Cryogenic Properties of Materials

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Goals

- Describe the issues associated with use of materials at cryogenic temperatures
- List suitable and unsuitable materials for use in cryogenic systems
- Give the physical explanation behind the variation of some material properties with temperature
- Provide pointers to material properties

Issues with Materials at Cryogenic Temperatures

- Material properties change significantly with temperature. These changes must be allowed for in the design.
- Many materials are unsuitable for cryogenic use.
- Material selection must always be done carefully. Testing may be required.

Material Selection

- Some suitable materials for cryogenic use include:
  - Austenitic stainless steels e.g. 304, 304L, 316, 321
  - Aluminum alloys e.g. 6061, 6063, 1100
  - Copper e.g. OFHC, ETP and phosphorous deoxidized
  - Brass
  - Fiber reinforced plastics such as G –10 and G –11
  - Niobium & Titanium (frequently used in superconducting RF systems)
    - But becomes brittle at cryogenic temperatures
  - Invar (Ni /Fe alloy) useful in making washers due to its lower coefficient of expansion
  - Indium (used as an O ring material)
  - Kapton and Mylar (used in Multilayer Insulation and as electrical insulation
  - Quartz (used in windows)

Material Selection

- Unsuitable materials include:
  - Martensitic stainless steels Undergoes ductile to brittle transition when cooled down.
  - Cast Iron – also becomes brittle
  - Carbon steels – also becomes brittle. Sometimes used in 300 K vacuum vessels but care must be taken that breaks in cryogenic lines do not cause the vacuum vessels to cool down and fail.
  - Rubber, Teflon and most plastics (important exceptions are Kel-F and UHMW used as seats in cryogenic valves)

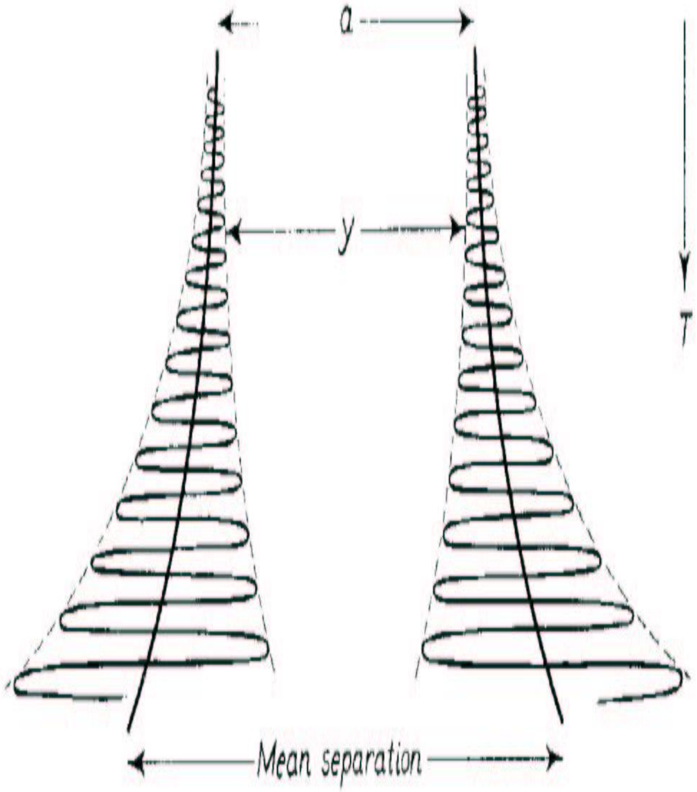
Thermal Expansivity

- Large amounts of contraction can occur when materials are cooled to cryogenic temperatures.
- Points to consider:
  - Impact on alignment
  - Development of interferences or gaps due to dissimilar materials
  - Increased strain and possible failure
  - Impact on wiring
  - Most contraction occurs above 77 K

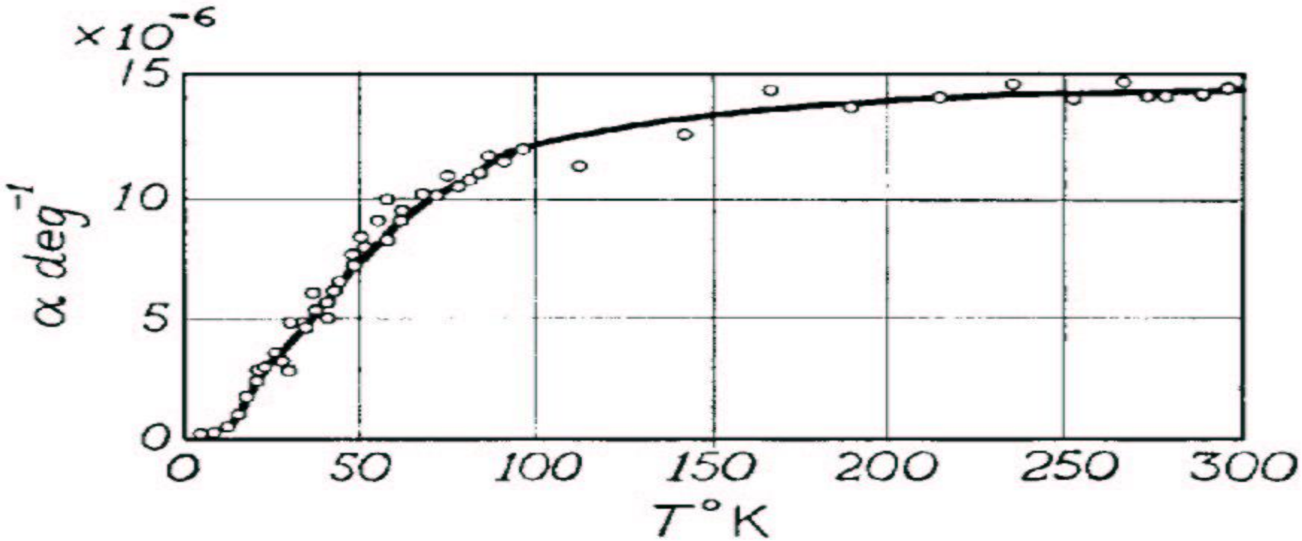
Thermal Expansivity

$\alpha = 1/L \, (\delta L/\delta T)$

Results from anharmonic component in the potential of the lattice vibration



Thermal Expansivity



- α goes to 0 at 0 slope as T approaches 0 K
- α is T independent at higher temperatures
- For practical work the integral thermal contraction is more useful

Integral Thermal Contraction

Material	$\Delta L / L$ (300 – 100)	$\Delta L / L$ (100 – 4)
Stainless Steel	296×10^{-5}	35×10^{-5}
Copper	326×10^{-5}	44×10^{-5}
Aluminum	415×10^{-5}	47×10^{-5}
Iron	198×10^{-5}	18×10^{-5}
Invar	40×10^{-5}	-
Brass	340×10^{-5}	57×10^{-5}
Epoxy/ Fiberglass	279×10^{-5}	47×10^{-5}
Titanium	134×10^{-5}	17×10^{-5}

Heat Capacity or Specific Heat of Solids

- $C = dU/dT$ or Q/mDT
- In general, at cryogenic temperatures, C decreases rapidly with decreasing temperature.
- This has 2 important effects:
  - Systems cool down faster as they get colder
  - At cryogenic temperatures, small heat leaks may cause large temperature rises
- Where is the heat stored ?
  - Lattice vibrations
  - Electrons (metals)
- The explanation of the temperature dependence of the specific heat of solids was an early victory for quantum mechanics

Lattice Contribution

- Dulong Petit Law
- Energy stored in a 3D oscillator = 3NkT = 3RT
- Specific heat = 3R = constant
  - Generally OK for T= 300 K or higher
  - Doesn't take into account quantum mechanics

Einstein & Debye Theories

- Einstein explains that atoms may only vibrate at quantized amplitudes. Thus:

$$U = \left(n + \tfrac{1}{2}\right) h\nu$$

- This results in a temperature dependent specific heat
- Debye theory accounts for the fact that atoms in a solid aren't independent & only certain frequencies are possible

Debye Theory

- The Debye theory gives the lattice specific heat of solids as:

$$C = 9R\left(\frac{T}{\Theta}\right)^3 \int_0^{x_{\max}} \frac{e^x x^4}{\left(e^x - 1\right)^2} dx$$

- As T ~ 300 K C~ 3R (Dulong Petit)
- At T< θ/10 C varies as T ^{3}

Impact of Electrons in Metals on Specific Heat

- Thermal energy is also stored in the free electrons in the metal
- Quantum theory shows that electrons in a metal can only have certain well defined energies
- Only a small fraction of the total electrons can be excited to higher states & participate in the specific heat
- It can be shown that $C_e = \gamma T$

Specific Heat of Solids

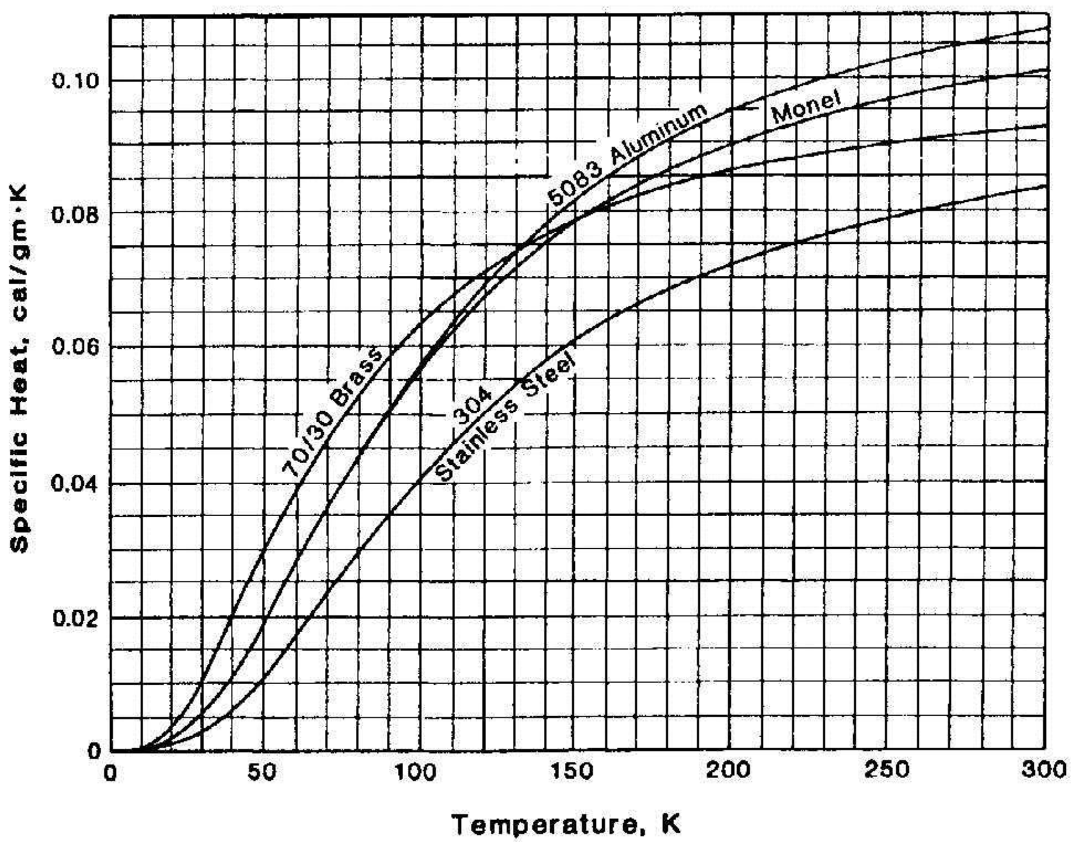
- The total specific heat of metals at <u>low temperatures</u> may be written:

$C = AT^3 + BT$ - the contribution of the electrons is only important at < 4 K

- Paramagnetic materials and other special materials have anomalous specific heats -always double check

Specific Heat of Common Metals

Transport Properties of Solids



Thermal Conductivity

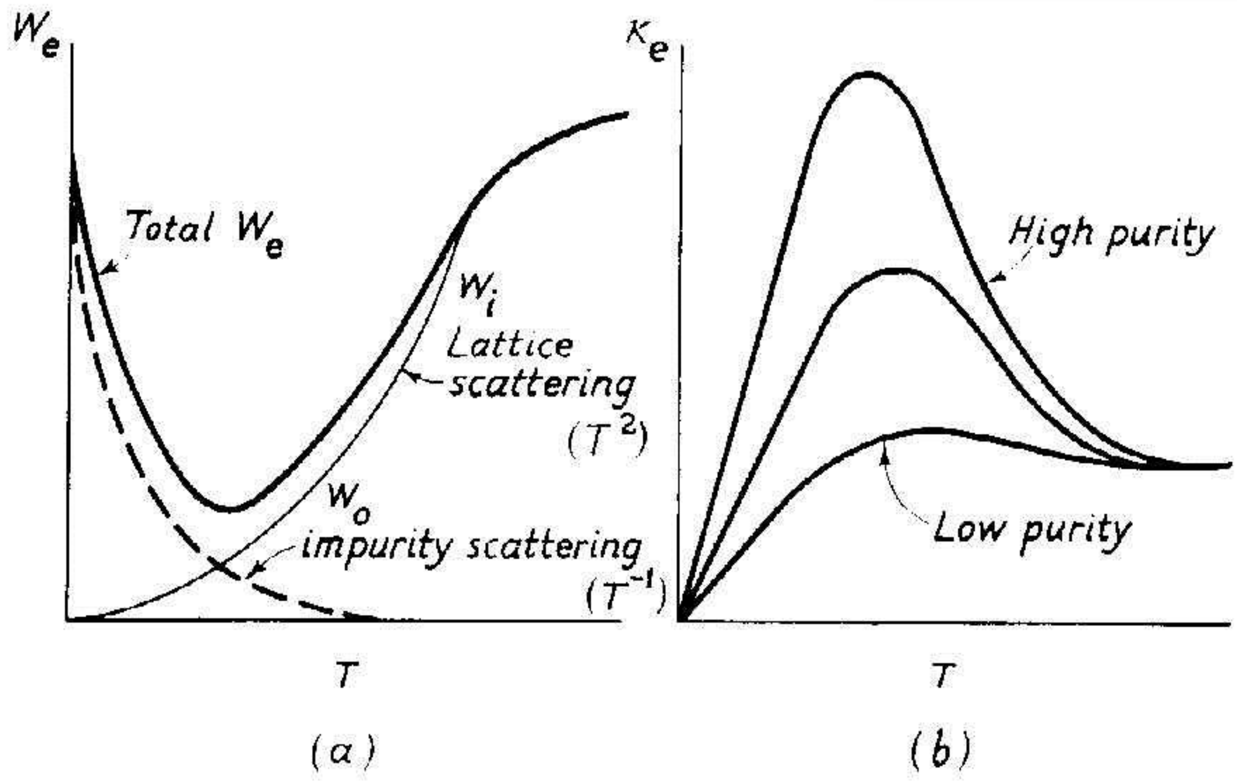
- $Q = -K(T)\, A(x)\, dT/dx$
- K Varies significantly with temperature
- Temperature dependence must be considered when calculating heat transfer rates

Thermal Conductivity of Metals

- Energy is transferred both by lattice vibrations (phonons) and conduction electrons
- In "reasonably pure" metals the contribution of the conduction electrons dominates
- There are 2 scattering mechanisms for the conduction electrons:
  - Scattering off impurities ($W_o = \beta/T$)
  - Scattering off phonons ($W_i = \alpha T^2$)
- The total electronic resistivity has the form :

$$W_e = \alpha T^2 + \beta/T$$

Thermal Conductivity of Metals Due to Electrons



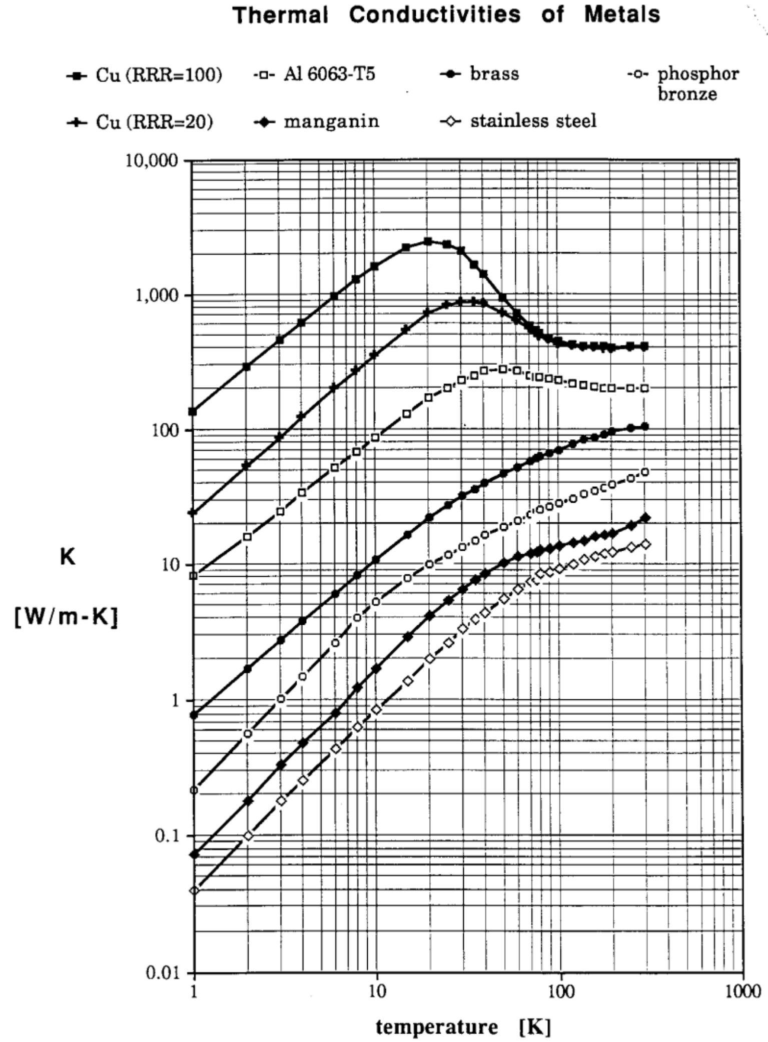
From Low Temperature Solid State Physics –Rosenburg

- The total electronic resistivity has the form : $W_e = aT^2 + b/T$ K~ 1/We

Heat Conduction by Lattice Vibrations in Metals

- Another mechanism for heat transfer in metals are lattice vibrations or phonons
- The main resistance to this type of heat transfer is scattering of phonons off conduction electrons
- This resistance is given by $W = A/T^2$
- Phonon heat transfer in metals is generally neglected

Thermal Conductivities of Metals



From Lakeshore Cryotronics

Thermal Conductivity Integrals

- The strong temperature dependence of K makes heat transfer calculations difficult
- The solution is frequently to use thermal conductivity integrals
- The heat conduction equation is written as:

$$Q = -G(\theta_2 - \theta_1)$$

Thermal Conductivity Integrals

- G is the geometry factor

$$G = \frac{1}{\int_{x_1}^{x_2} \frac{dx}{A(x)}}$$

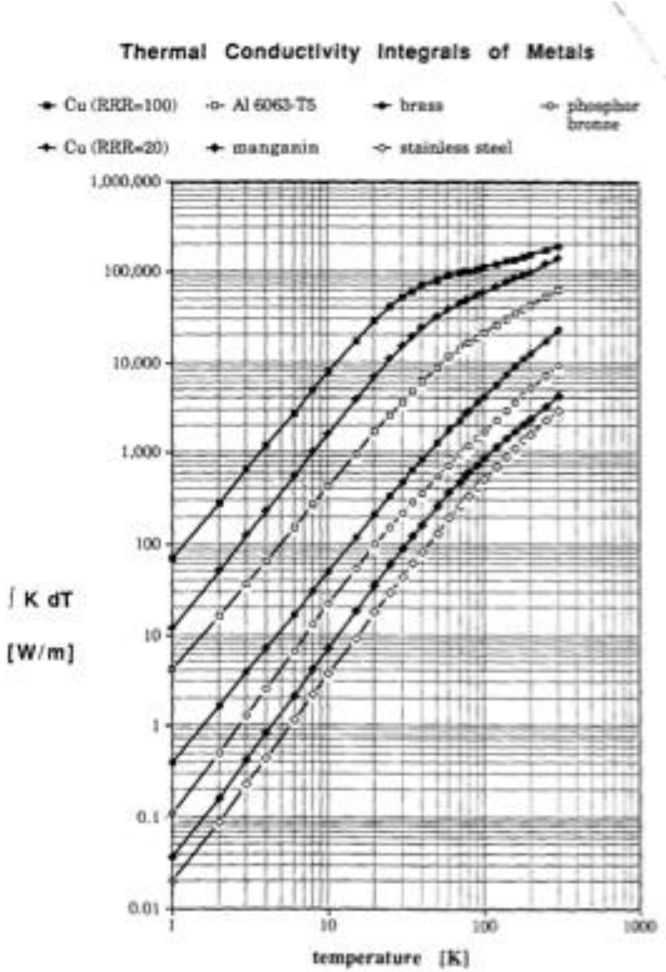
- θ is the thermal conductivity integral

$$\theta_i = \int_{0}^{T_i} K(T)\, dT$$

Thermal Conductivity Integrals

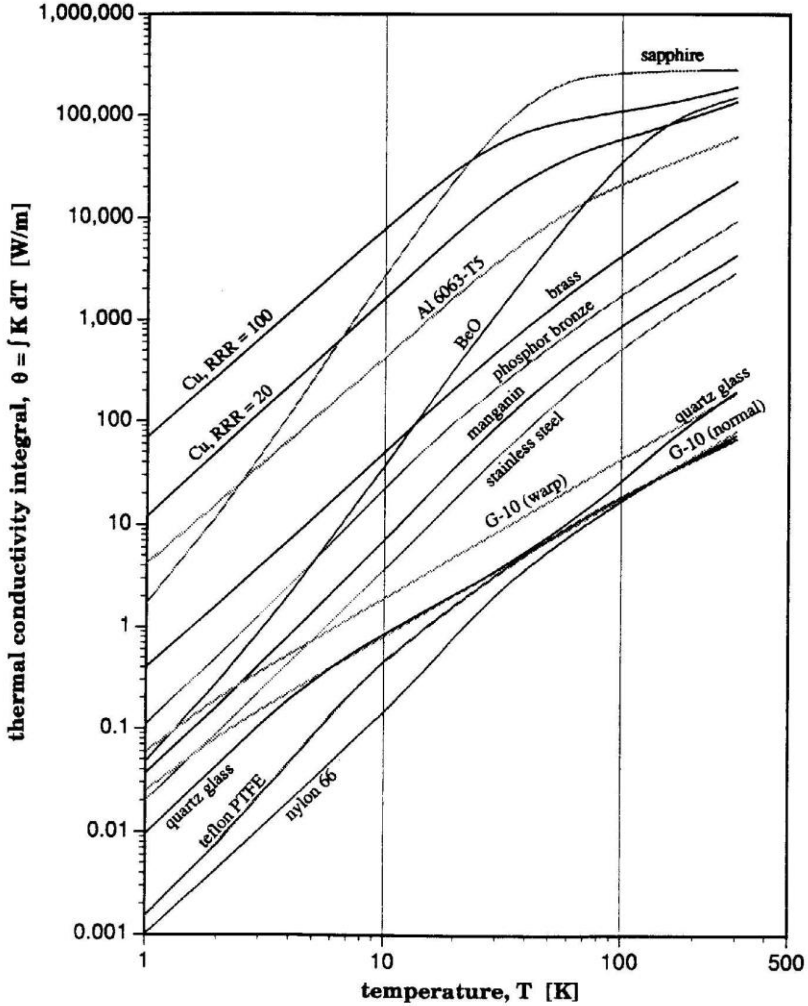
- Advantages:
  - Simple
  - Only end point temperatures are important. (assuming there are no intermediate heat sinks) The actual temperature distribution is not.
  - Thermal conductivity integrals have been calculated for many engineering materials
  - This is quite useful for heat leak calculations

Thermal Conductivity Integrals of Metals



From <u>Handbook of Cryogenic Engineering</u>, J. Weisend II (Ed)

Thermal Conductivity Integrals of Metals & Nonmetals



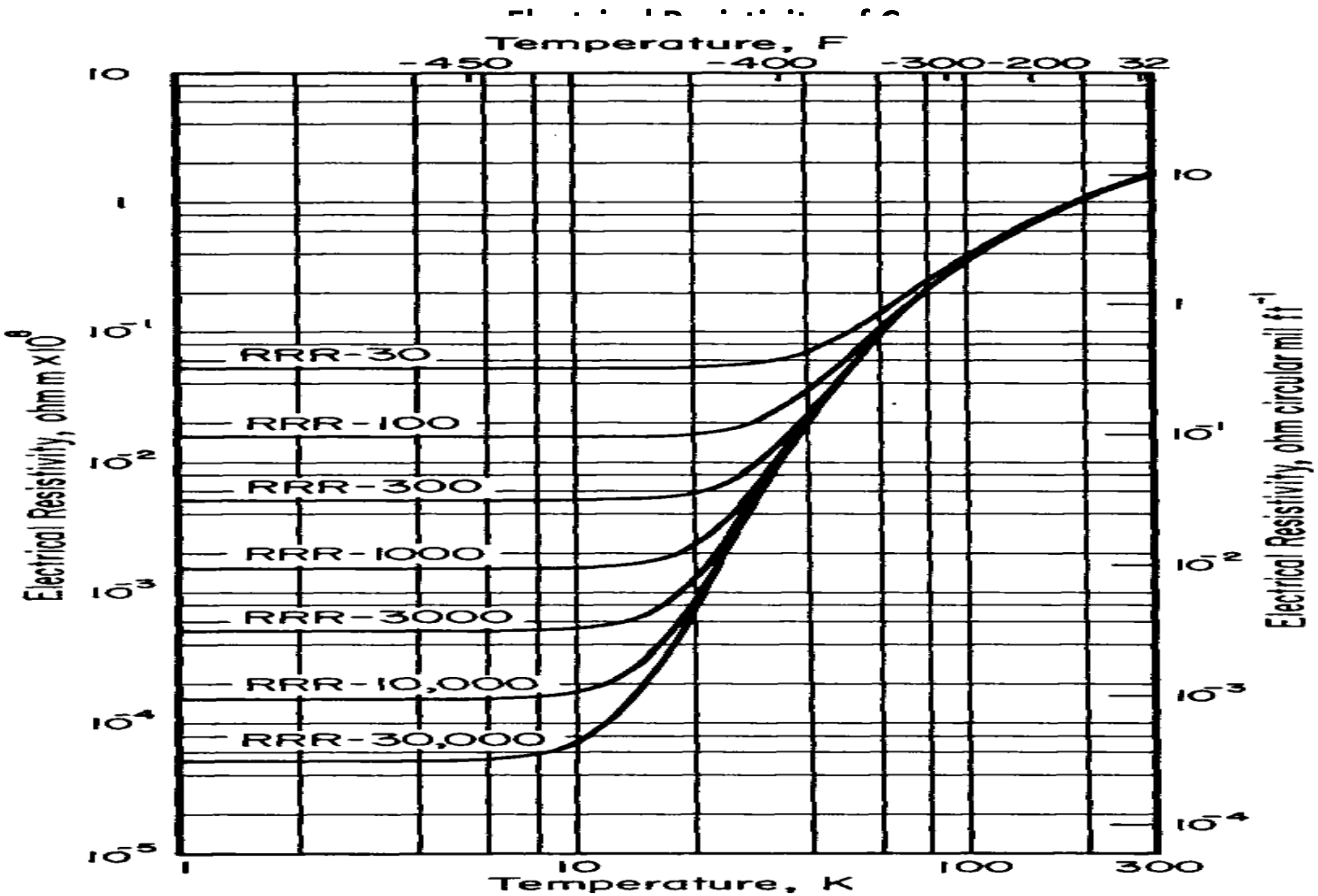
Electrical Resistivity

- Ohm's Law $V=IR$
  - $R=\rho L/A$ where ρ is the electrical resistivity
- Conduction electrons carry the current & there are 2 scattering mechanisms
  - Scattering of electrons off phonons
  - Scattering of electrons off impurities or defects (e.g. dislocations)

Electrical Resistivity of Metals

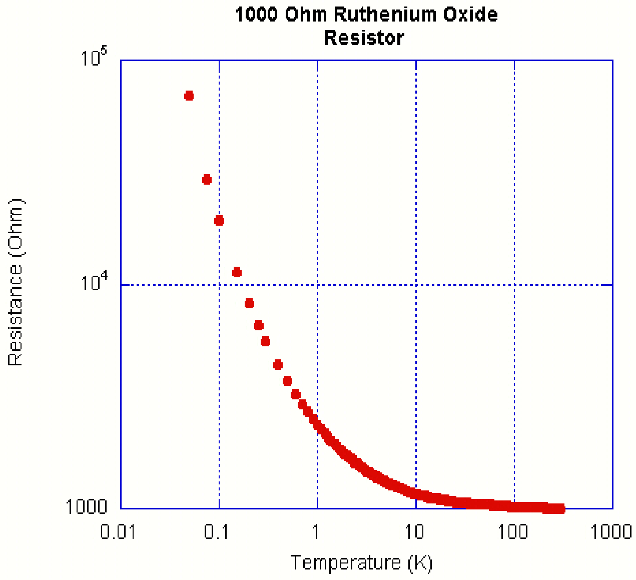
- For T ~ θ phonon scattering dominates
  - ρ is proportional to T
- For T<< θ impurity scattering dominates
  - ρ is constant
- Between these two regions (T~ $\theta/3$)
  - ρ is proportional to T^5 for metals
- RRR = ρ (300 K)/ρ (4.2K) an indication of metal purity

Electrical Resistivity of Copper



Electrical Resistivity of Other Materials

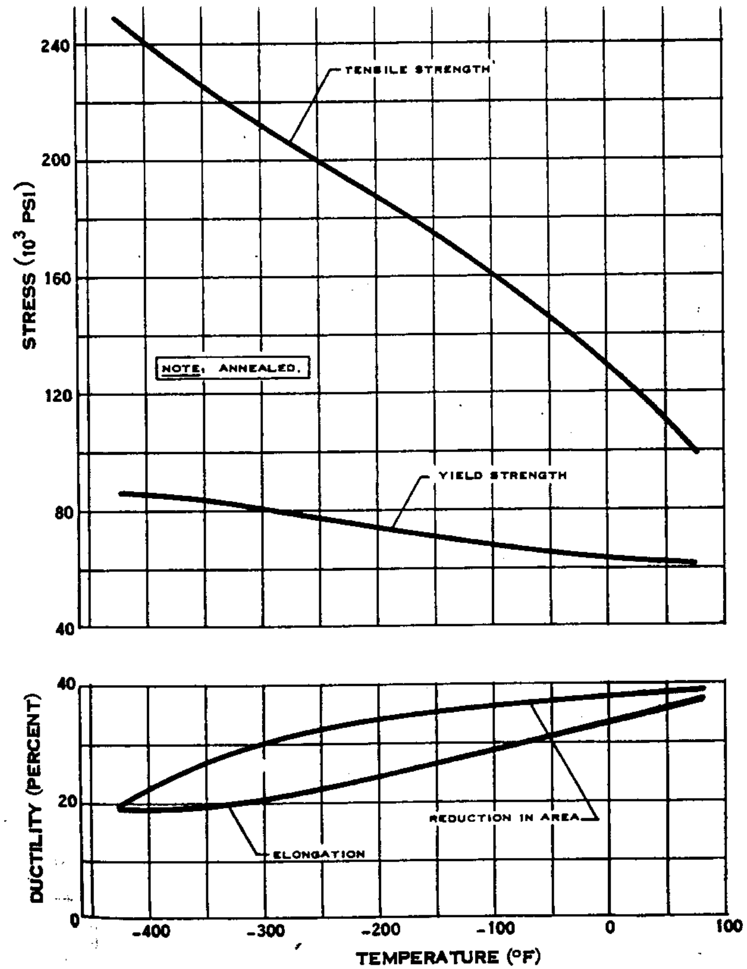
- Amorphous materials & semiconductors have very different resistivity characteristics than metals
- The resistivity of semiconductors is very non linear & typically **increases** with decreasing T due to fewer electrons in the conduction band
- Superconductivity – A later lecture



Material Strength

- Tends to increase at low temperatures (as long as there is no ductile to brittle transition)
- 300 K values are typically used for conservative design. Remember all systems start out at 300 K & may unexpectedly return to 300 K.
- Always look up values or test materials of interest

Typical Properties of 304 Stainless Steel
From Cryogenic Materials Data Handbook (Revised)
Schwartzberg et al (1970)



Sources of Data for the Cryogenic Properties of Material

- "A Reference Guide for Cryogenic Properties of Materials", Weisend, Flynn, Thompson; SLAC-TN-03-023
- Cryogenic Materials Data Handbook: Durham et al. C13.6/3.961 :
- MetalPak: computer code produced by CryoData

http://www.htess.com/software.htm

- CryoComp: computer Code produced by Eckels Engineering

http://www.eckelsengineering.com/

- Proceedings of the International Cryogenic Materials Conferences (ICMC)