

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.

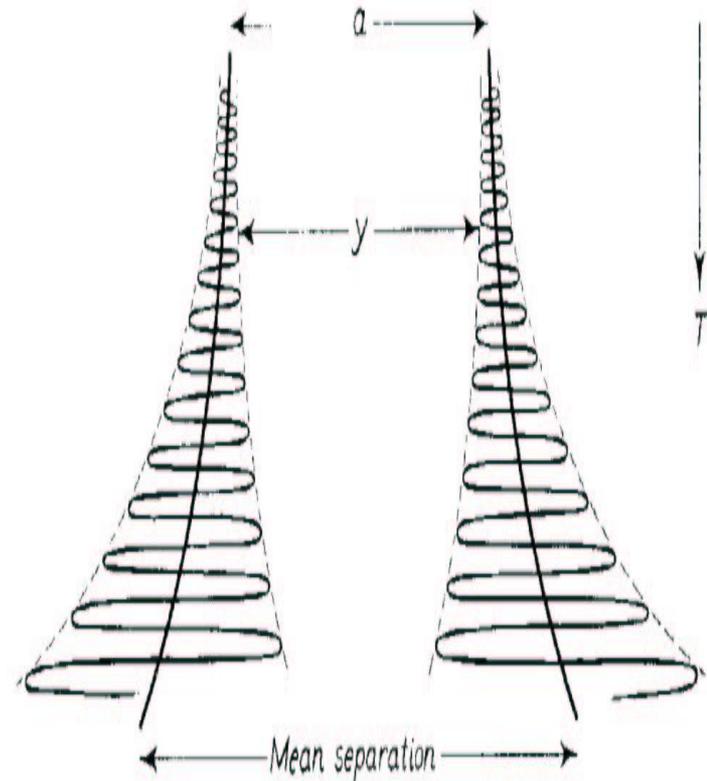
- Some suitable materials for cryogenic use include:
 - Austenitic stainless steels e.g. 304, 304L, 316, 321
 - Aluminum alloys e.g. 6061, 6063, 1100
 - Copper e.g. OFHC, ETP and phosphorous deoxidized
 - Brass
 - Fiber reinforced plastics such as G –10 and G –11
 - Niobium & Titanium (frequently used 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)

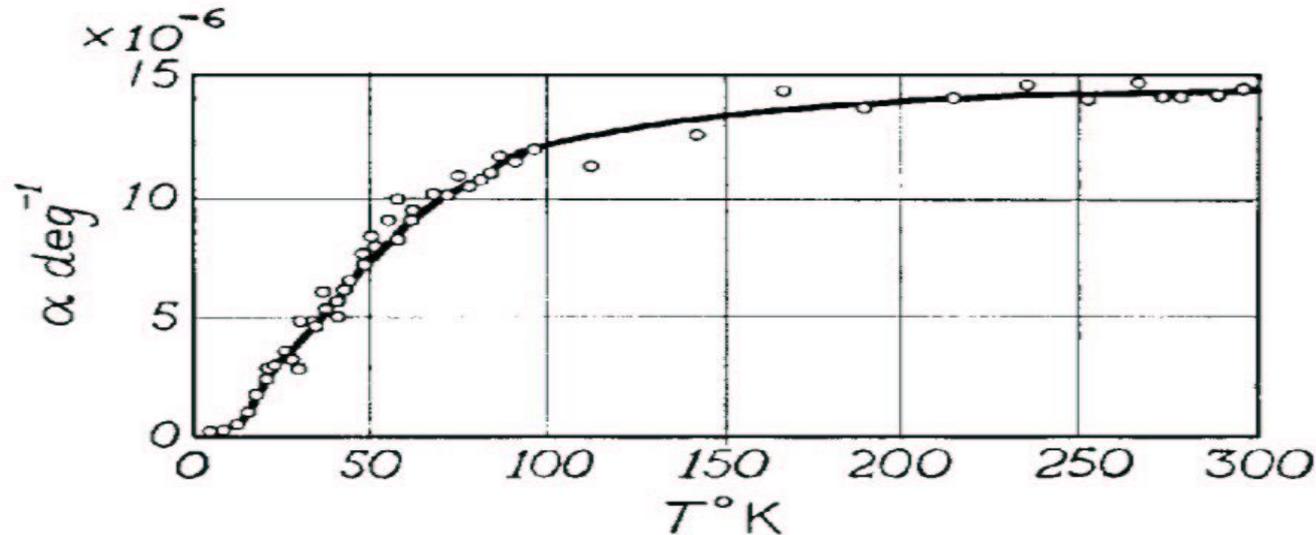
- Unsuitable materials include:
 - Martensitic stainless steels Undergoes ductile to brittle transition when cooled down.
 - Cast Iron – also becomes brittle
 - Carbon steels – also becomes brittle. Sometimes used in 300 K vacuum vessels but care must be taken that breaks in cryogenic lines do not cause 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)

- 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

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

Results from anharmonic component in the potential of the lattice vibration





- 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

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

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

Einstein & Debye Theories

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

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

- 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:

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

- As $T \sim 300 \text{ K}$ $C \sim 3R$ (Dulong Petit)
- At $T < \Theta/10$ C varies as T^3

Impact of Electrons in Metals on Specific Heat

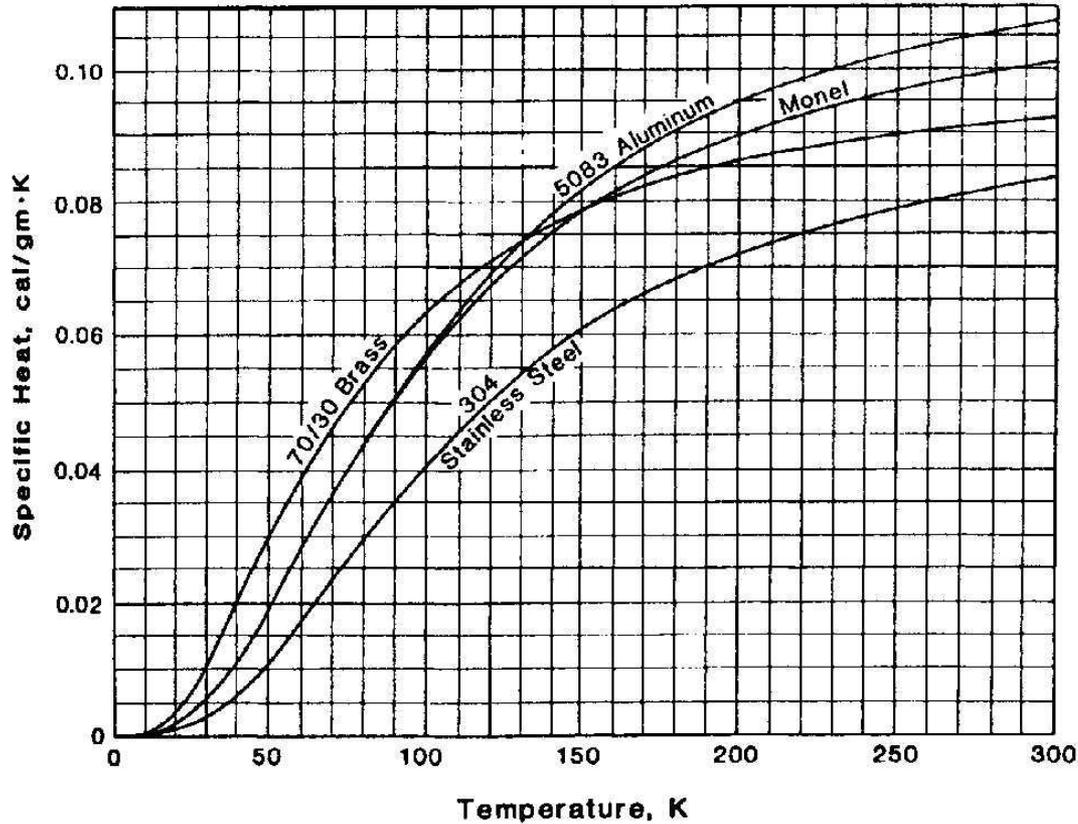
- Thermal energy is also stored in the free electrons in the metal
- Quantum theory shows that electrons in a metal can only have certain well defined energies
- Only a small fraction of the total electrons can be excited to higher states & participate in the specific heat
- It can be shown that $C_e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

- The total specific heat of metals at low temperatures 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

Transport Properties of Solids



Thermal Conductivity

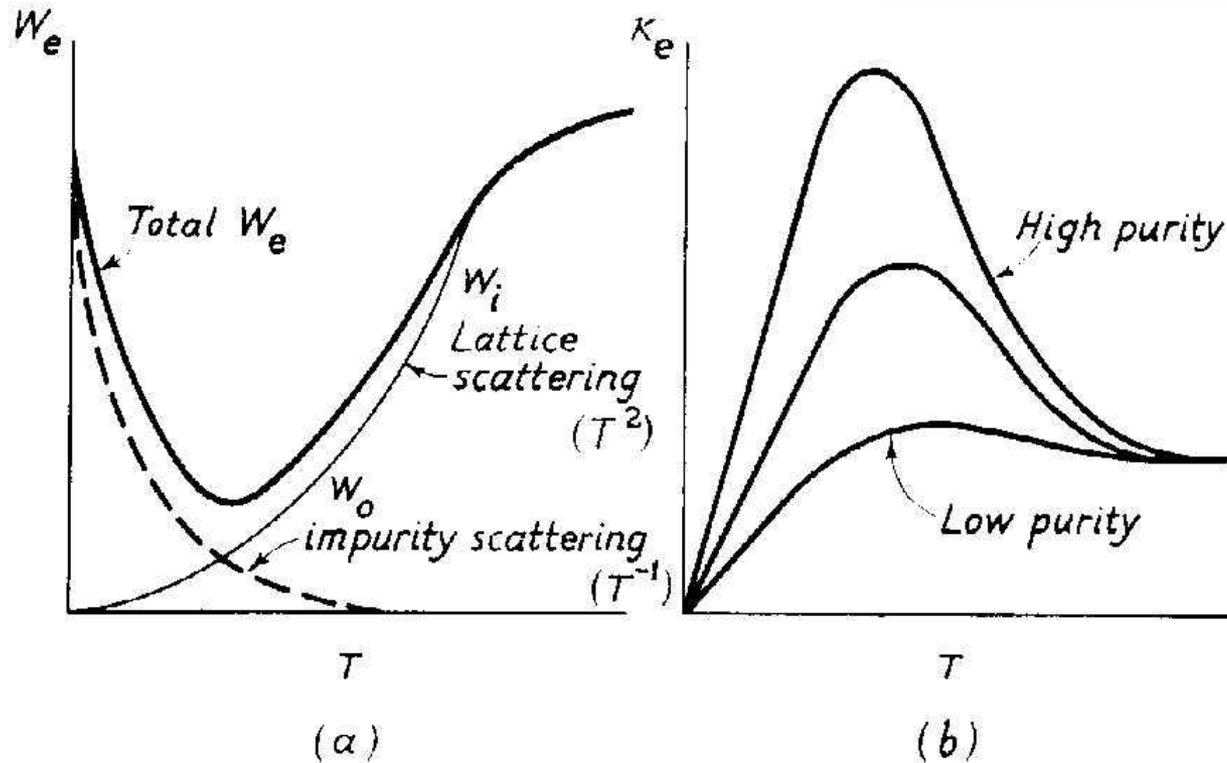
- $Q = -K(T) A(x) dT/dx$
- K Varies significantly with temperature
- Temperature dependence must be considered when calculating heat transfer rates

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

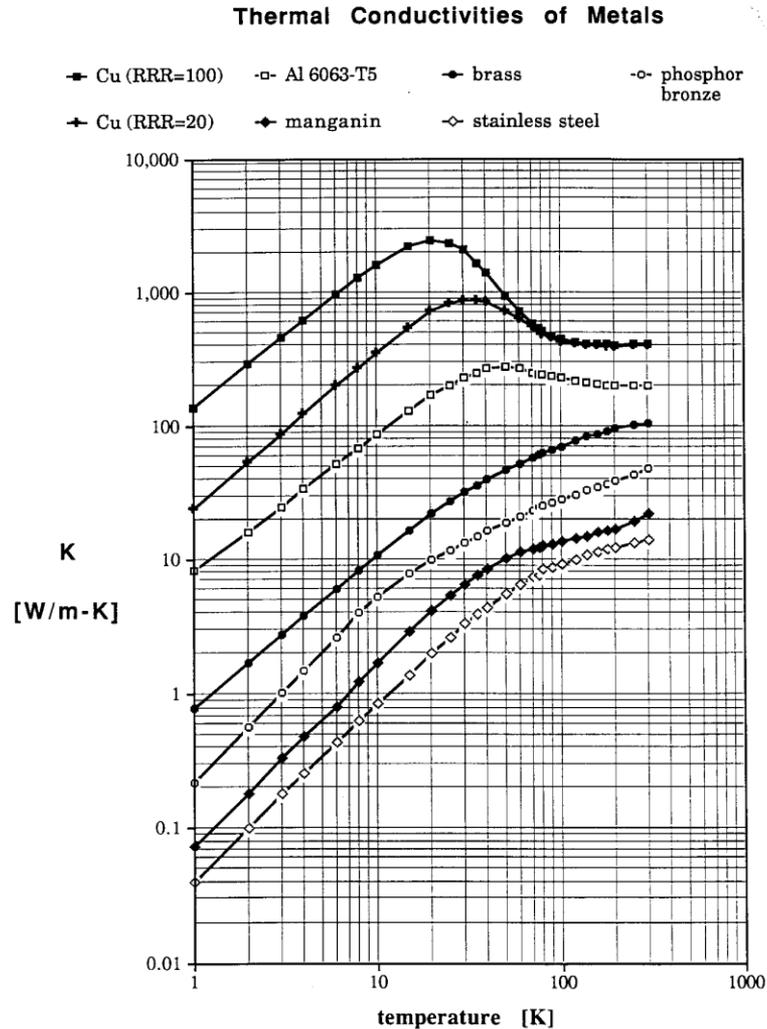


From Low Temperature Solid State Physics –Rosenburg

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

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



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

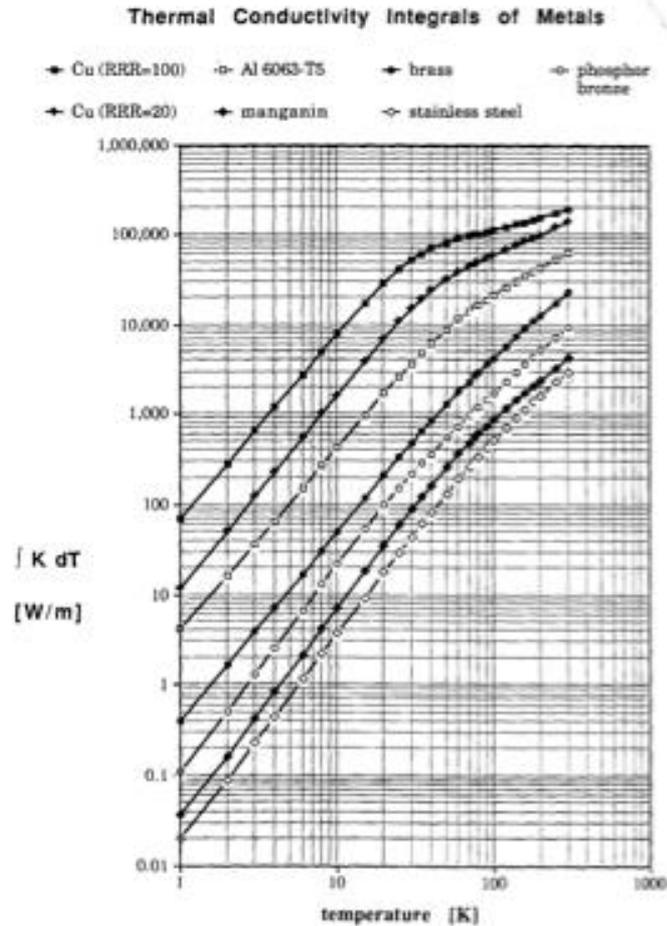
$$\theta_i = \int_0^{T_i} K(T) dT$$

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



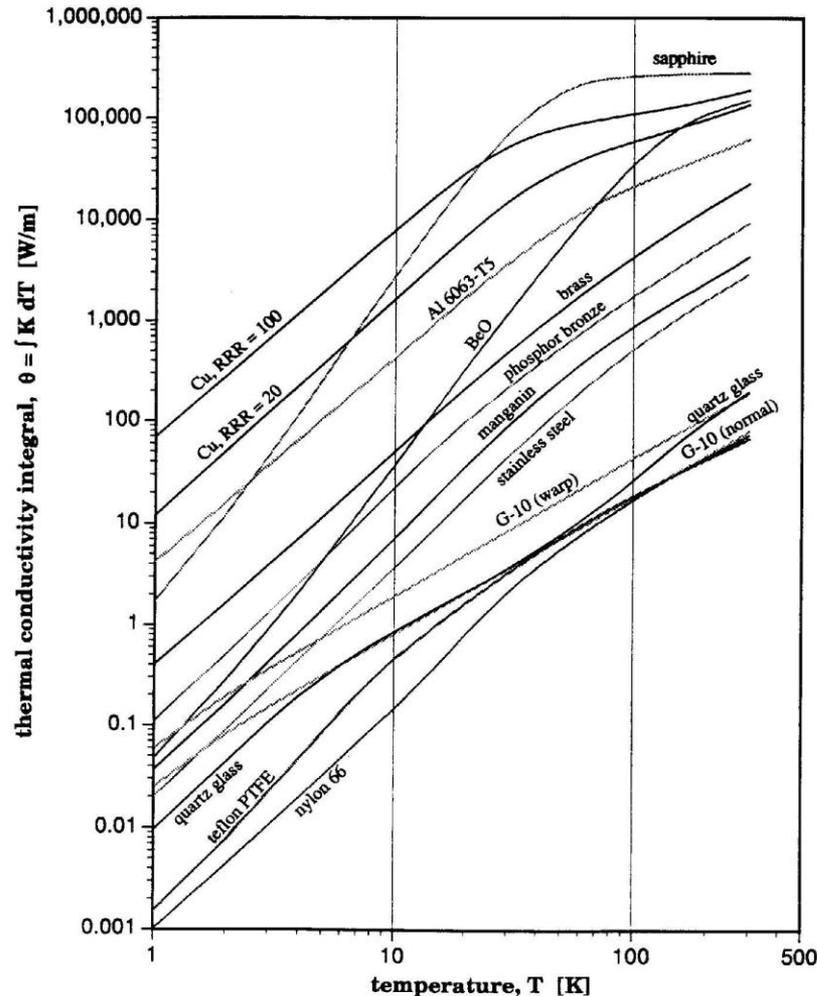
Thermal Conductivity Integrals of Metals



From Handbook of Cryogenic Engineering, J. Weisend II (Ed)



Thermal Conductivity Integrals of Metals & Nonmetals

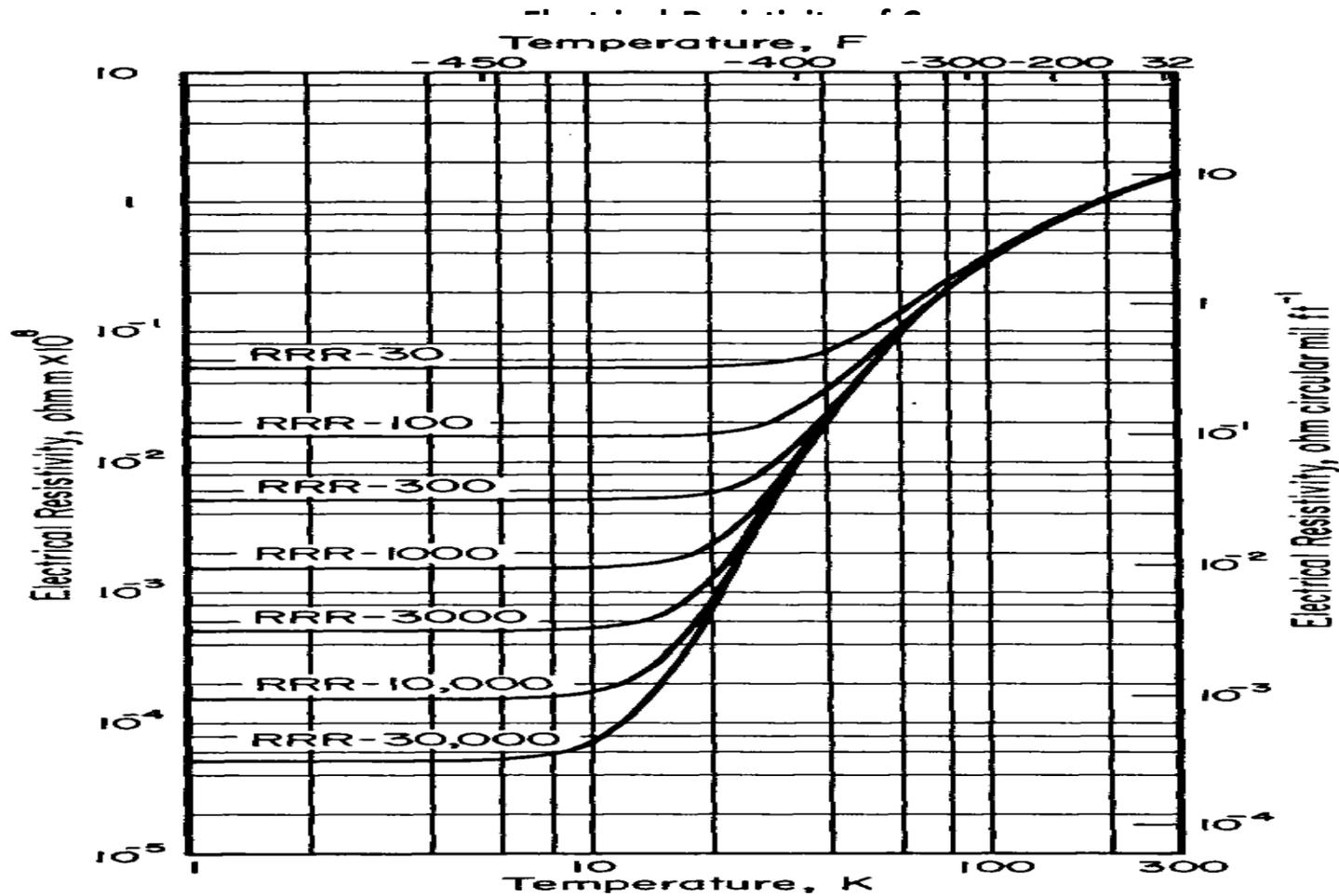


- Ohm's Law $V=IR$
 - $R=\rho L/A$ where ρ is the electrical resistivity
- Conduction electrons carry the current & there are 2 scattering mechanisms
 - Scattering of electrons off phonons
 - Scattering of electrons off impurities or defects (e.g. dislocations)

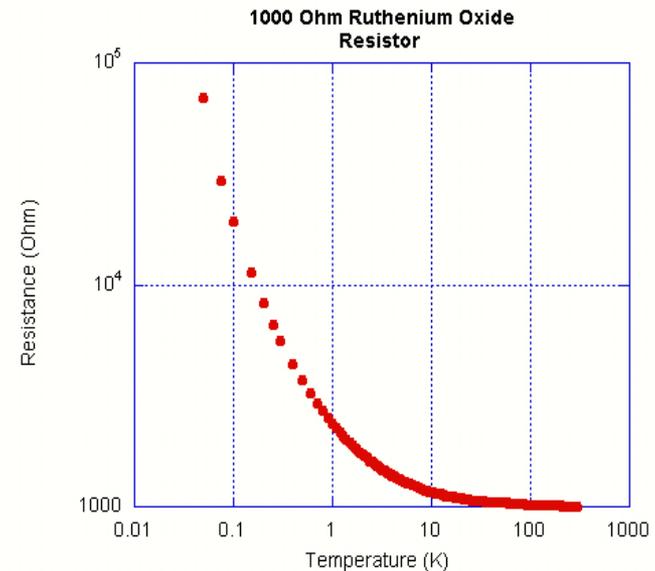
- For $T \sim \theta$ phonon scattering dominates
 - ρ is proportional to T
- For $T \ll \theta$ impurity scattering dominates
 - ρ is constant
- Between these two regions ($T \sim \theta/3$)
 - ρ is proportional to T^5 for metals
- $RRR = \rho(300\text{ K})/\rho(4.2\text{ K})$ an indication of metal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



Electrical Resistivity of Copper



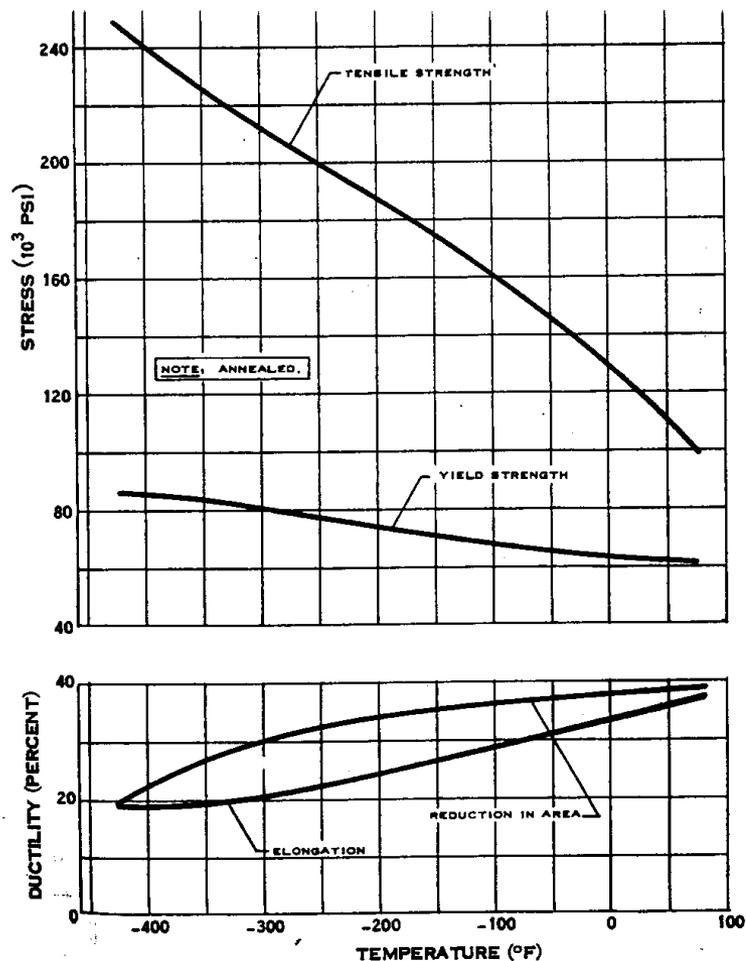
- Amorphous materials & semiconductors have very different resistivity characteristics than metals
- The resistivity of semiconductors is very non linear & typically **increases** with decreasing T due to fewer electrons in the conduction band
- Superconductivity – A later lecture



- 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)



- “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)