CHAPTER 7

Electrical Conduction in Metals and Alloys

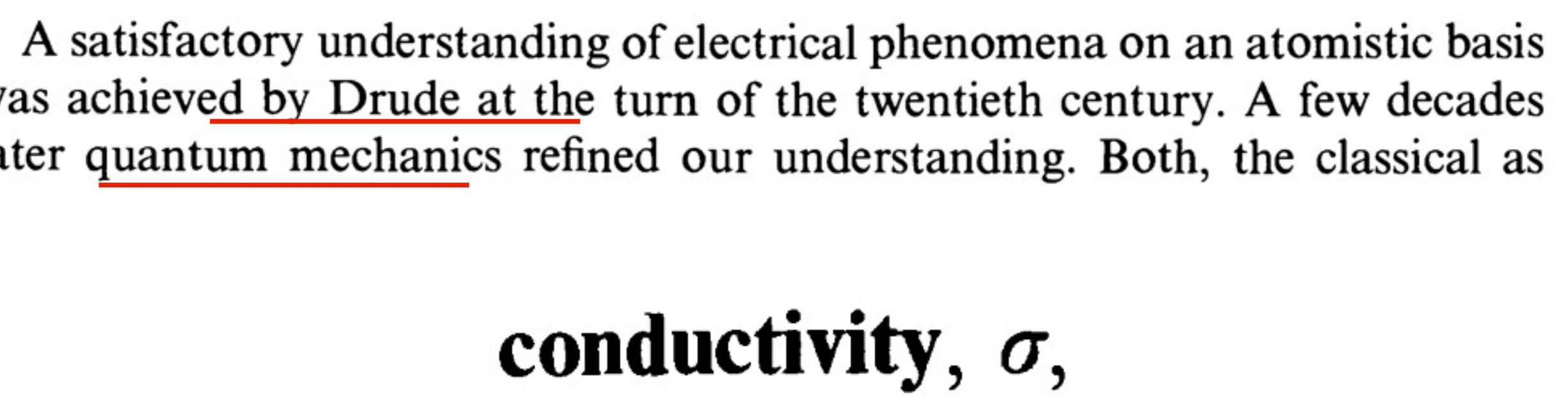
Thales of Miletus, a Greek philosopher, discovered around 600 BC that a piece of amber, having been rubbed with a piece of cloth, attracted feathers and other light particles. Very appropriately, the word *electricity* was later coined by incorporating the Greek word *elektron*, which means *amber*.

It was apparently not before 2300 years later that man became again interested in electrical phenomena. Stephen Gray found in the early 1700s that some substances conduct electricity whereas others do not. In 1733 DuFay postulated the existence of two types of electricity, which he termed *glass electricity* and *amber electricity* dependent on which material was rubbed. From then on a constant stream of well-known scientists contributed to our knowledge of electrical phenomena. Names such as Coulomb, Galvani, Volta, Oersted, Ampère, Ohm, Seebeck, Faraday, Henry, Maxwell, Thomson, and others, come to mind. What started 2600 years ago as a mysterious effect has been applied quite recently in an impressive technology that culminated in large-scale integration of electronic devices.

A satisfactory understanding of electrical phenomena on an atomistic basis was achieved by Drude at the turn of the twentieth century. A few decades later quantum mechanics refined our understanding. Both, the classical as

conductivity, σ,

conductivity of superconductors, measured at low temperatures, into consideration, this span extends to 40 orders of magnitude (using an estimated conductivity for superconductors of about 10^{20} $1/\Omega$ cm)



Room-temperature conductivity of various materials.

Ohm's law

$$V = RI$$

potential difference, V (in volts)
resistance, R (in ohms i.e. Ω)
electrical current, I (in amps)

current density

$$j = \sigma \mathscr{E}$$

$$j = \frac{I}{A}$$

the current per unit area (A/cm^2)

conductivity, σ ($1/\Omega$ cm)

electric field strength (V/cm)

The current density is frequently expressed by

$$j = Nve,$$

where N is the **number of electrons** (per unit volume), v their **velocity**, and e their **charge**

The resistance of a conductor

$$R = \frac{L\rho}{A}$$

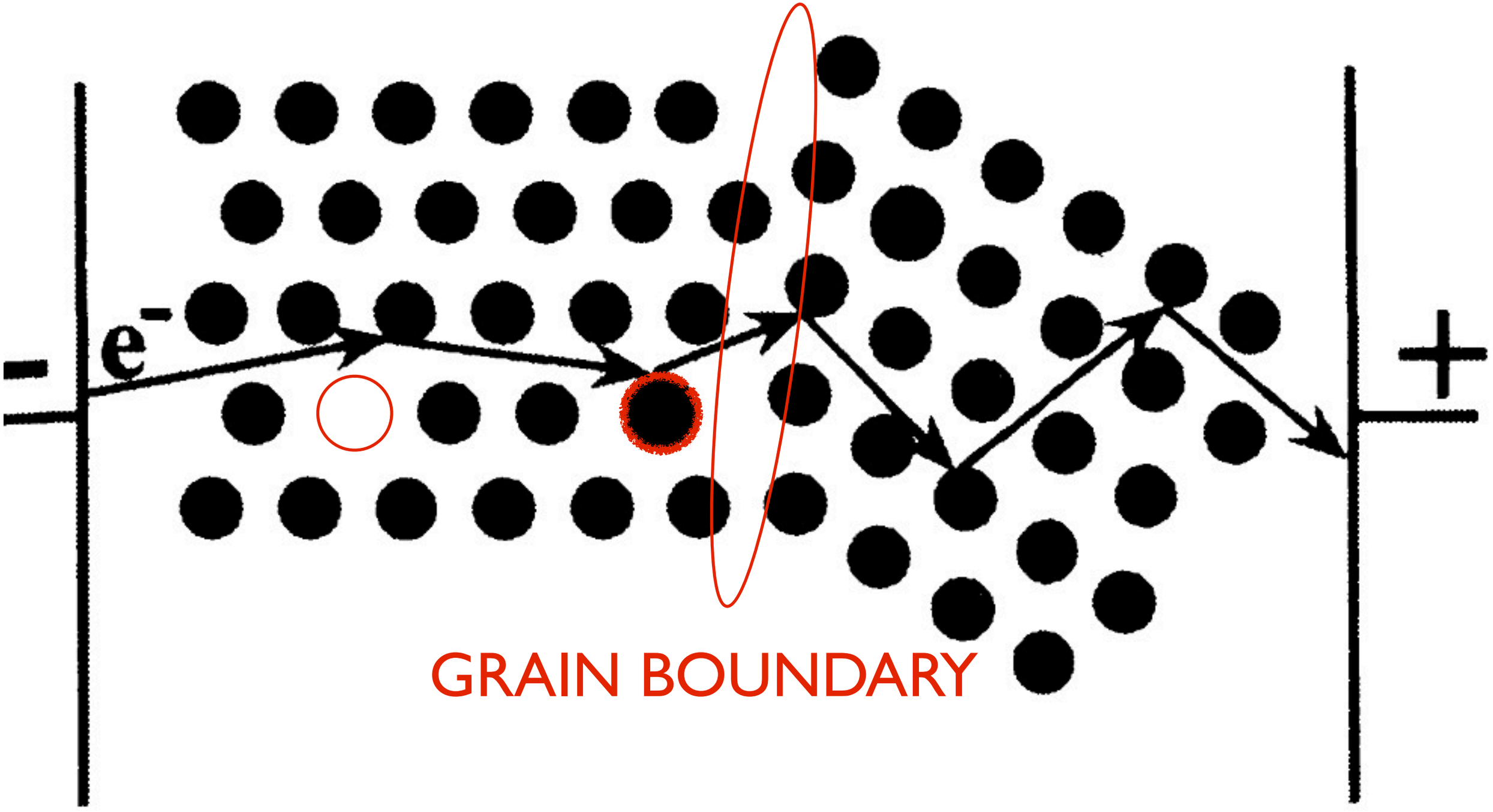
where L is the length of the conductor, A is its cross-sectional area, and ρ is the **specific resistance**, or **resistivity** (Ω cm)

$$\rho = \frac{1}{\sigma}$$

The reciprocal of the ohm (Ω) is defined to be 1 siemens (S)

Explanation of Resistance (Particle Nature)

one can explain the resistance by means of collisions of the drifting electrons with certain lattice atoms. The more collisions are encountered, the higher is the resistance. This concept qualitatively describes the increase in resistance with an increasing amount of lattice imperfections. It also explains the observed increase in resistance with increasing temperature: the thermal energy causes the lattice atoms to oscillate about their equilibrium positions (see Part V), thus increasing the probability for collisions with the drifting electrons.


-
e-
+
GRAIN BOUNDARY

Explanation of Resistance (Wave Nature)

The matter

waves may be thought to be scattered by lattice atoms. Scattering is the dissipation of radiation on small particles in all directions. The atoms absorb the energy of an incoming wave and thus become oscillators. These oscillators in turn re-emit the energy in the form of spherical waves. If two or more atoms are involved, the phase relationship between the individual re-emitted waves

coherent scattering (with perfect lattice)

incoherently scattered (with imperfect lattice)

The energy of incoherently scattered waves is smaller in the forward direction, that is, the matter wave loses energy. This energy loss qualitatively explains the resistance.

7.3. Conductivity—Classical Electron Theory

valence electrons of the individual atoms in a crystal

~ a free "electron gas" or "plasma,"

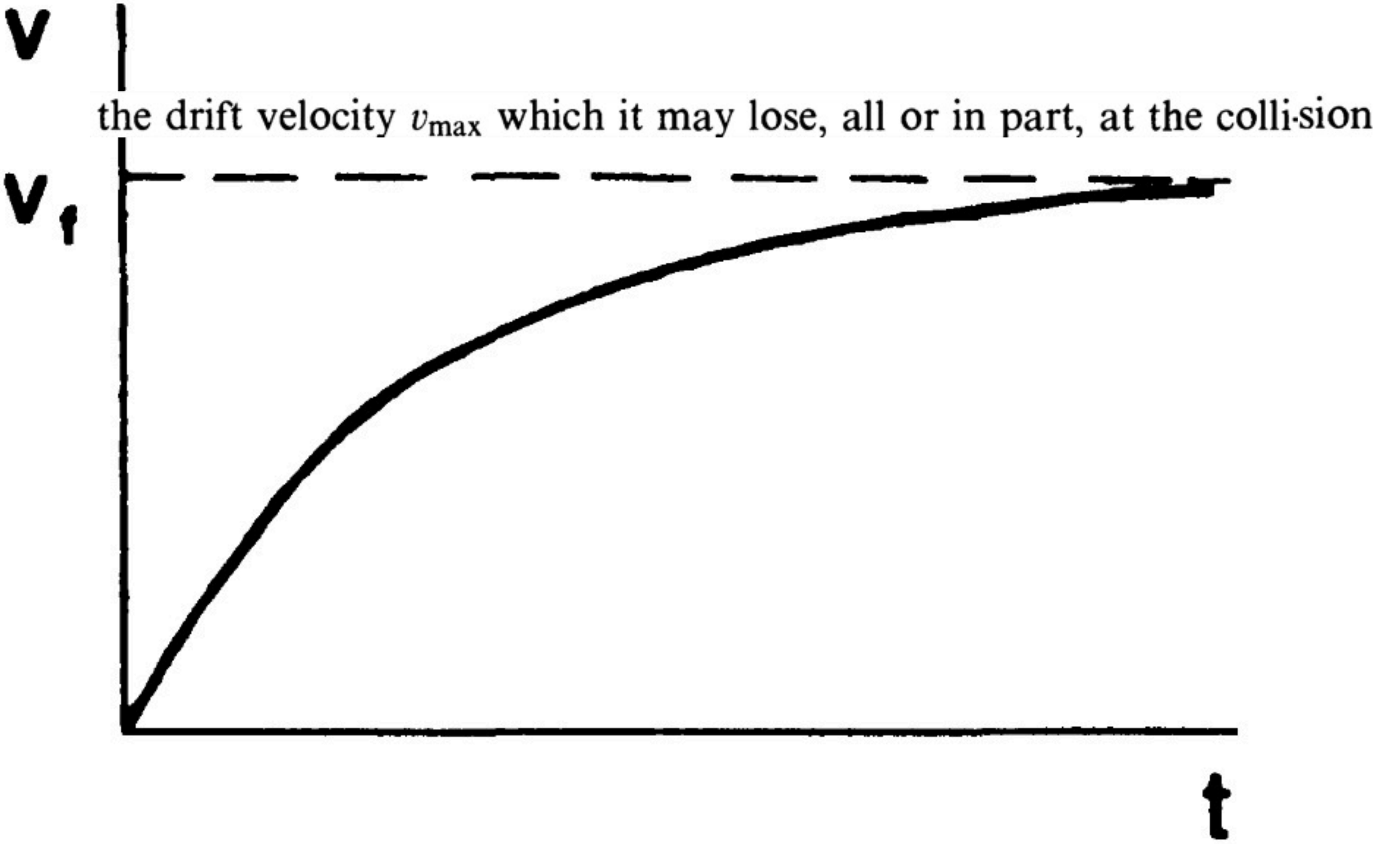
The electrons move randomly (in all possible directions) so that their individual velocities in the absence of an electric field cancel and no net velocity results.

electrons are then accelerated with a force $e\mathscr{E}$ towards the anode and a net **drift of the electrons** results

Newton's Law $$m\frac{dv}{dt} = e\mathscr{E}$$

where e is the charge of the electrons and m is their mass.

An electron, accelerated by an electric field, may be described to increase its **drift velocity** until it encounters a collision.



We postulate that the resistance in metals and alloys is due to interactions of the drifting electrons with some lattice atoms, i.e., essentially with the imperfections in the crystal lattice (such as impurity atoms, vacancies, grain boundaries, dislocations, etc.)

an electron motion to be counteracted by a "friction" force γv which opposes the electrostatic force $e\mathscr{E}$.

$$m\frac{dv}{dt} + \gamma v = e\mathscr{E},$$

where γ is a constant.

For the steady state case ($v = v_f$) we obtain $dv/dt = 0$.

$$\gamma = \frac{e\mathscr{E}}{v_f}.$$

$$m\frac{dv}{dt} + \frac{e\mathscr{E}}{v_f}v = e\mathscr{E}.$$

$$v = v_f\left[1 - \exp\left(-\left(\frac{e\mathscr{E}}{mv_f}t\right)\right)\right].$$

relaxation time (the average time between two consecutive collisions)

$$\tau = \frac{mv_f}{e\mathscr{E}}$$

$$j = N_f v_f e = \sigma \mathscr{E}$$

number of free electrons, N_f (per cm^3)

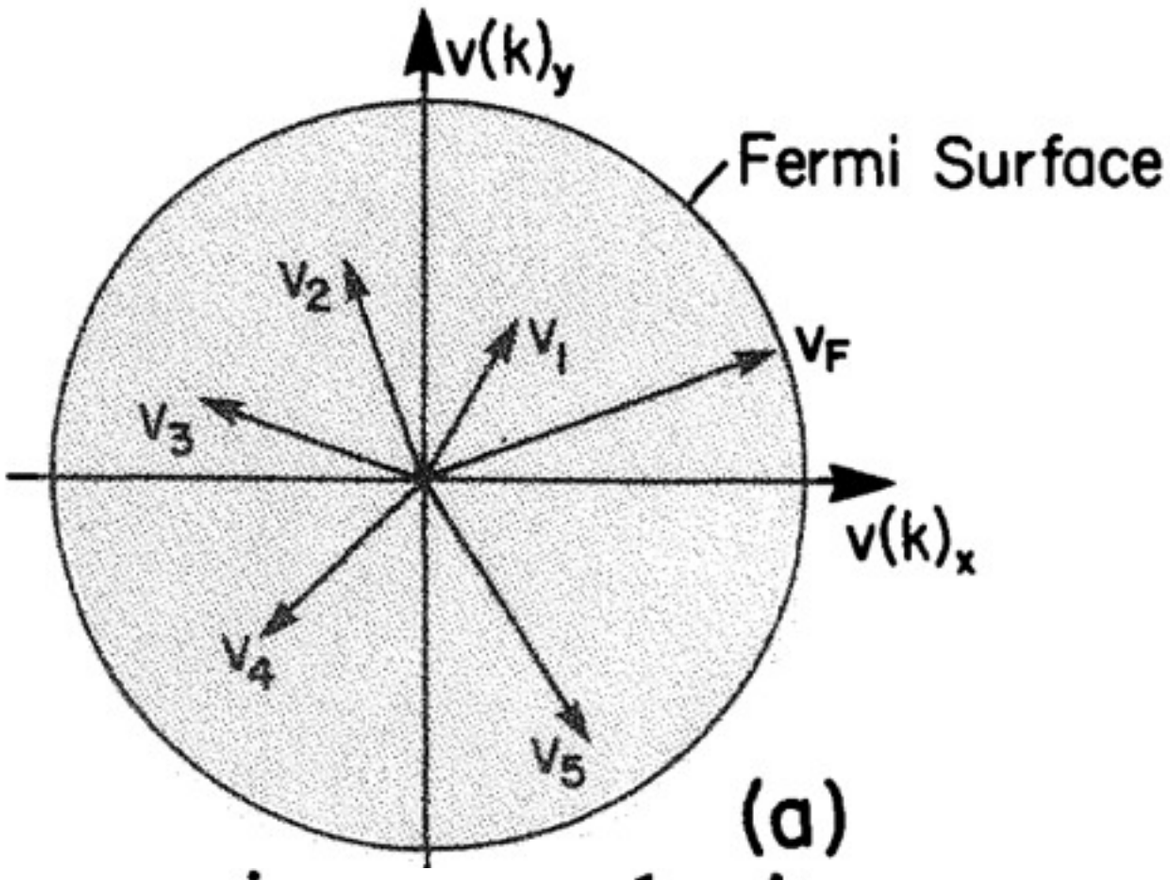
$$\sigma = \frac{N_f e^2 \tau}{m}.$$

the conductivity is large for a large number
of free electrons and for a large relaxation time

the mean free path between two consecutive collisions

$$l = v\tau$$

7.4. Conductivity—Quantum Mechanical Considerations



(a)

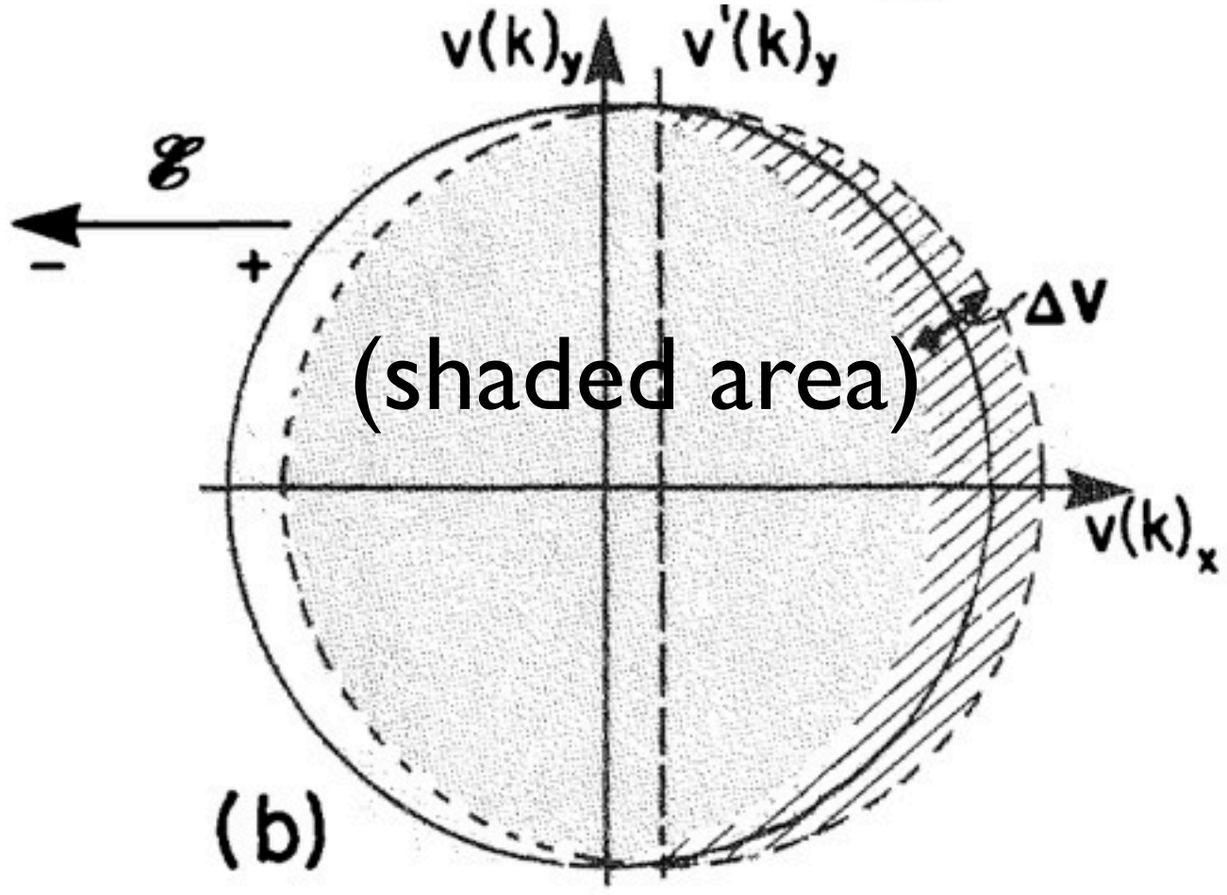
maximum velocity

Fermi velocity, v_F

the valence electrons perform, when in equilibrium,
random motions with no preferential velocity in any direction.

no net velocity

an electric field is applied



the Fermi sphere is displaced opposite to the field direction

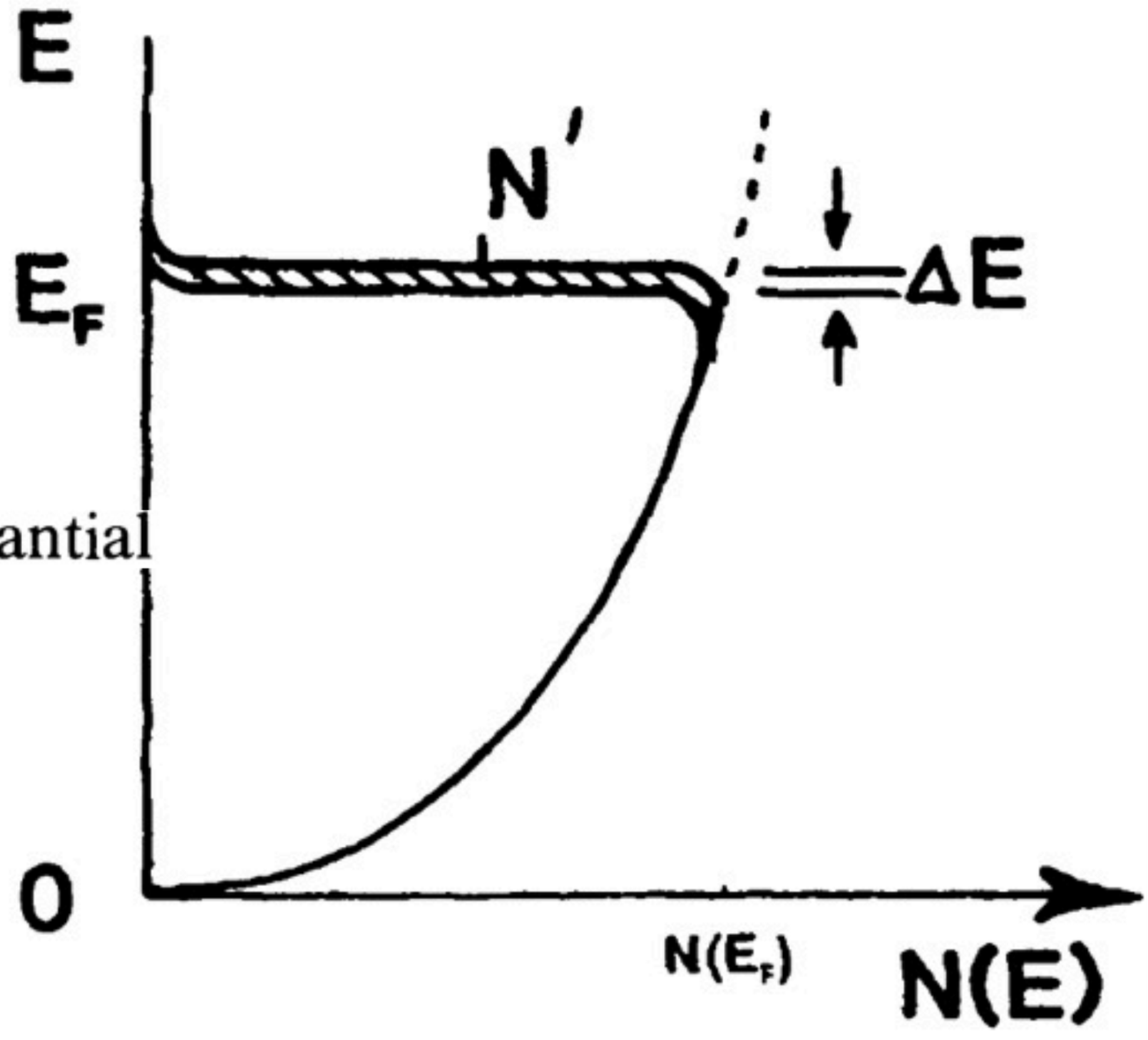
The shaded areas to the left and right of the $v(k)_y$-axis are of equal size. They cancel each other. The cross-hatched area remains uncompensated

Not all electrons have the same initial energy

displacement ΔE by an electric field
N' is the number of displaced electrons per unit volume

population density is highest around E_F

only a little extra
energy ΔE is needed to raise a substantial
number of electrons from the
Fermi level into slightly higher states



classical mechanics

Drude assume that *all* electrons drift, under the influence of an electric field, with a modest velocity.

Quantum mechanics

only specific electrons participate in conduction and that these electrons drift with a high velocity which is approximately the Fermi velocity v_F

electrons accelerated by the electric field $\mathscr{E}$ is only slightly larger than the Fermi energy E_F

$$j = v_{\mathrm{F}} e N'$$

The number of electrons displaced by the electric field $\mathscr{E}$ is

$$N' = N(E_{\mathrm{F}})\Delta E$$

$$j = v_{\mathrm{F}} e N(E_{\mathrm{F}})\Delta E = v_{\mathrm{F}} e N(E_{\mathrm{F}}) \frac{dE}{dk} \Delta k.$$

The factor dE/dk is calculated by using

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

$$\frac{dE}{dk} = \frac{\hbar^2}{m}k = \frac{\hbar^2 p}{m\hbar} = \frac{\hbar m v_F}{m} = \hbar v_F$$

$$j = v_F^2 e N(E_F)\hbar\Delta k$$

The displacement, Δk, of the Fermi sphere in k-space under the influence of an electric field

$$F = m\frac{dv}{dt} = \frac{d(mv)}{dt} = \frac{dp}{dt} = \hbar\frac{dk}{dt} = e\mathscr{E}$$

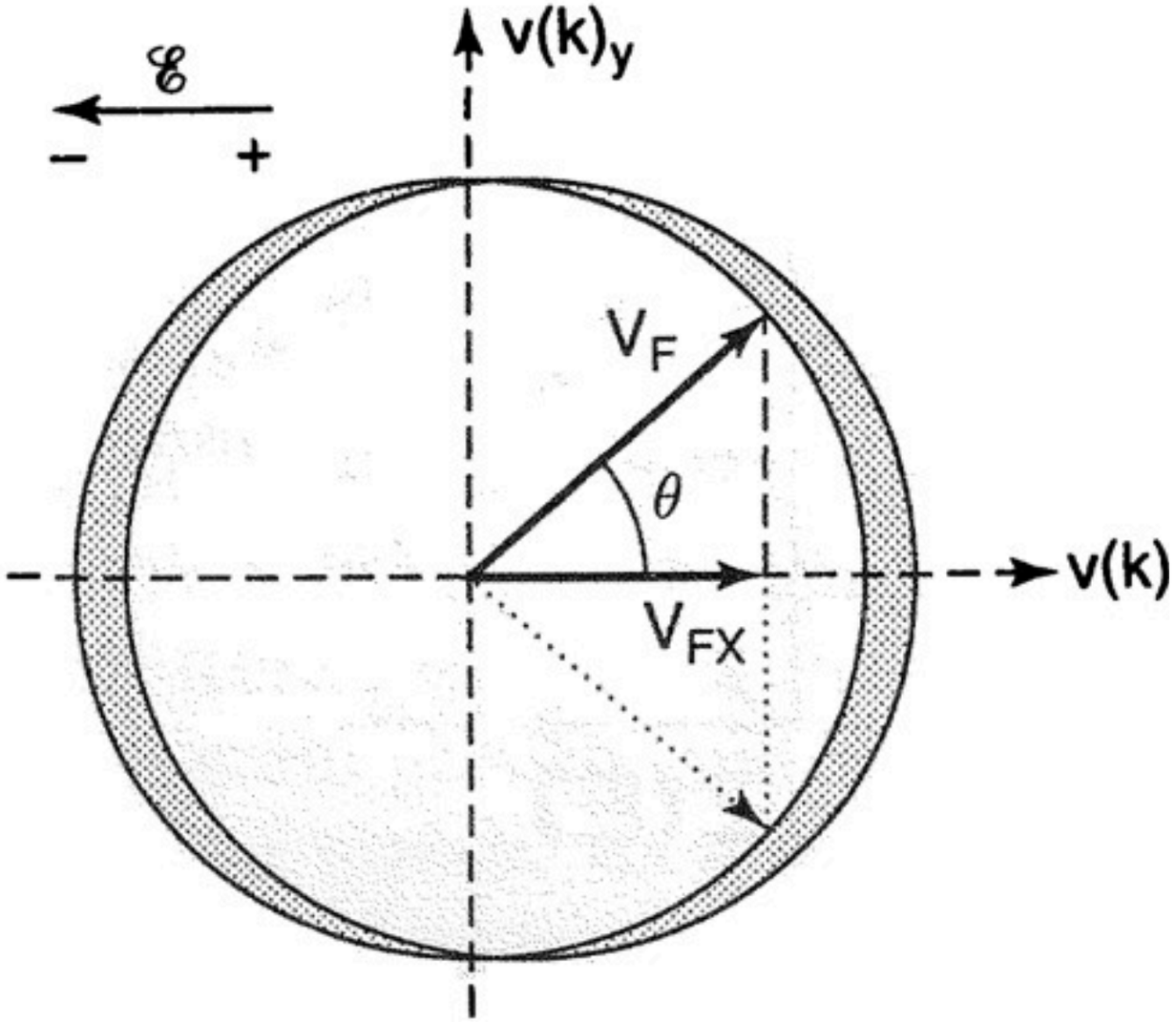
$$dk = \frac{e\mathscr{E}}{\hbar}\, dt$$

$$\Delta k = \frac{e\mathscr{E}}{\hbar}\Delta t = \frac{e\mathscr{E}}{\hbar}\tau$$

where τ is the time interval Δt between two "collisions" or the relaxation time

$$j = v_{\mathrm{F}}^2 e^2 N(E_{\mathrm{F}})\mathscr{E}\tau$$

only the projections of the velocities v_F on the positive $v(k)_x$-axis ($v_{Fx} = v_F \cos\theta$) contribute to the current



$$j = e^2 N(E_F)\mathscr{E}\tau \int_{-\pi/2}^{+\pi/2} (v_F \cos\theta)^2 \frac{d\theta}{\pi}$$

$$= e^2 N(E_F)\mathscr{E}\tau \frac{v_F^2}{\pi} \int_{-\pi/2}^{+\pi/2} \cos^2\theta \, d\theta$$

$$= e^2 N(E_F)\mathscr{E}\tau \frac{v_F^2}{\pi} \left[\frac{1}{4}\sin 2\theta + \frac{\theta}{2}\right]_{-\pi/2}^{+\pi/2},$$

$$j = \tfrac{1}{2} e^2 N(E_F)\mathscr{E}\tau v_F^2.$$

A similar calculation for a spherical Fermi surface yields

$$j = \tfrac{1}{3} e^2 N(E_\mathrm{F}) \mathscr{E} \tau v_\mathrm{F}^2$$

the conductivity finally becomes, with $\sigma = j/\mathscr{E}$

$$\boxed{\sigma = \tfrac{1}{3} e^2 v_\mathrm{F}^2 \tau N(E_\mathrm{F}).}$$

This quantum mechanical equation reveals that the conductivity depends on the Fermi velocity, the relaxation time, and the population density (per unit volume). The latter is, as we know, proportional to the density of states.

classical mechanics

$$\sigma = \frac{N_f e^2 \tau}{m}.$$

Quantum mechanics

$$\sigma = \tfrac{1}{3} e^2 v_F^2 \tau N(E_F).$$

(1) not *all* free electrons N_f are responsible for conduction

(2) depends to a large extent on the population density of the electrons near the Fermi surface

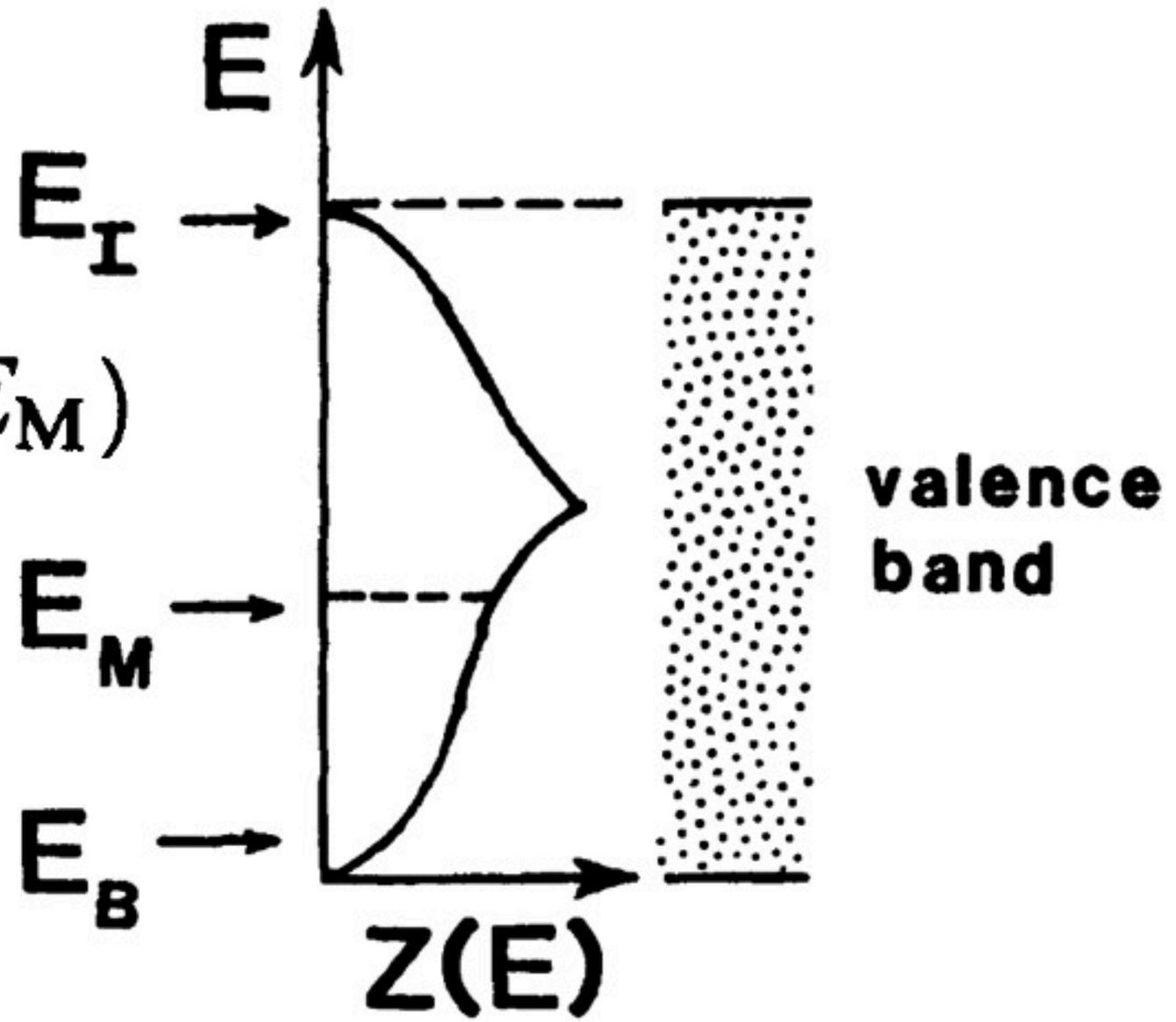
monovalent metals (such as
copper, silver, or gold) have partially filled valence bands

Their electron population densities near their Fermi energy are high
which results in a large conductivity

bivalent metal (E_B)

monovalent metal (E_M)

insulator (E_I)



bi-valent metals, on the other hand, are distinguished by an overlapping of the upper bands and by a small electron concentration near the bottom of the valence band the electron population near the Fermi energy is small which leads to a comparatively low conductivity

insulators and semiconductors have completely filled electron bands, which results in a virtu ally zero population density near the top of the valence band Thus, the conductivity in these materials is extremely small.

7.5. Experimental Results and Their Interpretation

7.5.1. Pure Metals

Matthiessen's rule

temperature independent

$$\rho = \rho_{\text{th}} + \rho_{\text{imp}} + \rho_{\text{def}} = \rho_{\text{th}} + \rho_{\text{res}}$$

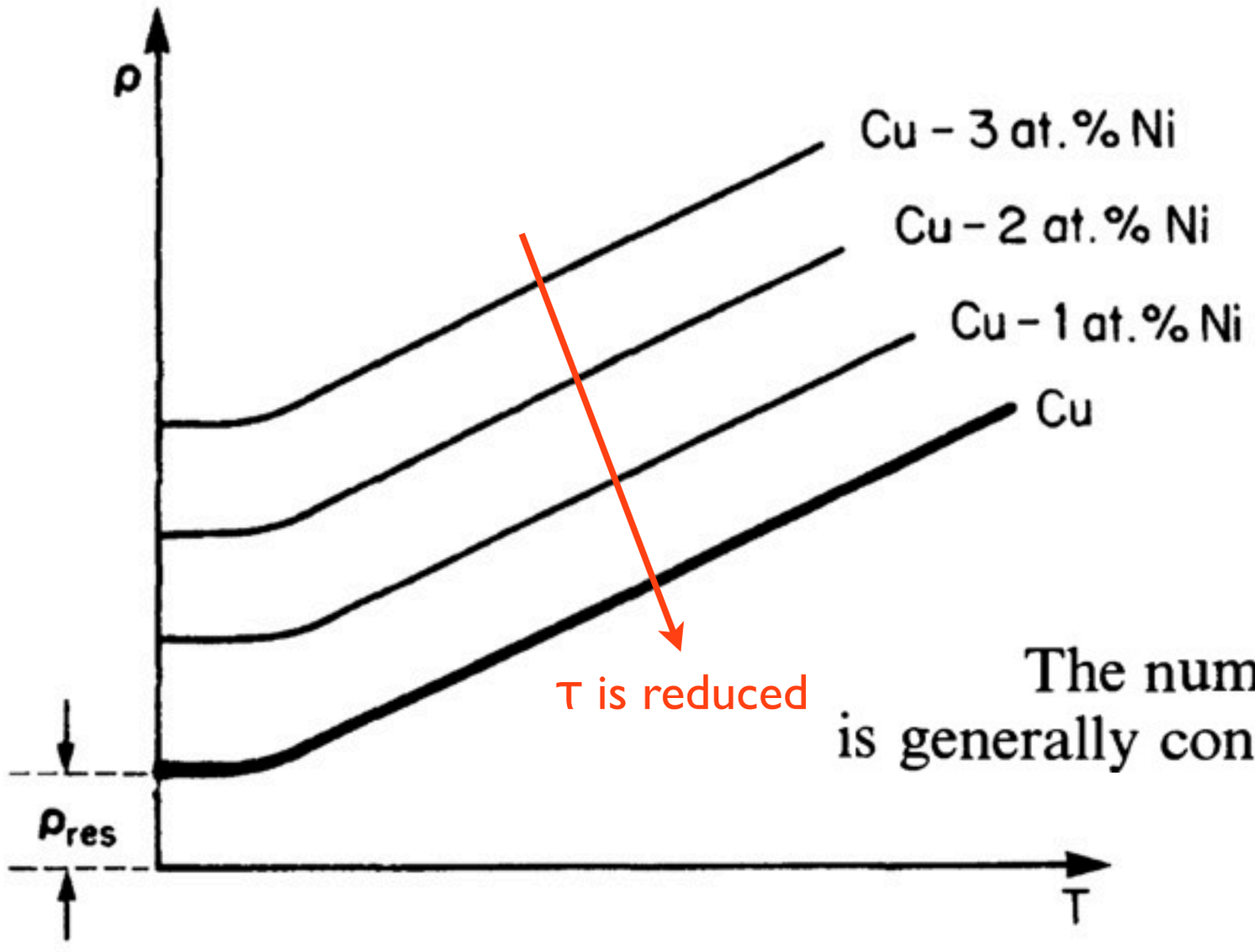
The resistivity of a metal (empirical equation)

$$\rho_2 = \rho_1[1 + \alpha(T_2 - T_1)]$$

where α is the linear temperature coefficient of resistivity.

thermal energy causes lattice atoms to oscillate about their equilibrium positions, thus increasing the incoherent scattering of the electron waves (or equivalently, increasing the number of electron-atom collisions)

ρ_{res}, is interpreted to be due to imperfections in the crystal such as impurities, vacancies, grain boundaries, or dislocations.
not temperature-dependent

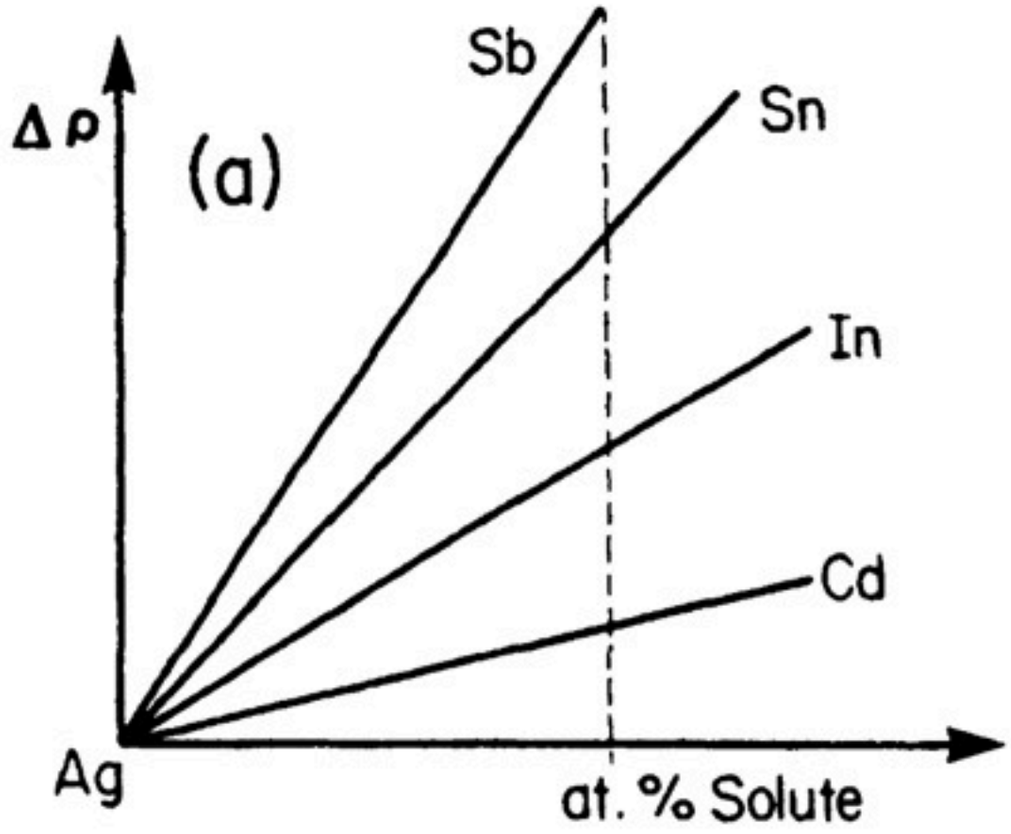


The number of impurity atoms
is generally constant in a given metal or alloy

resistivity vs. heat treatment

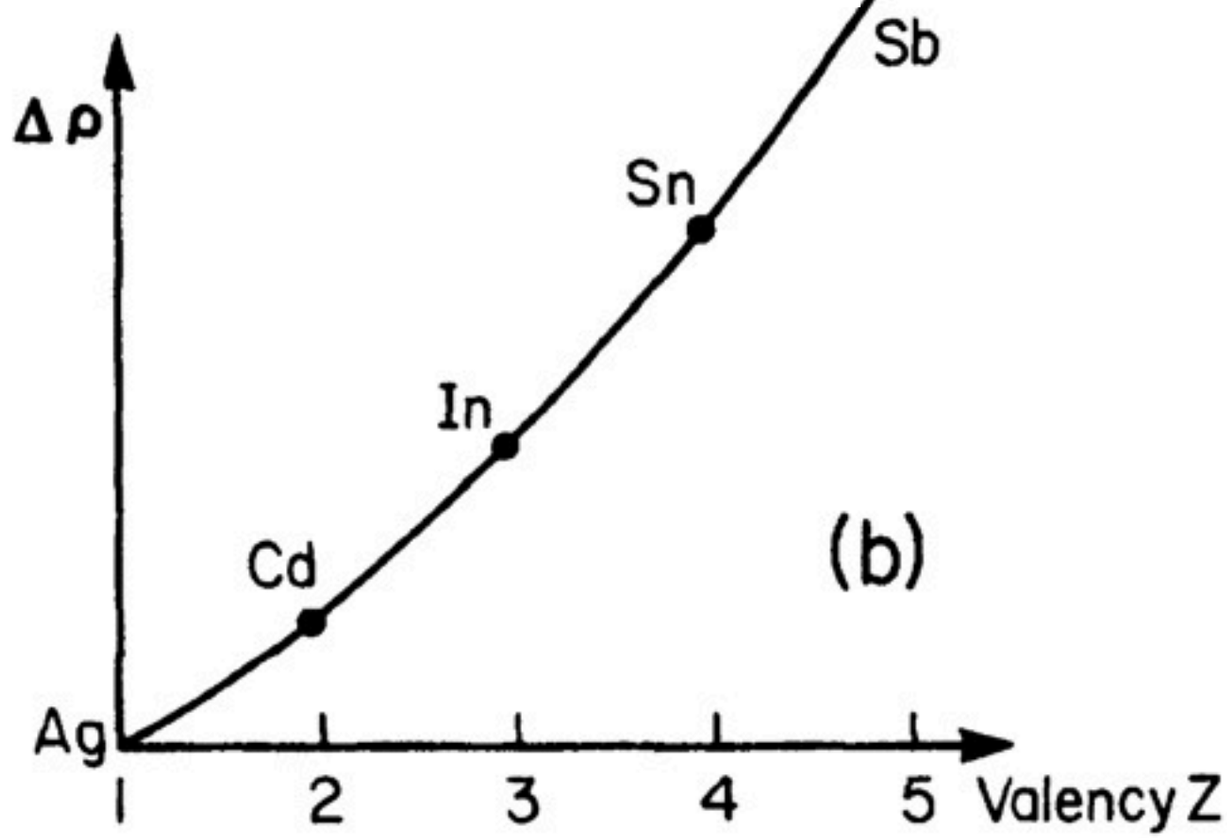
The number of vacancies or grain boundaries, however, can be changed by various heat treatments. For example, if a metal is annealed at temperatures close to its melting point and then rapidly quenched into water at room temperature, its room-temperature resistivity increases noticeably due to quenched-in vacancies. Frequently, this resistance increase diminishes during room-temperature aging or annealing at slightly elevated temperatures due to the annihilation of some vacancies. Likewise, recrystallization, grain growth, and many other metallurgical processes change the resistivity of metals. As a consequence of this, and due to its simple measurement, the resistivity is one of the most widely studied properties in materials research.

7.5.2. Alloys *dilute single-phase alloys*



atoms of different size cause
a variation in the lattice parameter

Linde's rule



- atoms having different valences
- different electron concentration
- alter the position of the Fermi energy
- changes the population density $N(E)$

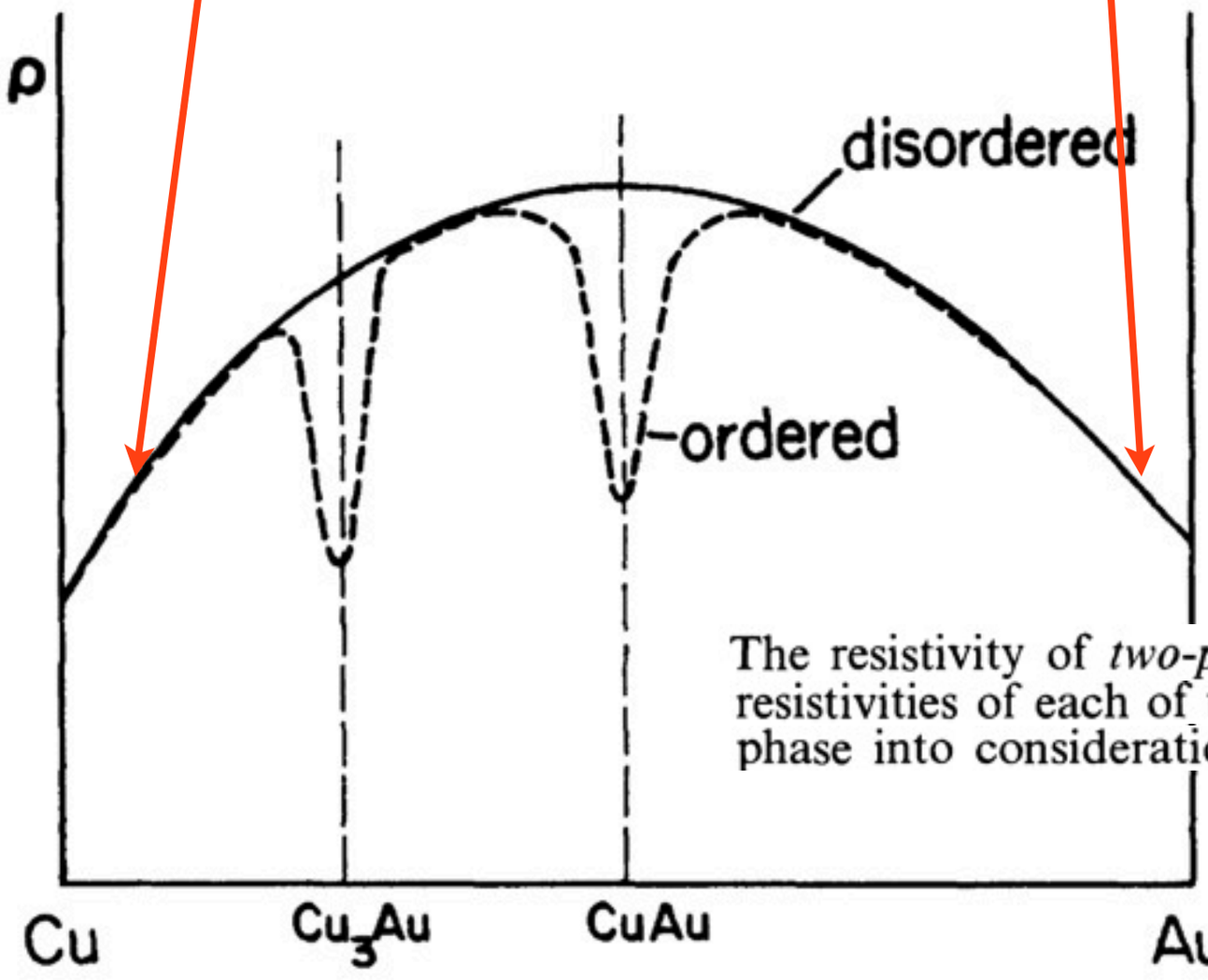
Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
* Lanthanoids			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
** Actinoids			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Nordheim's rule

Nordheim's rule holds strictly only for a few selected binary systems, because it does not take into consideration the changes in the density of states with composition. This is particularly true for alloys containing a transition metal.

$$\rho = X_A \rho_A + X_B \rho_B + C X_A X_B$$

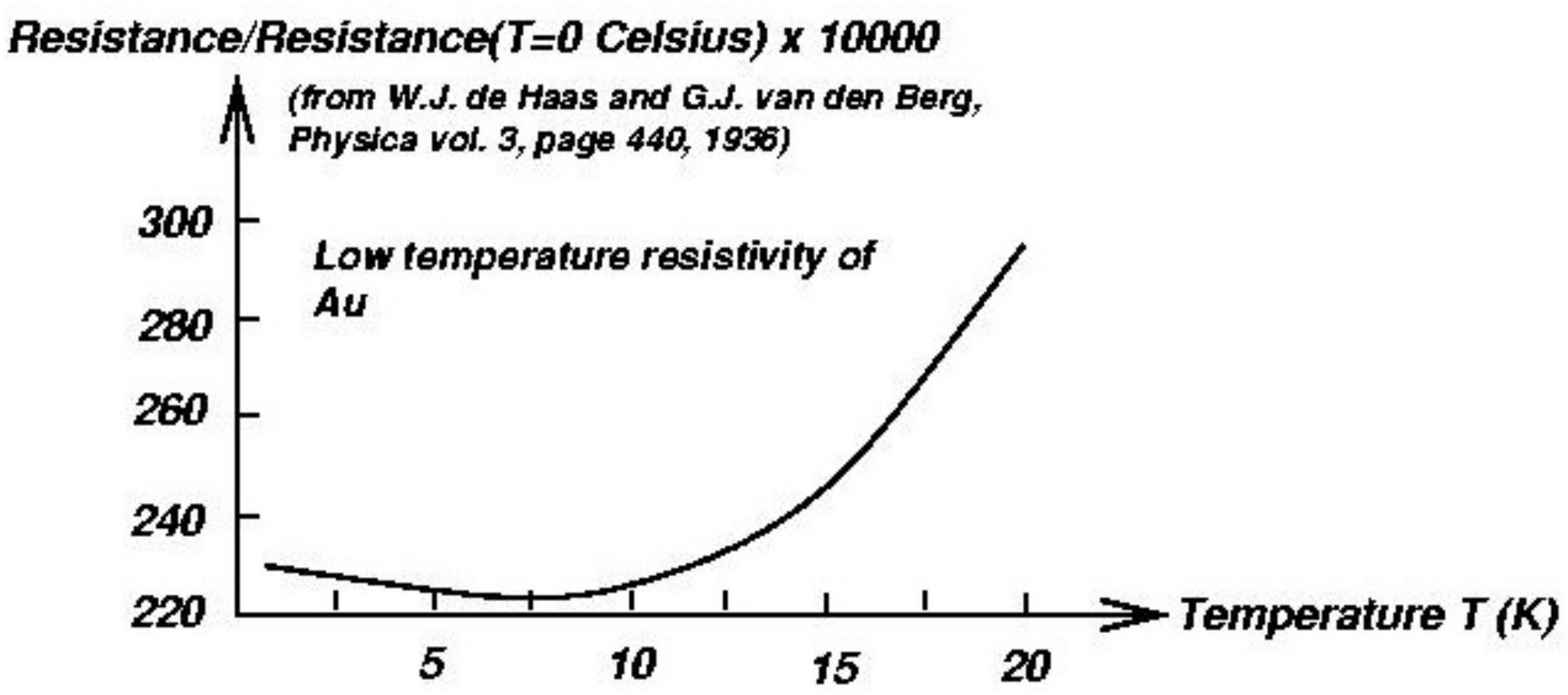
where C is a materials constant



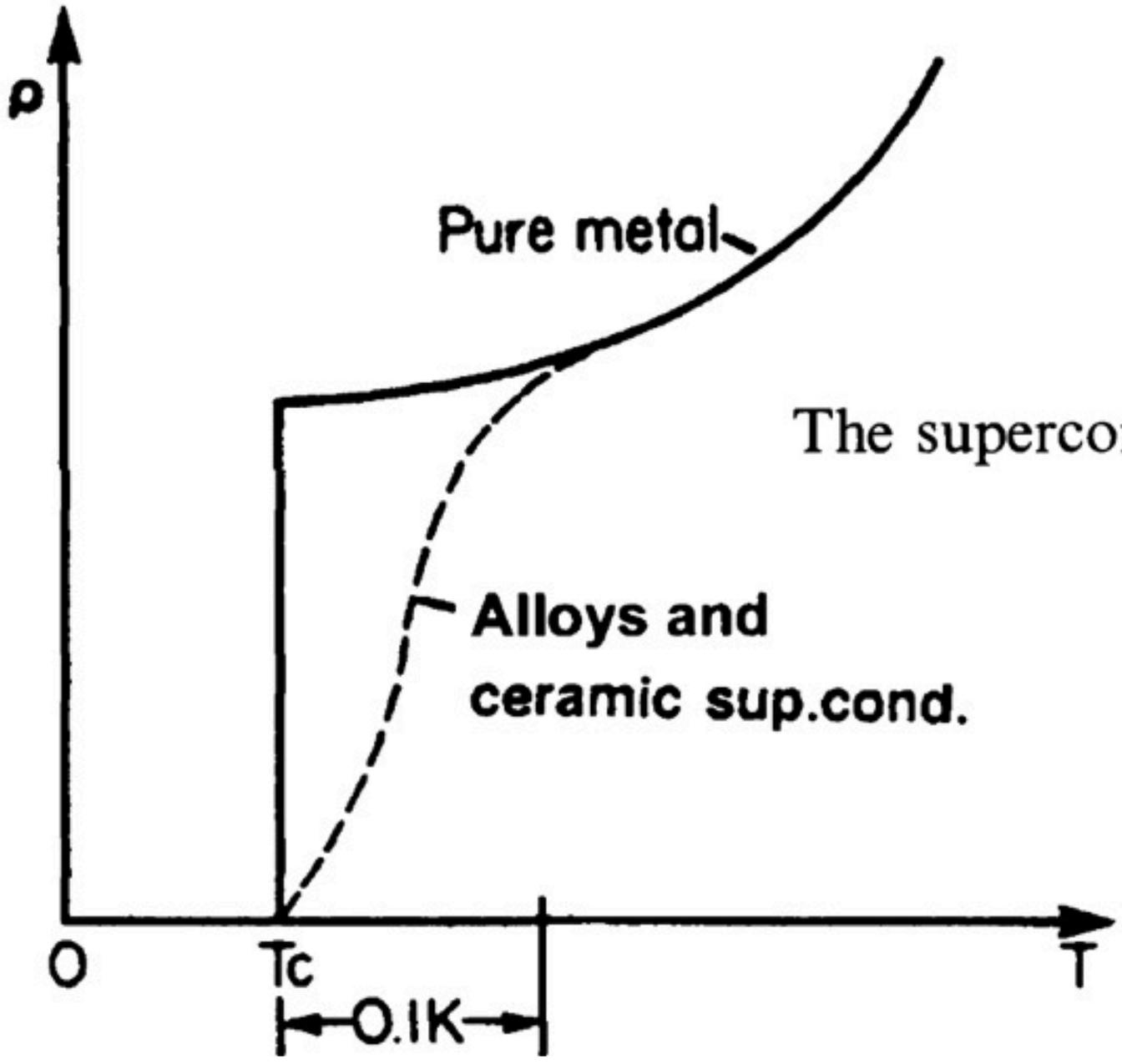
The resistivity of *two-phase alloys* is the sum of the resistivities of each of the components, taking the volume fractions of each phase into consideration

Kondo effect

Some alloys (copper with small amounts of iron, for example) show a minimum in the resistivity at low temperatures. This anomaly is due to additional scattering of electrons by the magnetic moments of the solutes and is a deviation from the Matthiessen rule (**Kondo effect**).



7.6. Superconductivity



The superconducting transition is reversible

T_c is the transition or critical temperature

Critical Temperatures of Some Superconducting Materials

Materials	T_c [K]	Remarks
Tungsten	0.01	—
Mercury	4.15	H.K. Onnes (1911)
Sulfur-based organic superconductor	8	S.S.P. Parkin et al. (1983)
Nb_3Sn and Nb–Ti	9	Bell Labs (1961), Type II
V_3Si	17.1	J.K. Hulm (1953)
Nb_3Ge	23.2	(1973)
La–Ba–Cu–O	40	Bednorz and Müller (1986)
$YBa_2Cu_3O_{7-x}$[a]	92	Wu, Chu, and others (1987)
$RBa_2Cu_3O_{7-x}$[a]	~92	R = Gd, Dy, Ho, Er, Tm, Yb, Lu
$Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$	113	Maeda et al. (1988)
$Tl_2CaBa_2Cu_2O_{10+\delta}$	125	Hermann et al. (1988)
$HgBa_2Ca_2Cu_3O_{8+\delta}$	134	R. Ott et al. (1995)

high-T_c superconductors

Superconductors having a T_c above 77 K (boiling point of liquid nitrogen) are technologically interesting because they do not require liquid helium (boiling point 4 K) or liquid hydrogen (boiling point 20 K) for cooling.

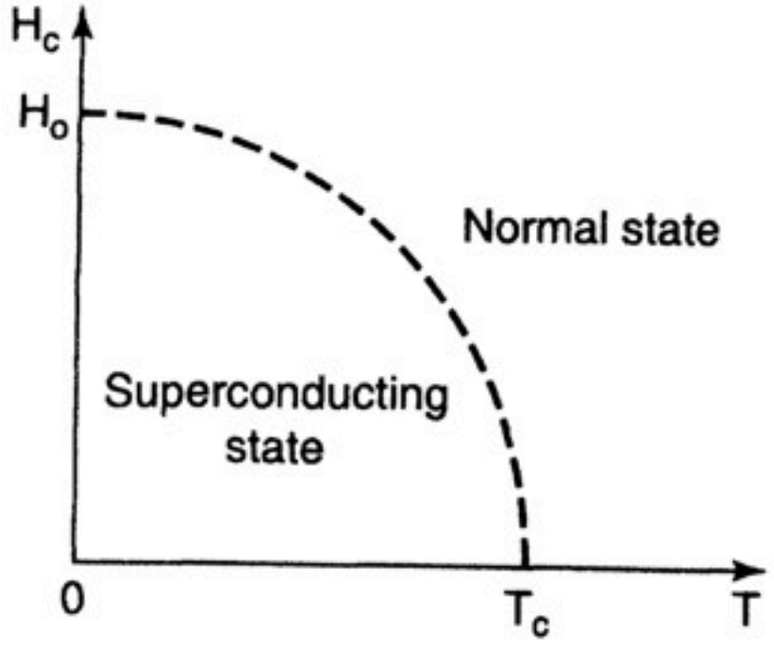
A zero resistance combined with high current densities makes superconductors useful for strong electromagnets, as needed, e.g., in magnetic resonance imaging devices (used in medicine), high-energy particle accelerators, or electric power storage devices. (The latter can be appreciated by knowing that once an electrical current has been induced in a loop consisting of a superconducting wire, it continues to flow without significant decay for several weeks.) Further potential applications are lossless power transmission lines, high-speed levitated trains, more compact and faster computers, or switching devices called cryotrons. (The latter device is based on the destruction of the superconducting state in a strong magnetic field, see below).

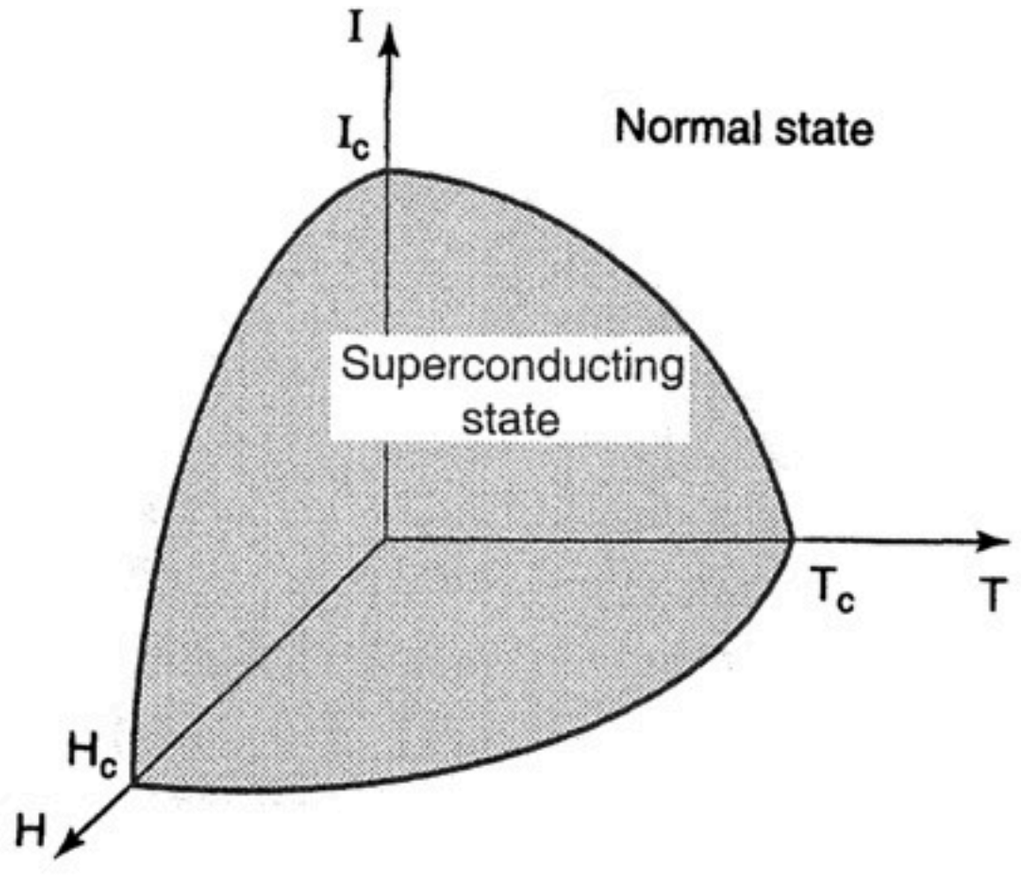
$$P = I^2 R$$

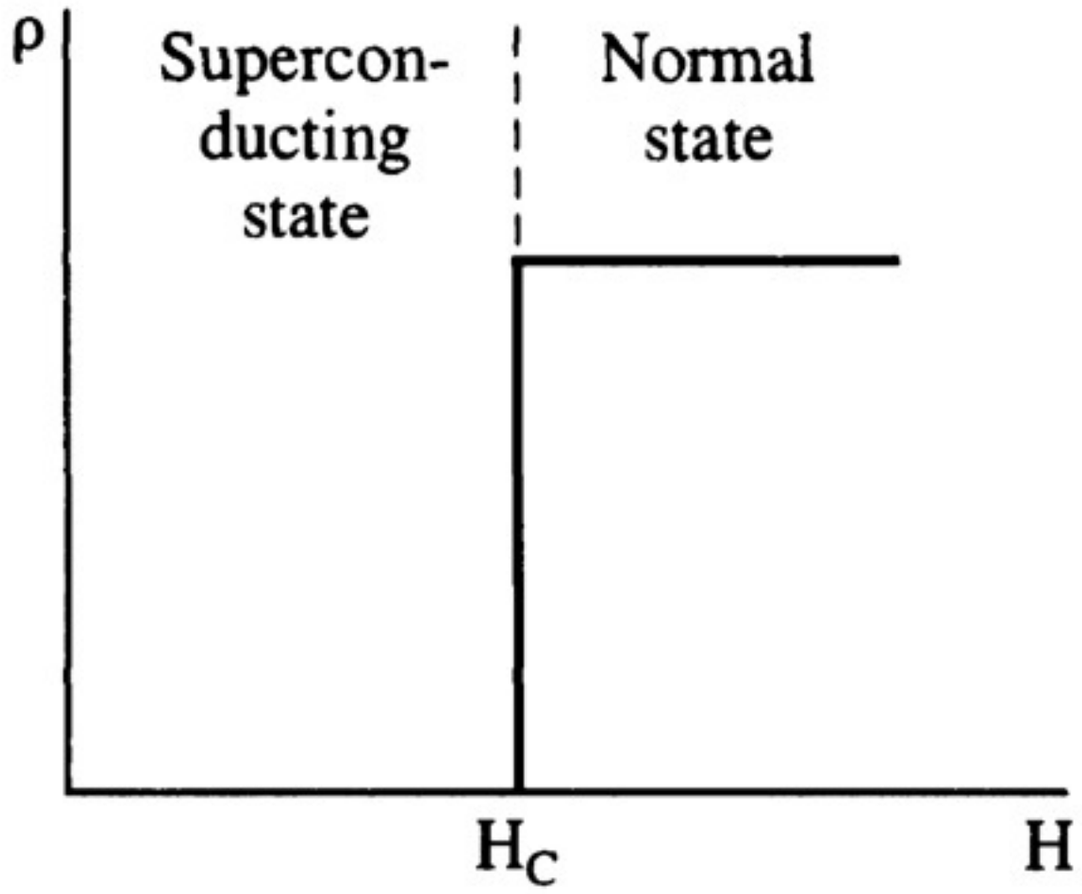
Elimination of the superconducting state does not only occur by raising the temperature, but also by subjecting the material to a strong magnetic field

$$H_c = H_0\left(1 - \frac{T^2}{T_c^2}\right)$$

where H_0 is the critical magnetic field strength at 0 K. Ceramic superconductors usually have a smaller H_c than metallic superconductors, i.e., they are more vulnerable to lose superconductivity by a moderate magnetic field.







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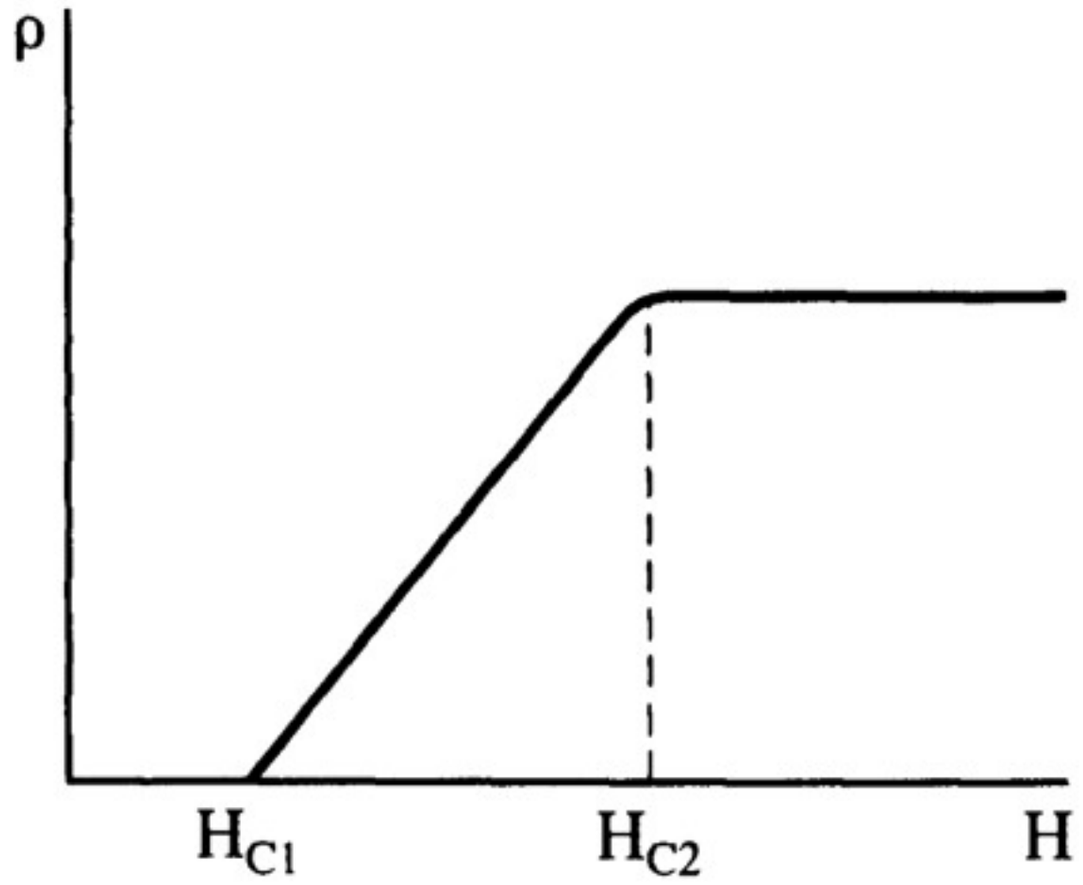

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