus,

$$\frac{1}{t_l} \int_0^{t_l} \frac{dp}{dt} dt = 0$$

$$\frac{1}{t_l} \int_0^{t_l} p dt = p_d$$

- Drudé Equation gives drift velocity:

$$p_d = \tau F$$
$$\implies v_d = \frac{\tau}{m} F \quad (\text{drift velocity})$$



Drudé Model

- Drift velocity in an electric field ($F = -eE$)

$$\mathbf{v}_d = -\frac{\tau e}{m} \mathbf{E}$$

- Current density

$$\mathbf{j} = -ne\mathbf{v}_d = \frac{ne^2\tau}{m} \mathbf{E}$$

- Electrical conductivity

$$\sigma = \frac{ne^2\tau}{m}$$



So What?

- The theory has a parameter τ
- How to calculate τ ?
- Well, we don't know yet!
- And...so, what?
- Calculate relaxation times from conductivity measurements
- What do you think it will be?



Relaxation Times

● Calculated relaxation times

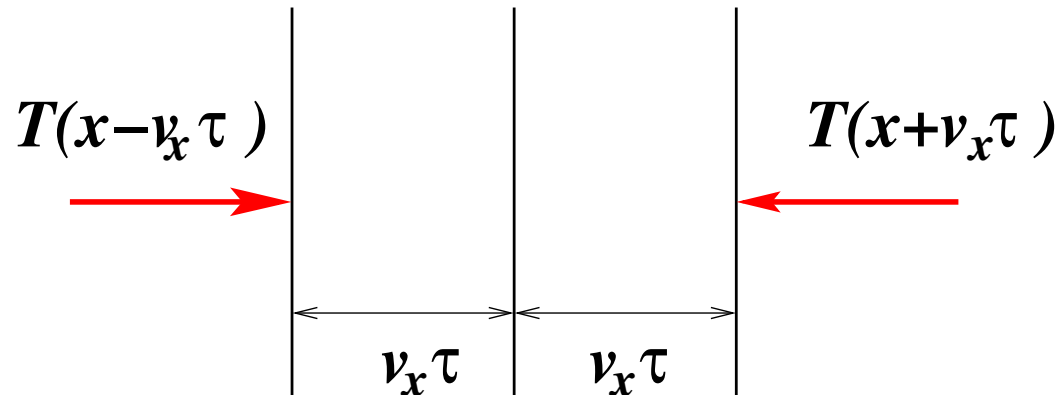
DRUDE RELAXATION TIMES IN UNITS OF 10^{-14} SECOND ^a			
ELEMENT	77 K	273 K	373 K
Li	7.3	0.88	0.61
Na	17	3.2	
K	18	4.1	
Rb	14	2.8	
Cs	8.6	2.1	
Cu	21	2.7	1.9
Ag	20	4.0	2.8
Au	12	3.0	2.1
Be		0.51	0.27
Mg	6.7	1.1	0.74
Ca		2.2	1.5
Sr	1.4	0.44	
Ba	0.66	0.19	
Nb	2.1	0.42	0.33
Fe	3.2	0.24	0.14
Zn	2.4	0.49	0.34
Cd	2.4	0.56	
Hg	0.71		
Al	6.5	0.80	0.55
Ga	0.84	0.17	
In	1.7	0.38	0.25
Tl	0.91	0.22	0.15
Sn	1.1	0.23	0.15
Pb	0.57	0.14	0.099
Bi	0.072	0.023	0.016
Sb	0.27	0.055	0.036

(Ashcroft-Mermin)



Thermal Conductivity

- Energy of an electron at temperature T , $E[T] = \frac{3}{2}k_B T$



- A (one-D) body with a temperature gradient
- Magnitude of velocity (speed) in x direction $= v_x$
- Heat flux from left to right $= \frac{n}{2} v_x E[T(x - v_x \tau)]$
- Heat flux from right to left $= \frac{n}{2} v_x E[T(x + v_x \tau)]$



Thermal Conductivity contd.

- Net heat flux towards positive x axis

$$\begin{aligned} \mathbf{q} &= \frac{n}{2} v_x (E[T(x - v_x \tau)] - E[T(x + v_x \tau)]) = n v_x \frac{\partial E}{\partial T} \left(-\frac{\partial T}{\partial x} \right) \\ &= -n \underbrace{v_x^2}_{\frac{k_B T}{m}} \underbrace{\frac{\partial E}{\partial T}}_{\frac{3}{2} k_B} \frac{\partial T}{\partial x} = - \left(\frac{3 n k_B^2 \tau T}{2 m} \right) \frac{\partial T}{\partial x} \end{aligned}$$

- Thermal conductivity:

$$\kappa = \frac{3 n k_B^2 T \tau}{2 m}$$



And now, Wiedemann-Franz!

- Ratio of thermal to electrical conductivity

$$\frac{\kappa}{\sigma} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 T$$

- It is linear in T !
- It is independent of the metal!
- What about the constant (Lorentz number)?

$$\frac{3}{2} \left(\frac{k_B}{e} \right)^2 = 1.11 \times 10^{-8} \text{ watt-ohm/K}^2$$

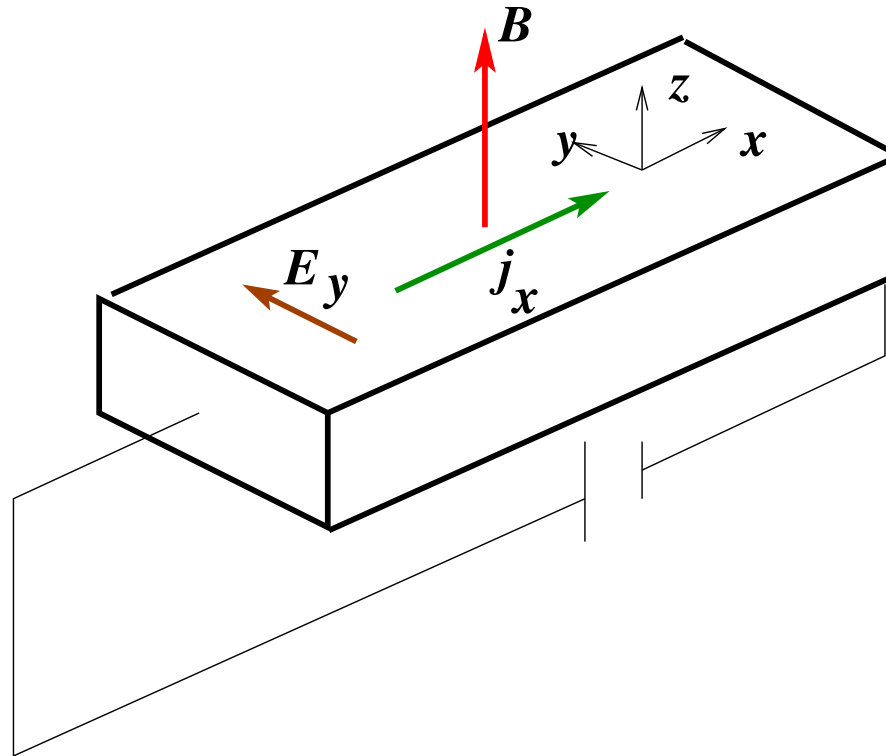
- Expt. value $\approx 2.3 \times 10^{-8} \text{ watt-ohm/K}^2$! Celebrations!



There is just one more thing...

- Dulong-Petit say specific heat is $3R$
- One mole of univalent metal contains one mole of ions and one mole of electrons
- Ionic specific heat = $3R$
- Electronic specific heat = $\frac{3}{2}R$ (ideal gas)
- Total specific heat = $\frac{9}{2}R$
- $\frac{9}{2} \neq 3$ for usual values of 2, 3, 9!
- Ok, turn the music down!

Hall Effect



- Electric field applied in the x direction – current flows j_x
- Magnetic field B applied in the z direction
- An electric field E_y develops in the y -direction



Hall Effect contd.

- Hall coefficient

$$R_H = \frac{E_y}{j_x B}$$

- Drudé value of Hall coefficient

$$R_H^D = -\frac{1}{ne}$$

(prove this!)

- Independent of relaxation time!



What about experiments?

- Ratio of theoretical and experimental Hall coefficients

HALL COEFFICIENTS OF SELECTED ELEMENTS
IN MODERATE TO HIGH FIELDS^a

METAL	VALENCE	$-1/R_H ne$
Li	1	0.8
Na	1	1.2
K	1	1.1
Rb	1	1.0
Cs	1	0.9
Cu	1	1.5
Ag	1	1.3
Au	1	1.5
Be	2	-0.2
Mg	2	-0.4
In	3	-0.3
Al	3	-0.3

(Ashcroft-Mermin)

- Ok for some metals, but suggests that electrons are positively charged in some metals! Oh, God!
- Stop the party!



Conclusions...and then...

- Classical theory is able to explain Wiedemann-Franz (Success!)
- Fails with specific heat (Ok, lets see!)
- Fails miserably with Hall coefficients (Surprise!)
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- Well, we DO NEED Quantum Mechanics!