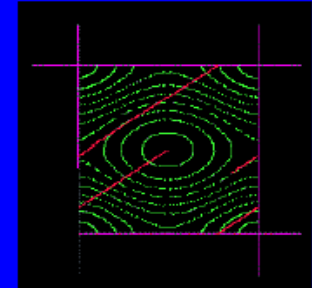
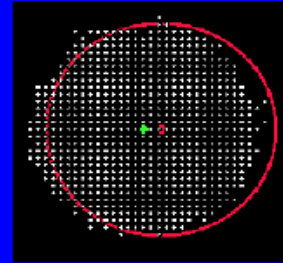
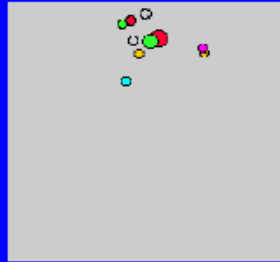
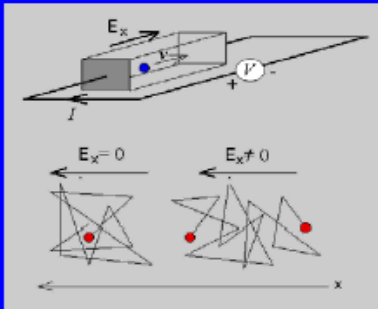


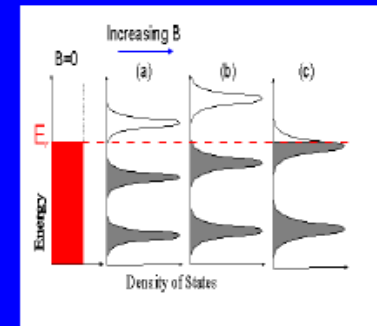
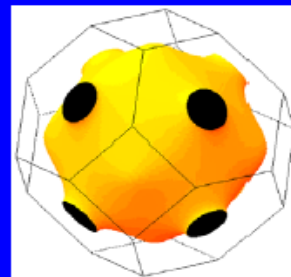
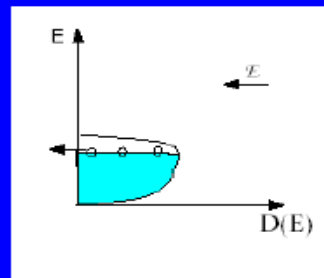
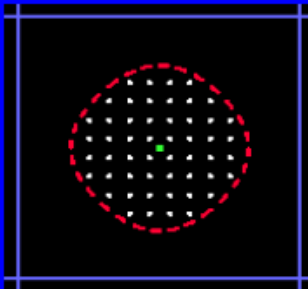
Transport Phenomena in Solids

Motions of electrons and transport phenomena



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

$$\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2} \sum_j \frac{\partial^2 E(\vec{k})}{\partial k_i \partial k_j}$$



Electrical conductivity

- Electrical resistivity due to electron-phonon interaction.
- Bloch-Gruneisen law
- Residual resistivity of metals
- Impurity effect in a metal

Relaxation time approximation:

This is based on the assumption that a nonequilibrium distribution $f(\mathbf{k}, \mathbf{r}, t)$ gradually returns to its equilibrium value within a characteristic time, the relaxation time $\tau(\mathbf{k})$, by the scattering of electrons with the wave vector \mathbf{k} into states \mathbf{k}' , and vice versa.

$$\left(\frac{\partial f}{\partial t}\right)_s = -\frac{f(\vec{k}) - f_0(\vec{k})}{\tau(\vec{k})}$$

The rate of return to equilibrium is proportional to $f(\vec{k}) - f_0(\vec{k})$

The proportionality coefficient

$$1/\tau$$

is a function of \vec{k} only

$$f = f_0 + f_1$$

$$f_1 = e \cdot \tau \cdot E \cdot v \cdot \frac{df_0}{d\varepsilon}$$

Electrical conductivity of metals

For steady state: $\left(\frac{\partial f}{\partial t}\right) = 0$

For a homogeneous Sommerfeld metal: $\nabla_r f = 0$

$$-\frac{e}{\hbar} \vec{E} \cdot \vec{\nabla}_k f = \left(\frac{\partial f}{\partial t}\right)_s$$

$$-\frac{e}{\hbar} \vec{E} \cdot \vec{\nabla}_k f = -\frac{f(\vec{k}) - f_0(\vec{k})}{\tau(\vec{k})}$$

$$\frac{\partial f_0}{\partial k} = \frac{\partial f_0}{\partial \varepsilon} \cdot \frac{\partial \varepsilon}{\partial k}$$

$$\varepsilon = \frac{\hbar^2 k^2}{2m}$$

$$\frac{\partial \varepsilon}{\partial k} = \frac{\hbar^2 k}{m}$$

$$v = \frac{p}{m} = \frac{\hbar k}{m}$$

$$f = f_0 + \frac{\tau(\vec{k}) e E}{\hbar} \cdot \nabla_k f_0$$

Electron-phonon interaction

Reading:

1. Ch. 26, Ashcroft & Mermin
2. Ch. 7, Kittel

Small oscillations

$$\vec{R}_\alpha = \vec{R}_\alpha^0 + \vec{u}_\alpha$$

(See Mizutani)

The ions oscillations create changes in the crystalline periodic potential



Changes in the electron wave functions

Hamiltonian of the solid: electrons and phonons

$$H = H_e + H_{ph} + H_{e-ph} + H_{e-e} + H_{ph-ph}$$

$$H_e = \sum_{\vec{k}, \sigma} \epsilon_{\vec{k}} c_{\vec{k}, \sigma}^+ c_{\vec{k}, \sigma}$$

In harmonic approximation

$$H_{ph-ph} = 0$$

$$H_{ph} = \sum_{\vec{q}, \lambda} \hbar \omega_{\vec{q}, \lambda} a_{\vec{q}, \lambda}^+ c_{\vec{q}, \lambda} c_{\vec{q}, \lambda}$$

Electron-electron interaction



Screening

Electron-phonon interaction

$$H = H_e + H_{ph} + H_{e-ph}^{eff}$$

Fröhlich

$$H_{e-ph}^{eff} = \sum_{\vec{k}, \vec{q}, \sigma} \left\{ A_q^{eff} a_{\vec{q}}^+ c_{\vec{k}+\vec{q}, \sigma}^+ c_{\vec{k}, \sigma} + A_q^{eff*} a_{\vec{q}}^+ c_{\vec{k}-\vec{q}, \sigma}^+ c_{\vec{k}, \sigma} \right\}$$

electron $\vec{k} \rightarrow \vec{k}' = \vec{k} \pm \vec{q}$

emission and absorption of phonons

$$A_q^{eff} = -iDq \left(\frac{\hbar}{2\rho\omega_q} \right) \propto U(q)$$

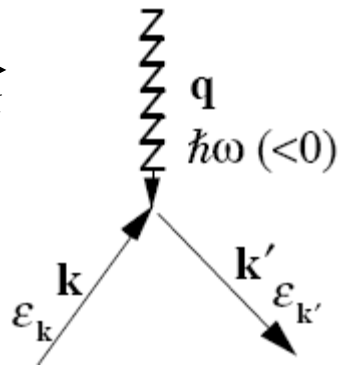
$$D = \frac{2}{3} Z \varepsilon_F^0$$

$$a_{\vec{q}}^+ c_{\vec{k}+\vec{q}, \sigma}^+ c_{\vec{k}, \sigma}$$

- An electron in state \vec{k} disappears

- A phonon in state \vec{q} disappears

- An electron in state $\vec{k}' = \vec{k} + \vec{q}$ appears

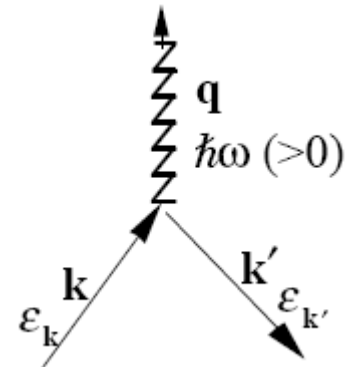


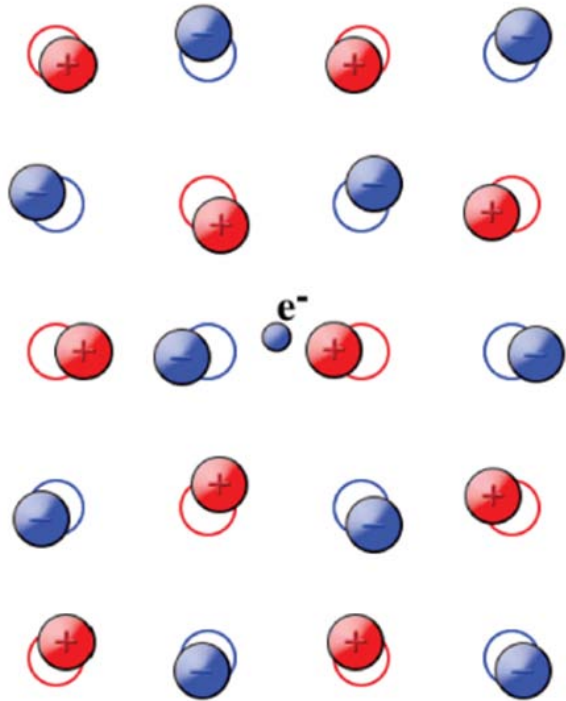
$$a_{\vec{q}}^+ c_{\vec{k}-\vec{q}, \sigma}^+ c_{\vec{k}, \sigma}$$

- An electron in state \vec{k} disappears

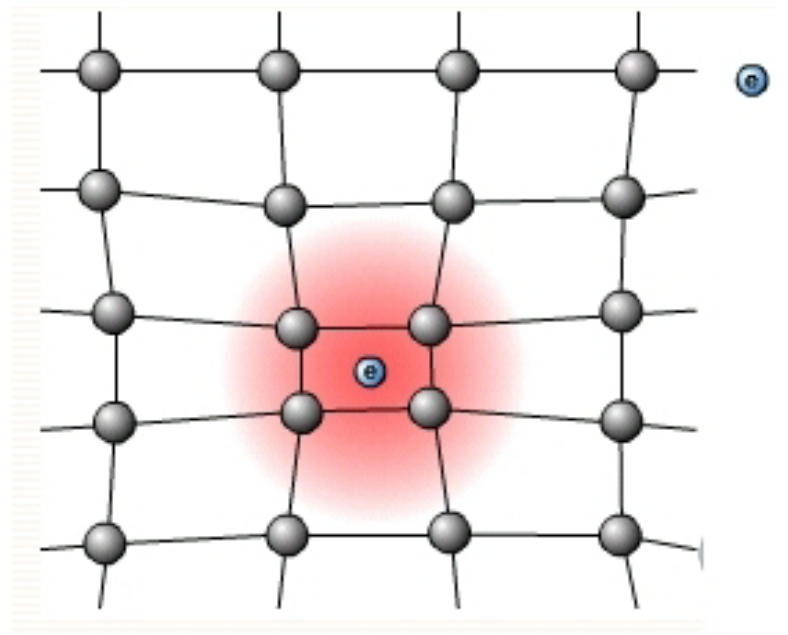
- A phonon in state \vec{q} appears

- An electron in state $\vec{k}' = \vec{k} - \vec{q}$ appears





Solid State Course by Mark Jarrel (Louisiana Univ.),



Electrical resistivity due to electron-phonon interaction

see Mizutani

We presume the electron-phonon interaction is coulombian

The Fourier transform of the interaction potential

$$U(\vec{R}_\alpha) \implies U_{\vec{q}} = \frac{4\pi Ze^2}{\Omega q^2}$$

Ω : volume per atom

DC electrical conductivity due to inelastic electron-phonon interaction

the Boltzmann transport equation for an isotropic metal consisting of only a single element:

$$\left(-\frac{\partial f_0}{\partial \varepsilon} \right) \mathbf{v}_{\mathbf{k}} \cdot (-e)\mathbf{E} = \left(\frac{V}{8\pi^3} \right) \int \{f(\mathbf{k}') [1 - f(\mathbf{k})] - f(\mathbf{k}) [1 - f(\mathbf{k}')] \} Q(\mathbf{k}, \mathbf{k}') d\mathbf{k}'.$$

$$Q(\mathbf{k} \rightarrow \mathbf{k}') = \frac{2\pi}{\hbar} \sum_f \left| \langle \mathbf{k}', f | \sum_{\mathbf{l}} U_p(\mathbf{r} - \mathbf{R}_{\mathbf{l}}) | \mathbf{k}, i \rangle \right|^2 \delta(\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}} + E_f - E_i)$$

$$\left\langle \mathbf{k}', f \left| \sum_{\mathbf{l}} U_p(\mathbf{r} - \mathbf{R}_{\mathbf{l}}) \right| \mathbf{k}, i \right\rangle = \frac{1}{N} \langle f | \sum_{\mathbf{l}} e^{-i\mathbf{K} \cdot \mathbf{R}_{\mathbf{l}}} | i \rangle \cdot U_p(\mathbf{K})$$

where \mathbf{K} is the scattering vector defined as $\mathbf{K} = \mathbf{k}' - \mathbf{k}$.

$$U_p(\mathbf{K}) = (N/V) \int e^{-i\mathbf{K} \cdot \mathbf{r}'} U_p(\mathbf{r}') d\mathbf{r}'$$

$$\left(\frac{\partial f(\mathbf{k})}{\partial t}\right)_{\text{scatter}} = -\left(\frac{2\pi}{N}\right) \int_{-\infty}^{\infty} d\omega \sum_{\mathbf{k}'} \left| U_{\text{p}}(\mathbf{K}) \right|^2 a(\mathbf{K}, \omega) f(\mathbf{k}) [1 - f(\mathbf{k}')] \delta(\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}} + \hbar\omega)$$

$$a(-\mathbf{K}, -\omega) = e^{-\beta\hbar\omega} a(\mathbf{K}, \omega)$$

We get:

$$\left(\frac{\partial f(\mathbf{k})}{\partial t}\right)_{\text{scatter}} = \left(\frac{2\pi}{N}\right) \int_{-\infty}^{\infty} d\omega \sum_{\mathbf{k}'} \left| U_{\text{p}}(\mathbf{K}) \right|^2 a(\mathbf{K}, \omega) \{ e^{-\beta\hbar\omega} f(\mathbf{k}') [1 - f(\mathbf{k})] - f(\mathbf{k}) [1 - f(\mathbf{k}')] \} \delta(\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}} + \hbar\omega).$$

If the relaxation time approximation is employed again, the Boltzmann transport equation is simplified as:

$$\begin{aligned} (-e)(\mathbf{v}_{\mathbf{k}} \cdot \mathbf{E}) \left(-\frac{\partial f_0}{\partial \varepsilon_{\mathbf{k}}} \right) &= \frac{2\pi}{\hbar N} \int_{-\infty}^{\infty} d\omega \sum_{\mathbf{k}'} \left| U_{\text{p}}(\mathbf{K}) \right|^2 a(\mathbf{K}, \omega) \\ &\quad \times (-e) \{ \tau_{\mathbf{k}}(\mathbf{v}_{\mathbf{k}} \cdot \mathbf{E}) - \tau_{\mathbf{k}'}(\mathbf{v}_{\mathbf{k}'} \cdot \mathbf{E}) \} \\ &\quad \times \left(-\frac{\partial f_0}{\partial \varepsilon_{\mathbf{k}}} \right) \delta(\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}} + \hbar\omega) \beta \omega n(\omega), \end{aligned}$$

where

$$n(\omega) = 1/(e^{\beta\hbar\omega} - 1)$$

To simplify further, the relaxation time $\tau_{\mathbf{k}}$ is assumed to be independent of the wave vector \mathbf{k} and is denoted as τ .

Then, the Boltzmann transport equation is reduced to:

$$\frac{1}{\tau} = \left(\frac{2\pi}{N} \right) \int d\omega \sum_{\mathbf{k}'} \left| U_{\mathbf{p}}(\mathbf{K}) \right|^2 a(\mathbf{K}, \omega) (1 - \cos\theta_{\mathbf{k}\mathbf{k}'}) \delta(\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}} + \hbar\omega) \beta \omega n(\omega),$$

If a spherical Fermi surface is assumed for an isotropic metal, the summation over the wave vector \mathbf{k}' can be replaced by the integration over the whole of \mathbf{k}' -space.

$$\rho = \left(\frac{3\pi\Omega_0}{4e^2\hbar v_{\text{F}}^2 k_{\text{F}}^4} \right) \int_0^{2k_{\text{F}}} K^3 \left| U_{\mathbf{p}}(K) \right|^2 dK \int_{-\infty}^{\infty} a(K, \omega) \beta \omega n(\omega) d\omega,$$

$$\rho = \frac{m}{ne^2\tau}.$$

Bloch-Grüneisen law

(See Mizutani)

The displacement of atoms from their equilibrium positions disrupts the periodicity of the lattice and contributes to the resistivity through inelastic scattering of electrons with the absorption or emission of phonons.

we need to evaluate the dynamical structure factor

$$a(\mathbf{K}, \omega) = \frac{1}{N} \sum_{\mathbf{l}, \mathbf{l}'} e^{i\mathbf{K} \cdot (\mathbf{l} - \mathbf{l}')} \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\omega t} \langle e^{-i\mathbf{K} \cdot \mathbf{u}_{\mathbf{l}'}(t)} e^{i\mathbf{K} \cdot \mathbf{u}_{\mathbf{l}}(0)} \rangle_T,$$

Phonon absorption depends on the phonon density $n(q)$, while phonon emission depends on the factor $1+n(q)$.

consideration of the **inelastic** electron–phonon interaction is essential in treating electron transport phenomena in both periodic and non-periodic metals at finite temperatures.

- phonon energies are small compared to the Fermi energy
- only electrons close to the Fermi surface can participate in scattering events.

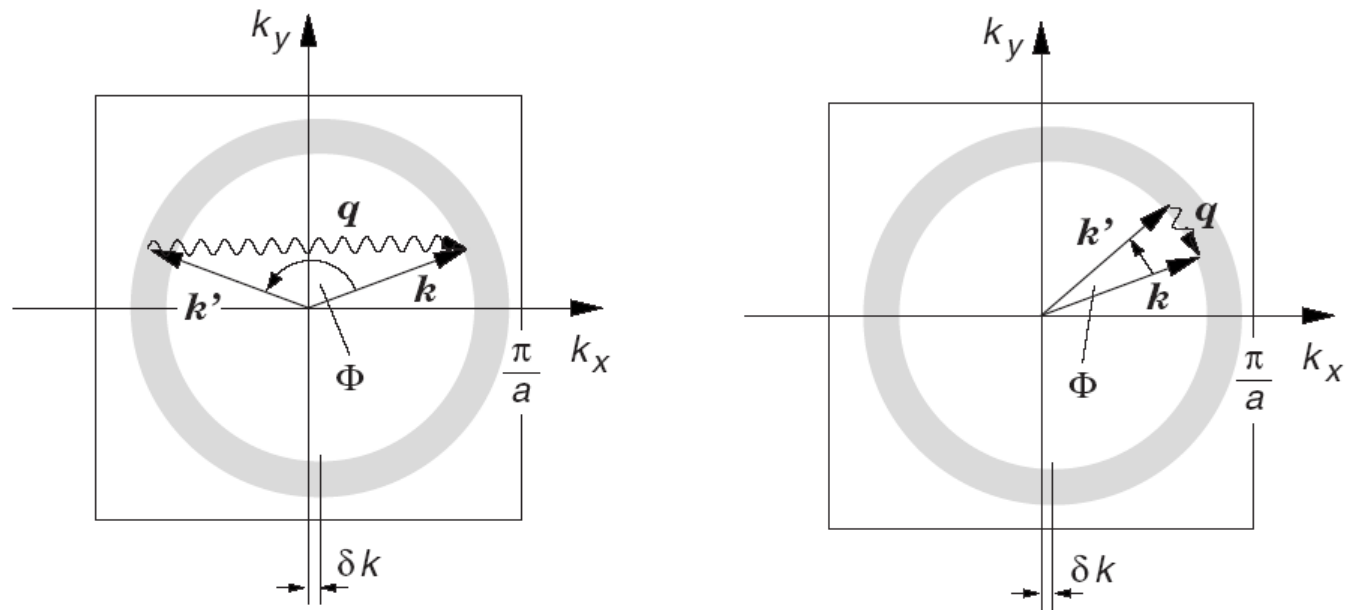


Fig. 7.7. Illustration of electron–phonon scattering processes in a free-electron gas. The electronic wave vectors are represented by *straight arrows*, those of the phonons by *wavy arrows*. The blurring of the Fermi surface is indicated by *tinted areas*. The collision of an electron with (a) a short-wavelength phonon (high temperature), and with (b) a long-wavelength phonon (low temperature) are shown

from Mizutani

Normal (N) and Umklapp (U) processes

Large angle scattering dominates at high temperature

Small angle scattering is important at low temperature

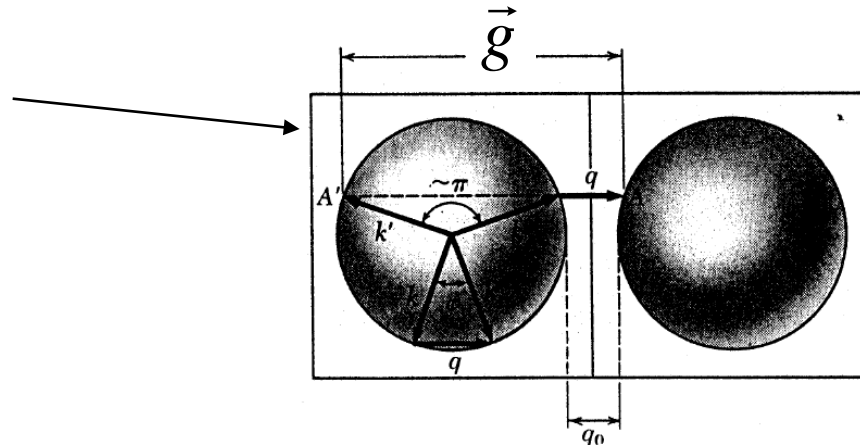
The structure factor remains finite when $\mathbf{K} \pm \mathbf{q} = \mathbf{g}$ or $\mathbf{k} - \mathbf{k}' \pm \mathbf{q} = \mathbf{g}$.

\vec{g} Is a reciprocal lattice vector

The process with: $\mathbf{g} = 0$ and, hence, $\mathbf{K} = \pm \mathbf{q}$ is a normal process

Umklapp process

$$\vec{k}' - \vec{k} = \pm \vec{q}$$



from Kittel

The scattering process with $\mathbf{g} \neq 0$ is called the Umklapp process.

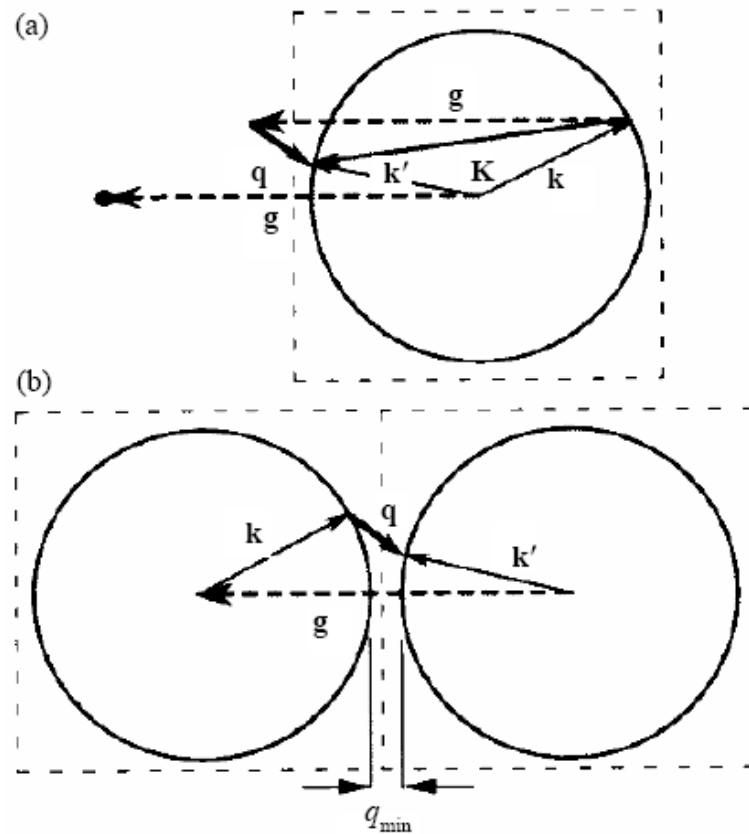


Figure 10.8. Umklapp process in electron–phonon interaction. (a) Large-angle scattering is made possible even at low temperatures with the assistance of the reciprocal lattice vector. Note that the phonon wave vector \mathbf{q} is small at low temperatures. (b) Umklapp process in the repeated zone scheme. A minimum wave number q_{\min} is required to allow the Umklapp process to occur. [J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, 1964)]

- The umklapp process becomes important when the temperature dependence of the resistivity of a metal needs to be quantitatively evaluated.

In the present discussion, we consider only the normal process and discuss qualitatively the temperature dependence of the electrical resistivity of a crystal metal.

- the resistivity due to the inelastic one-phonon normal process is deduced to be

$$\rho = \left(\frac{3\pi\Omega_0}{4e^2\hbar v_F^2 k_F^4} \right) \left(\frac{1}{M} \right) \int_0^{q_{\max}} q^5 |U_p(q)|^2 \beta n(\omega_q) [n(\omega_q) + 1] dq,$$

- we take the ratio of resistivity at temperature T over that at the Debye temperature Θ_D .

$$\frac{\rho(T)}{\rho(\Theta_D)} = \left(\frac{T}{\Theta_D}\right)^5 \frac{\int_0^{\Theta_D/T} |U_p(x)|^2 x^5 \frac{e^x}{(e^x - 1)^2} dx}{\int_0^1 |U_p(x)|^2 x^5 \frac{e^x}{(e^x - 1)^2} dx}.$$

Bloch-Grüneisen law

where $x = \hbar\omega/k_B T = (\omega/\omega_D)/(T/\Theta_D) = (q/q_D)(\Theta_D/T)$

the maximum value of x at any temperature T is replaced by Θ_D/T ,
since $q_{\max} = q_D$.

This indicates that the temperature-dependent resistivity can be normalized with respect to that at the Debye temperature.

At high temperatures $T \geq \Theta_D$, all phonon modes are excited. Since the relation $\hbar\omega \leq \hbar\omega_D < k_B T$ or $\beta\hbar\omega < 1$ holds, we have

$$\beta n(\omega_q) \{n(\omega_q) + 1\} = \frac{\beta}{e^{\beta\hbar\omega} - 1} \cdot \frac{e^{\beta\hbar\omega}}{e^{\beta\hbar\omega} - 1} = \left(\frac{\beta}{e^{\beta\hbar\omega} - 1} \right)^2 \cdot \frac{e^{\beta\hbar\omega}}{\beta} \approx \left(\frac{1}{\hbar\omega} \right)^2 k_B T.$$

$$\rho = \frac{3\pi\Omega_0}{4e^2\hbar v_F^2 k_F^4} \int_0^{q_D} q^5 |U_p(q)|^2 \frac{k_B T}{(\hbar s q)^2} dq = \frac{3\pi\Omega_0}{4e^2\hbar v_F^2 k_F^4} \left(\frac{q_D^2 T}{k_B \Theta_D^2} \right) \int_0^{q_D} q^3 |U_p(q)|^2 dq \propto \frac{T}{\Theta_D^2},$$

where the upper limit is replaced by the Debye radius corresponding to the available maximum wave number in the Debye model

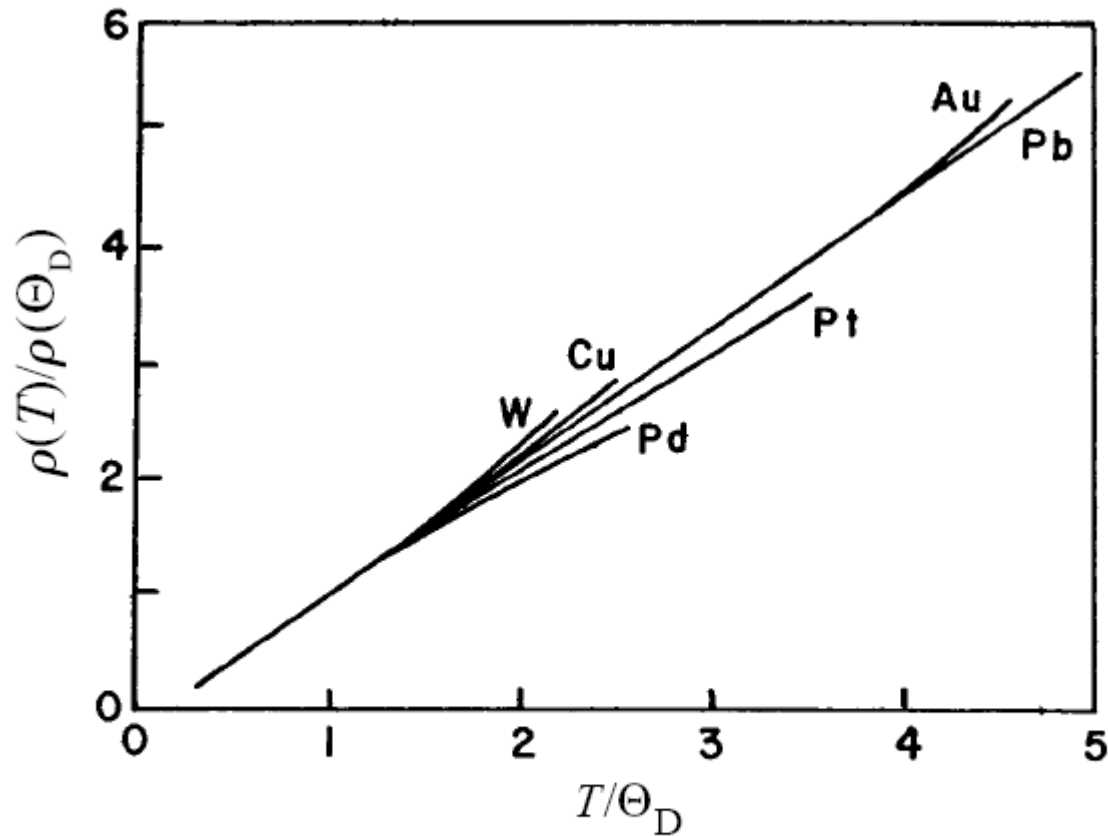


Figure 10.10. Normalized electrical resistivity versus normalized temperature for pure metals in high-temperature range. [K. Schröder, *Handbook of Electrical Resistivities of Binary Metallic Alloys* (CRC Press, Florida, 1983)]

For example, pure Cu with $\Theta_D=333$ K exhibits an almost linear temperature dependence in the temperature range from 80 K up to about 800 K.

With decreasing temperature below Θ_D , phonons having smaller wave vectors become dominant and, hence, the magnitude of the scattering vector \mathbf{K} is also decreased in the one-phonon normal process. Thus, the resistivity at $T \leq \Theta_D$ turns out to be

$$\rho = \frac{3\pi\Omega_0}{4e^2\hbar v_F^2 k_F^4} \left(\frac{1}{M}\right) \left(\frac{T}{\Theta_D}\right)^6 \left(\frac{\hbar}{k_B T}\right) q_D^6 |U_p(0)|^2 \int_0^{\Theta_D/T} x^5 \frac{e^x}{(e^x - 1)^2} dx \quad \boxed{\propto T^5}$$

where $|U_p(K)|^2$ is replaced by $|U_p(0)|^2$,

normally below about 20 K.

$$\int_0^{\infty} x^5 \frac{e^x}{(e^x - 1)^2} dx = \int_0^{\infty} x^5 e^{-x} (1 + 2e^{-x} + 3e^{-2x} + 4e^{-3x} + \dots) dx \quad \text{from Mizutani}$$

$$= 5! \left(\frac{1}{1^5} + \frac{1}{2^5} + \frac{1}{3^5} + \frac{1}{4^5} + \dots \right) = 5! \zeta(5) \cong 120 \times 1.0369 = 124.428,$$

where $\zeta(5)$ is the Riemann zeta function

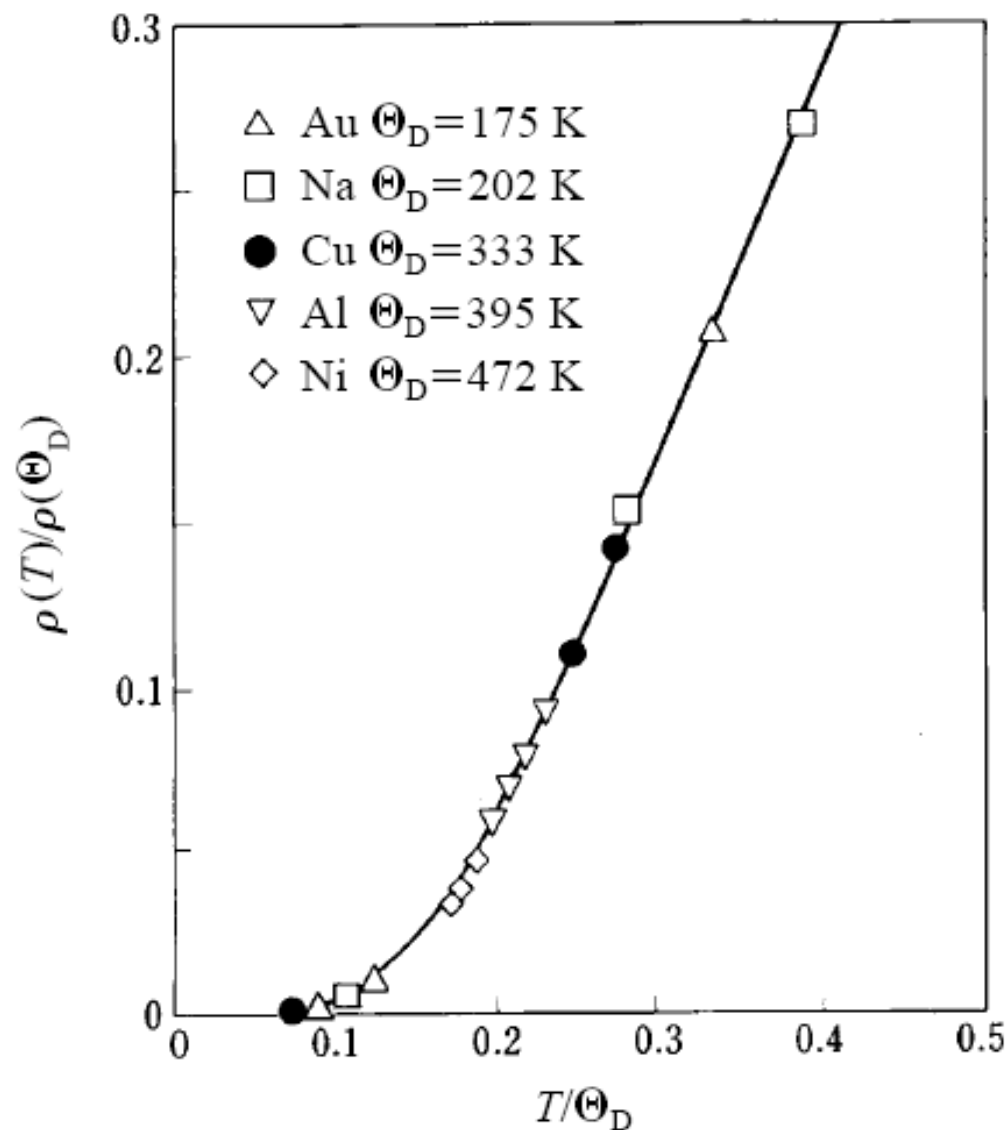


Figure 10.9. Temperature dependence of the electrical resistivity for various metals. The Debye temperature is deduced so as to fit the experimental data to equation (10.107). There is reasonable agreement with the Debye temperature deduced from the low-temperature specific heat (see Table 3.1). [J. Bardeen, *J. Appl. Phys.* **11** (1940) 88]

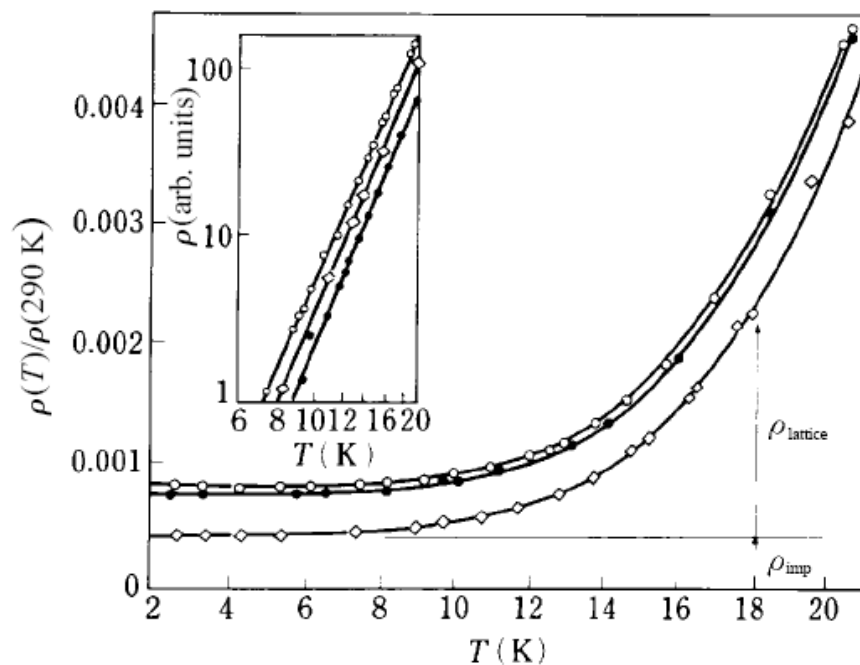


Figure 10.5. Temperature dependence of the electrical resistivity for pure Na at low temperatures. The temperature-dependent part of the resistivity due to electron-phonon interaction is denoted as ρ_{lattice} . Three different data sets yield different residual resistivities owing to a slight difference in purity of the samples. The inset shows a log-log plot for the temperature-dependent ρ_{lattice} . The relation $\rho_{\text{lattice}} = T^5$ holds well for pure Na. [D. K. C. MacDonald and K. Mendelssohn, *Proc. Roy. Soc. (London)* **A202** (1950) 103]

Only lattice waves with long wavelengths or shorter wave vectors can survive in a perfect crystal at low temperatures.

- the scattering angle becomes smaller and smaller with decreasing temperature.
- The Bloch-Grüneisen law, particularly the T^5 -law, is a phenomenon characteristic of a crystalline metal, where the mean free path of the conduction electron is much longer than the atomic distance.
- The Bloch-Grüneisen law breaks down in non-periodic solids like amorphous alloys and quasicrystals, where the mean free path of the conduction electron is shortened because of the failure of the Bloch theorem and often becomes comparable to an average atomic distance.

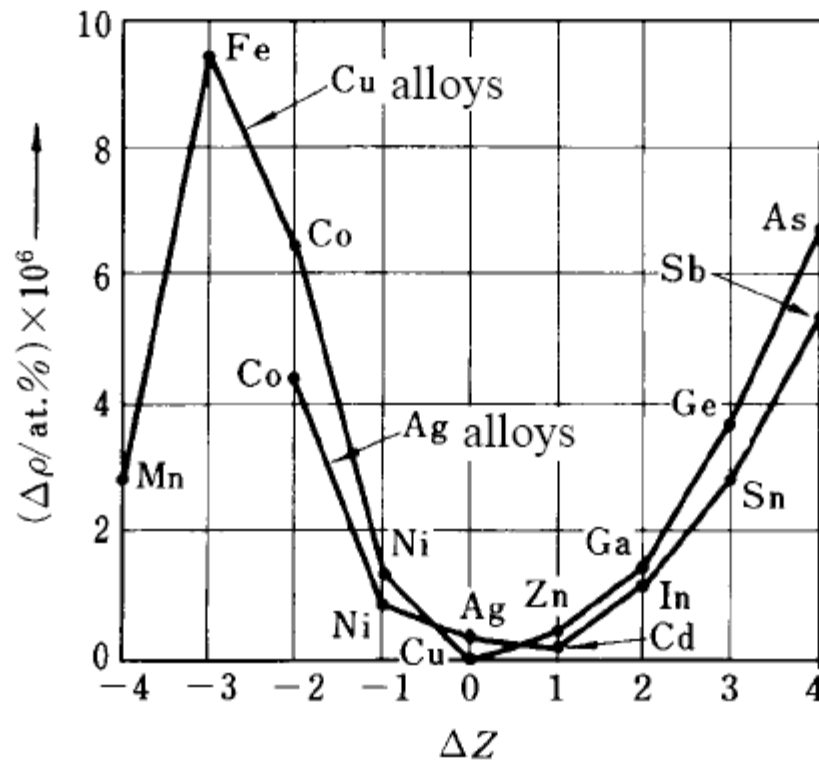


Figure 9.2. The Linde law. The ΔZ dependence of the increment of resistivity upon adding 1 at.% of various elements (as indicated) to Cu and Ag. ΔZ is the difference in valency between the solute and the noble metal matrix. The value of ΔZ is taken to be 0, -1, -2 and -3, for Ni, Co, Fe and Mn, respectively. [F. Seitz, *The Modern Theory of Solids* (McGraw-Hill, New York, 1940)]

Linde law no longer holds when the solute concentration exceeds about 5 at.%.

the impurity-impurity interaction cannot be ignored.

All these compounds form a completely periodic structure, since the lattice sites which Au and Cu atoms occupy are uniquely assigned.

superlattice or superstructure.

the resistivity drops sharply when an intermetallic compound is formed.

- This is due to the restoration of the periodic potential, resulting in a substantial reduction in the scattering of conduction electrons

Electrical conductivity of metals

Matthiessen's rule

$$\frac{1}{\tau} = \frac{1}{\tau_{def}} + \frac{1}{\tau_{e-e}} + \frac{1}{\tau_{ph}} + \frac{1}{\tau_{mag}} + \frac{1}{\tau_{CEF}} + \dots$$

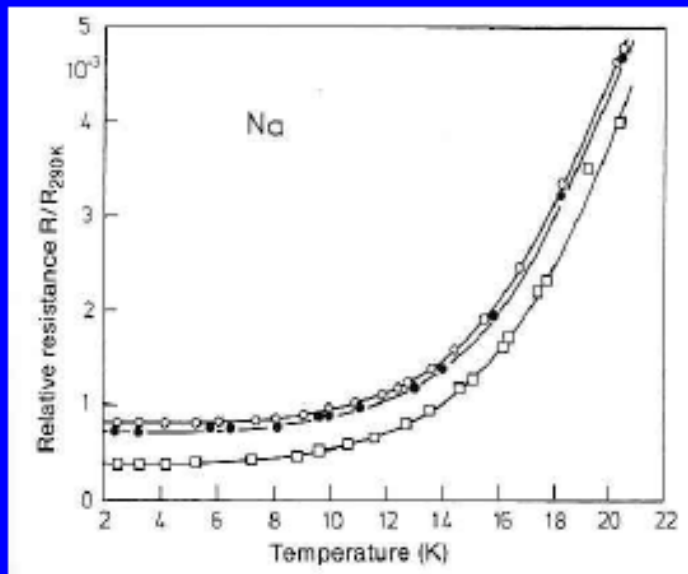
$$\rho = \rho_0 + \rho_{e-e} + \rho_{ph} + \rho_{mag} + \rho_{CEF} + \dots$$

from UvA-VU Master Course: Advanced Solid State Physics by Anne de Visser (University of Amsterdam)

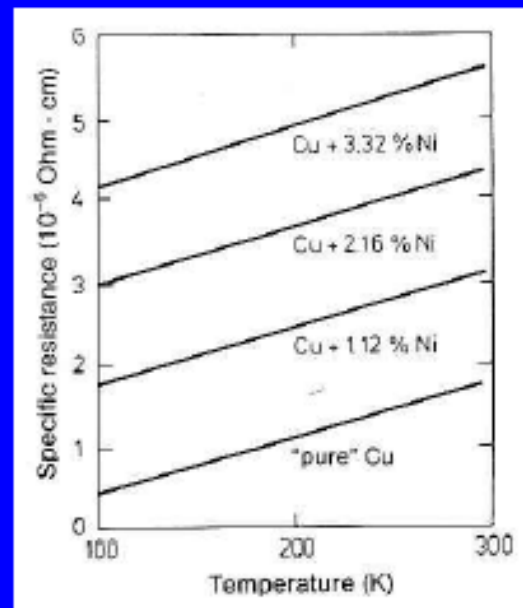
$$\rho_0 = \text{constant}$$

$$\rho_{e-e} = AT^2$$

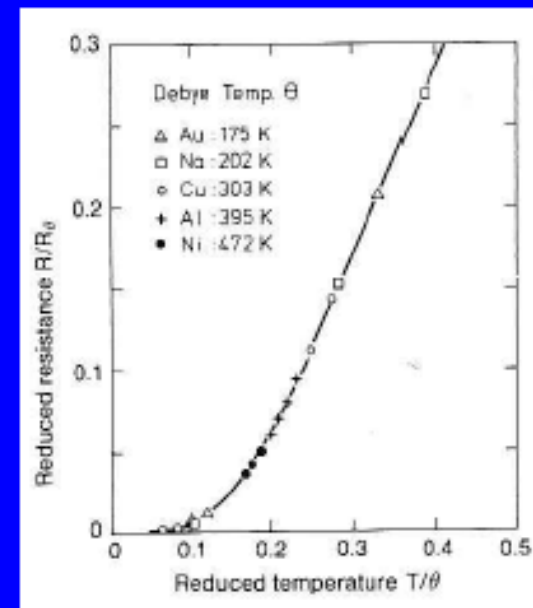
$$\rho_{ph} = a(T/\theta)^5 \int_0^{\theta/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})}$$



resistance of sodium
3 diff. defect concentrations

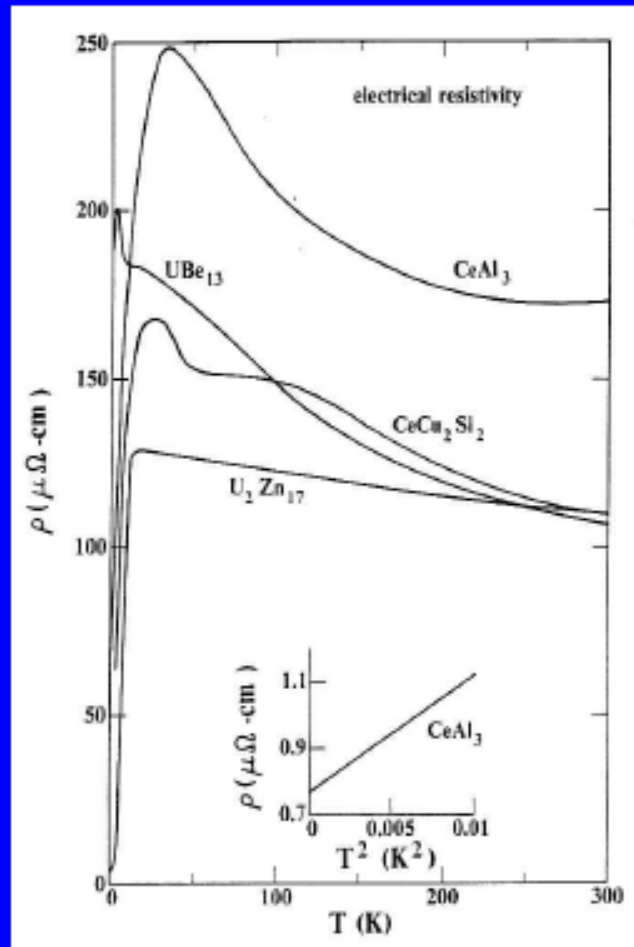


resistivity of copper-nickel alloys



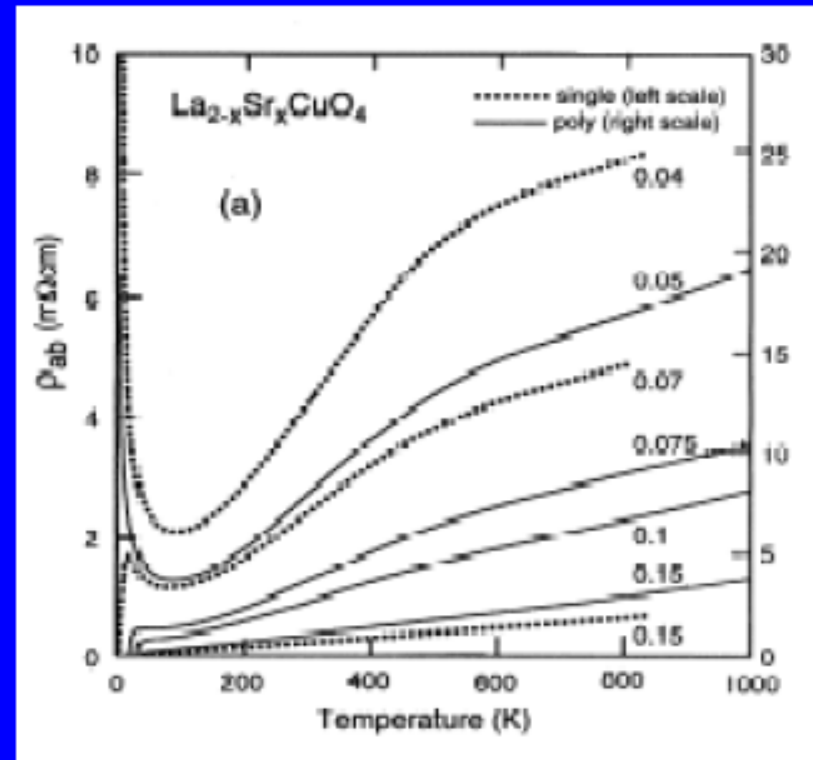
phonon (Debye) resistance

Electrical conductivity of metals: examples



resistivity of heavy-fermion compounds

from UvA-VU Master Course: Advanced Solid State Physics by Anne de Visser (University of Amsterdam)



resistivity of superconducting cuprates: $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$