Electrical Transport in Liquid Metals

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ELECTRICAL TRANSPORT IN LIQUID METALS

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These are preliminary lecture notes, intended only for distribution to participants. Missing or extra copies are available from Room 230.

I) Introductory remarks

These lecture notes contain a short summary of the main ideas and equations for the course on transport in liquid metals. More details will be given in the course or in seperate discussions. Sections II to IV present the more or less "well established" approach to transport in disordered metals and is limited in the applications to liquid metals. In section V some new approaches to strong disorder are presented which are perhaps more important for amorphous metals, besides their general interest.

Since this is a "pedagogical" text rather than a complete review on the subject, the choice of references may be biased by the author's judgement of their importance as a help to understand the main ideas and is certainly incomplete. Here is a list of important textbooks and recent conference proceedings:

J.M. ZIMAN	Electrons and Phonons (Clarendon Press, Oxford, 1960)
W. JONES, N.H. MARCH	Theoretical Solid State Physics (Wiley, Interscience Monographs, vol. 27, 1973) vol. 2
J.M. ZIMAN	Models of Disorder (Cambridge Univ. Press, 1979)
M. SHIMOJI	Liquid Metals (Acad. Press, 1977).

"Liquid and amorphous metals", NATO Adv. Study Institute, Series E36; Sijthoff and Noordhoff, 1980; eds. : E. Lüscher, H. Coufal.

"Liquid metals", M. Shimoji, Acad. Press, 1977.

"Glassy metals", Springer, Topics in applied physics, vol. 46, 1981; eds. : H.-J. Güntherodt, H. Beck.

"LAM 4", Conference Proceedings, Journal de Physique C-8, tome 41, August 1980.

"Liquid metals", Inst. of Physics Conf. Series 30, 1976; eds. : R. Evans, D.A. Greenwood.

II.) Basic notions

A metal is a two-component system of ions of charge Ze and valence electrons, described by the following Hamiltonian:

$$H = H_{el} + H_{ion} + H_{el-ion} \tag{2.1}$$

$$H_{el} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{ij}{}' \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \tag{2.2}$$

$$H_{ion} = \sum_n \frac{P^2(n)}{2M} + \frac{1}{2} \sum_{nm}{}' \frac{(Ze)^2}{|\vec{R}_n - \vec{R}_m|} \tag{2.3}$$

$$H_{el-ion} = \sum_{in} V(\vec{r}_i - \vec{R}_n) + \sum_{in} J(\vec{r}_i - \vec{R}_n)\, \vec{\sigma}_i \cdot \vec{S}_n \tag{2.4}$$

Here and in the following $\vec{P}_n, \vec{R}_n$ and $\vec{S}_n$ denote ionic momenta, positions and spins, respectively, whereas position, momentum and spin of the i-th electron are denoted by $\vec{r}_i, \vec{p}_i$ and $\vec{\sigma}_i$. Before specifying the electron-ion interaction in more detail let us sketch the aims of a complete theory of liquid metals:

(a) Equilibrium properties: Hamiltonian (2.1) should provide the electronic density of states, the equilibrium charge densities and information about the one-electron stationary states. Moreover the electronic screening will lead to effective interactions between the ions, which determine the ionic structure and their dynamics [These topics are dealt with in the lectures by Gautier, Hafner, March, Finney, Hansen].

(b) Non-equilibrium phenomena: This field comprises electrical conductivity and other transport coefficients like thermopower and Hall coefficient and ionic transport [see the lectures by Gerl)

For discussing electrical transport in a disordered metal we may assume the ionic structure to be given. For many purposes it is sufficient to know the static ionic structure factor defined by

$$S(q) \equiv \frac{1}{N} \sum_{n,m} e^{i\vec{q}\cdot(\vec{R}_n - \vec{R}_m)} - N \delta_{\vec{q},\vec{0}} \qquad (2.5)$$

which is the Fourier transform of the pair correlation function g (Ω_0 = atomic volume):

$$S(q) - 1 = \frac{1}{\Omega_0} \int d\vec{r}^{\,3}\, e^{i\vec{q}\cdot\vec{r}} \left[g(r) - 1 \right] \qquad (2.6)$$

For a crystal $S(\vec{q})$ consists of sharp "Bragg peaks" at all the reciprocal lattice vectors, which is characteristic of long range translational order. For a liquid metal of macroscopic volume $S(q)$ is a smooth function, whose structure describes the short range order of such a system (see Fig. 1)

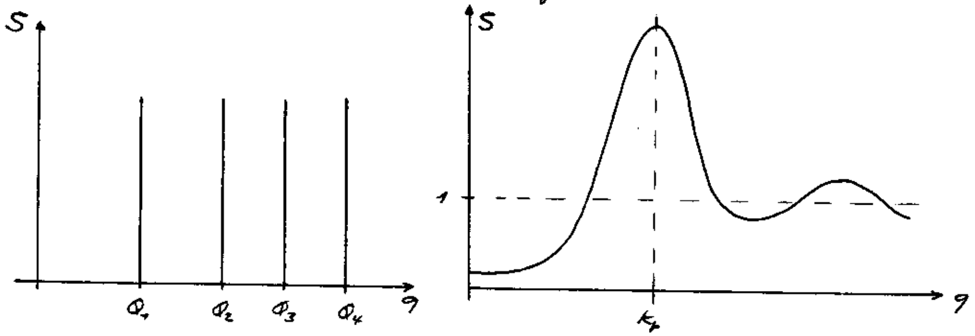


Fig. 1: Static structure factor for a crystal (in some direction of $\vec{q}$-space)

Typical static structure factor of a liquid metal (k_p = position of the first peak)

The sums in (2.5) can be taken over the ionic positions of one given metal sample (at some time t). Often

it is more convenient to define $S(q)$ and $g(r)$ as configurational averages over an ensemble of systems with the same macroscopic properties [1].

The temperature dependence of $S(q)$, which will be of importance later on, is shown in Fig. 2

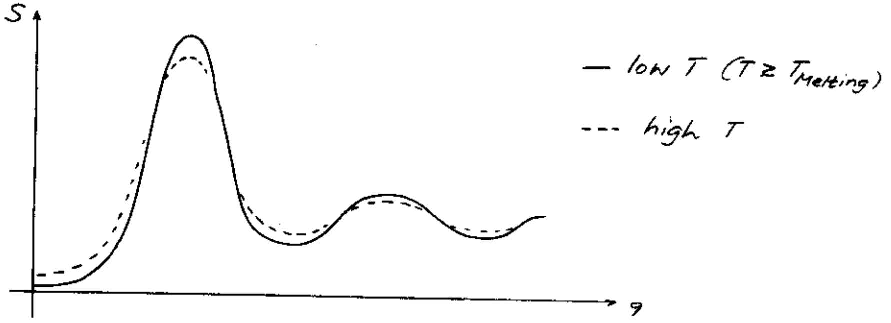


Fig. 2: Schematic T-dependence of $S(q)$

For an alloy containing N_α ions of species α, partial structure factors can be defined [1]:

$$S_{\alpha\beta}(q) \equiv (N_\alpha N_\beta)^{-\frac{1}{2}} \sum_{n_\alpha=1}^{N_\alpha} \sum_{n_\beta=1}^{N_\beta} e^{i\vec{q}\cdot(\vec{R}_{n_\alpha} - \vec{R}_{m_\beta})} - (N_\alpha N_\beta)^{1/2} \delta_{\vec{q},\vec{0}} \qquad (2.7)$$

Later on dynamic structure factors

$$S(q,\omega) \equiv \frac{1}{N} \sum_{n,m} \int dt\, e^{-i\omega t} e^{i\vec{q}\cdot(\vec{R}_n(t) - \vec{R}_m(0))} \qquad (2.8)$$

(and correspondingly the partials) will also be important

Structure factors can be measured by neutron or x-ray diffraction. Where such experimental results are not available (specially for alloys where only few partials have been measured) model forms can be used, such as the Percus-Yevick result for hard spheres.

When we consider the ionic positions as given parameters (at some time t) the electrons move in a fixed random potential given by (2.4). For the electron-ion interaction we distinguish two cases:

(a) "Simple" metals (examples see below)

V(r) is given by a (weak) pseudopotential (see Hafner's lectures). In its simplest (local and energy independent) form it is given by a Coulomb tail and some constant value inside the ionic core.

(b) Transition metals, rare earths

Here V(r) will be an "atomic" potential (such as it is used for bandstructure calculations) containing the nuclear attraction and repulsion, exchange and correlation with the core electrons.

(c) Magnetic ions

If the ions carry a magnetic moment, due to localized f (or d) electrons, its effect on the conduction electrons can be represented by an "exchange function" J(r). More details will be given in the application to liquid Gd in section IV.

Finally, in the spirit of a local density functional approach the explicit electron-electron interaction in (2.2) is replaced by introducing screened electron-ion interactions. For simple metals linear screening amounts to replacing the Fourier transform $\tilde{V}(q)$ of the pseudopotential by $\tilde{V}(q)/\varepsilon(q)$, where ε is a suitable dielectric function of the homogeneous interacting electron gas [2]. In the "atomic" potentials screening is built in from the beginning by the electrostatic and the exchange and correlation interactions with the core electrons. Screening by the conduction electrons can be taken into account by using atomic wave functions, or by using self-consistently screened potentials obtained from band structure calculations for the corresponding crystalline solids. In practice one usually adopts the "muffin-tin" picture: each ion is surrounded by a sphere and the potential within such a sphere is calculated on the basis of the total charge density contained in it. The potential outside the spheres (which should not overlap) is assumed to be constant. For the practical evaluation of such potentials atomic wave functions tabulated by Herman and Skillman [4] can be used, following the "Mattheiss procedure" [5]. Alternatively, self-consistent potentials from band-structure calculations are now also available [6].

We have thus reduced our problem to one of non-interacting electrons in a given external potential U:

$$H_e = \sum_i \left[\frac{p_i^2}{2m} + U(\vec{r}_i, \vec{\sigma}_i)\right] \qquad (2.9)$$

with

$$U(\vec{r}, \vec{\sigma}) = \sum_n \left[V(\vec{r} - \vec{R}_n) + J(\vec{r} - \vec{R}_n)\,\vec{\sigma}\cdot\vec{S}_n\right] \qquad (2.10)$$

The price we have to pay for the simplicity of (2.10) is that U should be determined self-consistently through the equilibrium electronic charge densities.

Before dealing with transport problems we should now determine the equilibrium electronic structure on the basis of (2.9). This is already a difficult problem owing to the disorder in the ionic positions (and possibly their spins). In the absence of systematic theoretical results we shall take the following point of view:

(a) For simple metals we shall use the free electron approximation for the conduction electrons. Photoemission experiments have indeed shown that in many cases the density of states is well represented by its free electron form. Deviations could in principle be calculated by a perturbation expansion with respect to V or by introducing phenomenologically some parameters like an effective mass.

(b) In the case of metals with unfilled atomic d-states it will turn out to be crucial to take into account at least some general features of the electronic structure in order to develop a consistent picture of transport phenomena. Typically the band structure of, say, a crystalline transition or noble metal shows the following overall features (see Fig. 3):

(i) At low energies (near the bottom of what is called the "conduction band") and at high energies the dispersion is quite free-electron like. The corresponding (s-like) density of states forms some sort of "background" extending through the whole band.

(ii) At intermediate energies we find many rather flat bands made up predominantly by d-states. They contribute to a high d-like density of states

Such a behavior is easily understood, at least qualitatively, in a tight binding scheme, where we start from atomic s- (and possibly p) and d-states and allow for hybridization.

In a disordered metal we expect to find an electron structure which is not totally different, since — again in the tight binding approach — many features of the electron states are determined by short range rather than long range ionic order [7]. This is corroborated by the fact that the electronic density of states $D(E)$ does not change drastically when going from a crystalline to a disordered form of the same metal

(except that fine structures caused by van Hove singularities are usually washed out) as photoemission experiments often show. Indeed, experimental data for $D(E)$ are often reproduced qualitatively by band structure calculations for the crystalline phase [8]. Moreover, various multiple scattering calculations (see section III) for $D(E)$ have produced some kind of isotropic "average band structure" for liquid transition or noble metals, which again shows the main properties of a hybridized s-d band [9].

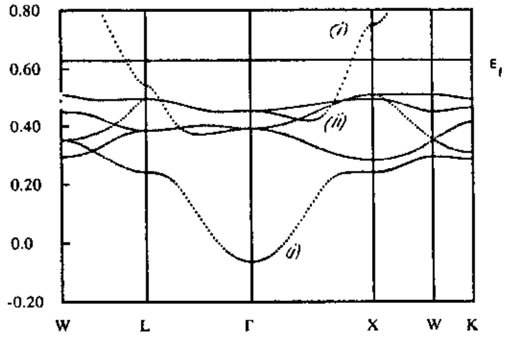
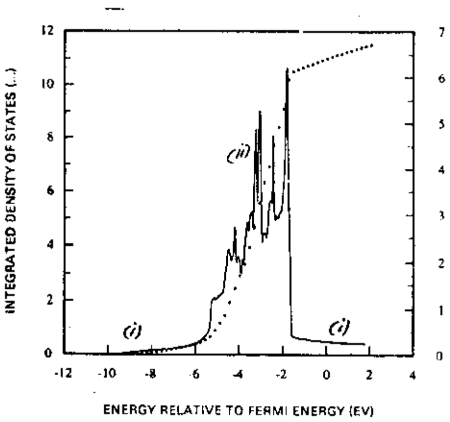


Fig. 3

Band structure of crystalline Cu [6]



Density of electronic states of crystalline Cu [6].

At the end of this section let us present a classification of the various metals which will be discussed subsequently:

(a) Simple metals (weak "scatterers"):

- Alkali metals (Li, Na, K, Rb, Cs)
- Alkaline earths (Be, Mg, Ca, ...)
  (some of the heavier ones are actually strong scatterers!)
- Polyvalent metals (Al, Ga, In, Si, Ge, Sn, Pb, Sb, Bi, ..)

(b) Non-simple metals (strong electron scatterers)

- Noble metals (Cu, Ag, Au)
- Early transition metals (TM), (Sc, Y, Ti, Zr, V, Nb ...)
- Late transition metals (Fe, Co, Ni, Pd, ...)
- Rare earths (RE)
- Actinides

III) General transport theory

Measurements of transport coefficients are done by applying external fields to the system (electric field $\vec{E}$, temperature gradient $\vec{\nabla}T$, etc.) and measuring the current $\vec{j}$ flowing in response to this external perturbation. For our system, described by (2.9), the electrical current operator can be defined in second quantization by

$$\vec{j}(\vec{r}) = -e \sum_{\vec{k}\vec{q}} \sum_{s} e^{i\vec{q}\cdot\vec{r}} \frac{\vec{k}}{m} a^{+}_{\vec{k}+\frac{1}{2}\vec{q},s}\, a_{\vec{k}-\frac{1}{2}\vec{q},s} \qquad (3.1)$$

where $a^{+}_{\vec{p}s}$ $(a_{\vec{p}s})$ is a creation (annihilation) operator of an electron with momentum $\vec{p}$ and spin s (i.e z-component of the spin with respect to some axis). Therefore the basic quantity to be calculated is the electronic distribution function

$$f_s(\vec{k},\vec{r},t) = \sum_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} \left\langle a^{+}_{\vec{k}+\frac{1}{2}\vec{q},s}\, a_{\vec{k}-\frac{1}{2}\vec{q},s} \right\rangle_t \qquad (3.2)$$

where $\langle\cdot\rangle_t$ is a quantum mechanical average over a density matrix whose time evolution includes the effect of the external field. We briefly sketch two different approaches to evaluating (3.2): a (non-equilibrium) "scattering approach" and a linear response approach involving equilibrium correlation functions.

3.1) "Scattering approach"

Suppose the metallic sample M, described by (2.9), is embedded in a "free electron sea" (Fig. 4). The electron states outside M are plane waves, which are scattered by M. The probability per unit time of a transition from $(\vec{k}s)$ to $(\vec{k}'s')$ is given by

$$W(\vec{k}s,\vec{k}'s') = \frac{v(\vec{k}s)}{\Omega} \frac{d\sigma}{d\Omega} \qquad (3.3)$$

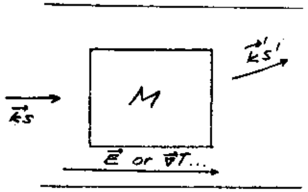


Fig. 4: Plane wave scattered from a piece of metal.

where Ω = volume, $\frac{d\sigma}{d\Omega}$ = scattering cross-section of M, $v(\vec{k}s) = \frac{\hbar k}{m}$ = velocity of the incoming electron stream.

Now, our distribution function f_s will be given by the Fermi distribution N_0 plus a deviation φ_s. For small external fields the latter will obey a linear Boltzmann equation (see, e.g., [10]):

$$\frac{\partial\varphi_s}{\partial t} + \vec{v}\cdot\frac{\partial\varphi_s}{\partial\vec{r}} - e\vec{E}\cdot\frac{\partial N_0}{\partial\vec{k}} + \vec{v}\cdot\vec{\nabla}T\,\frac{\partial N_0}{\partial T} = \int d^3k' \sum_{s'} W(\vec{k}s,\vec{k}'s')\left[\varphi_s(\vec{k}) - \varphi_{s'}(\vec{k}')\right] \tag{3.4}$$

This equation is simplified if we consider a homogeneous steady state situation and by introducing the spin sum, which has to be done in (3.1):

$$\varphi \equiv \sum_s \varphi_s \quad \text{and} \quad \overline{W} \equiv \frac{1}{2}\sum_{ss'} W(s,s'). \tag{3.5}$$

Then, the transport equation

$$-e\vec{E}\cdot\frac{\partial N_0}{\partial\vec{k}} + \vec{v}\cdot\vec{\nabla}T\,\frac{\partial N_0}{\partial T} = \int d^3k'\,\overline{W}(\vec{k},\vec{k}')\left[\varphi(\vec{k}) - \varphi(\vec{k}')\right] \tag{3.6}$$

describes the balance between the external forces and the collisions inside M. If the scatterer M is macroscopically isotropic (i.e. $\overline{W}$ depends only on k and on $q = |\vec{k}-\vec{k}'|$), eq. (3.6) can be solved exactly [10] by introducing the relaxation time

$$\tau^{-1}(k) \equiv \frac{2\pi}{\Omega}\int_{-1}^{+1} d(\cos\theta)\,(1-\cos\theta)\,\overline{\frac{d\sigma}{d\Omega}}(k,q) \tag{3.7}$$

where θ is the scattering angle between $\vec{k}$ and $\vec{k}'$. The

current is then linearly related to the driving forces:

$$\vec{j} = L_1\vec{E} + L_2\vec{\nabla}T \tag{3.8}$$

with

$$L_1 = -|e|\sum_{\vec{k}} \vec{v}\cdot\frac{\partial N_0}{\partial\vec{k}}\,\tau(k) \tag{3.9}$$

$$L_2 = |e|\sum_{\vec{k}} v^2(k)\,\frac{\partial N_0}{\partial T}\,\tau(k) \tag{3.10}$$

For calculating the electrical (isothermal) conductivity σ, we put $\vec{\nabla}T = 0$ and identify σ with L_1, whereas the thermopower Q is given by L_2/L_1. The Hall coefficient will be discussed later in this section.

This result is (in some sense) exact [11]. For practical calculations we have to find approximations for $\frac{d\sigma}{d\Omega}$.

(a) Weak scattering limit

If the electron-ion interaction is given by a weak (screened) pseudopotential $\hat{V}$, as it is assumed for simple metals, the cross-section can be evaluated in Born approximation; by using (2.10) with $J=0$:

$$\begin{aligned} \overline{\frac{d\sigma}{d\Omega}}(|\vec{k}|,q) \propto \left|\langle\vec{k}|\,U\,|\vec{k}'\rangle\right|^2 &= \left|\int d^3r\, e^{i\vec{q}\cdot\vec{r}}\,U(\vec{r})\right|^2 \\ &= \int d^3r\,d^3r'\, e^{i\vec{q}\cdot(\vec{r}-\vec{r}')}\sum_{nm}\hat{V}^*(\vec{r}-\vec{R}_n)\,\hat{V}(\vec{r}'-\vec{R}_m) \\ &= \sum_{nm} e^{i\vec{q}\cdot(\vec{R}_n-\vec{R}_m)}\,|\hat{V}(\vec{q})|^2 \\ &= N\,S(q)\,|\hat{V}(q)|^2 \end{aligned} \tag{3.11}$$

Inserting this into (3.9,10) and using the free electron relation $k_F^3 = 3\pi^2\Omega_0$ (Ω_0 = atomic volume) yields, at low T:

$$\text{Resistivity} \quad \rho \equiv \sigma^{-1} = \frac{3\pi\Omega_0 m^2}{4e^2\hbar^3 k_F^6}\int_0^{2k_F} dq\, q^3\, S(q)\,|\hat{V}(q)|^2 \tag{3.12}$$

Thermopower: $$Q = \frac{\pi^2 k_B T}{3|e|} \left.\frac{\partial \ln \rho(E)}{\partial E}\right|_{E=E_F} \qquad (3.13)$$

with $$\rho(E) = E^{-3} \int_0^{2\sqrt{\frac{\hbar E}{m}}} dq\, q^3 S(q) \left|\hat{V}(q)\right|^2 . \qquad (3.14)$$

These are the results of what is called "Ziman theory" or "diffraction model" or "weak scattering limit" of electronic transport in liquid metals. There are two immediate generalizations:

(i) For a liquid alloy partial structure factors show up in the "Ziman integral", e.g. in the resistivity:

$$\rho = \frac{3\pi^2 \Omega_0 m^2}{4 e^2 \hbar^3 k_F^6} \int_0^{2k_F} dq\, q^3 \sum_{\alpha\beta} (x_\alpha x_\beta)^{1/2} \hat{V}_\alpha(q) \hat{V}_\beta^*(q) S_{\alpha\beta}(q) \qquad (3.15)$$

where $\hat{V}_\alpha$ and x_α are pseudopotential and concentration of species α.

(ii) A more complete theory takes account of inelastic electron-ion collisions [12]. The result is the same as (3.12)-(3.14), but the static structure factor is replaced by an integral over the dynamic one:

$$S(q) \longrightarrow \int d\omega\, S(q,\omega) \frac{\hbar\beta\omega}{e^{\hbar\beta\omega} - 1} \qquad \left(\beta = \frac{1}{k_B T}\right) \qquad (3.16)$$

This generalization due to Baym [12] is used for calculating transport coefficients for amorphous metals, specially at low T. In liquid metals T is above the Debye temperature, so the factor $\hbar\beta\omega/[e^{\hbar\beta\omega}-1]$ can be replaced by unity and we are back to $S(q)$. It is interesting to note that in this temperature domain where the restrictions on the inelastic processes — due to the Bose factor in (3.16) — are no more important, integrating over all inelastic collisions (all ω) yields the same result as our static theory which led to (3.11).

(b) Multiple scattering expansion

Formally, in scattering theory, the cross-section $\frac{d\sigma}{d\Omega}$ is determined by the T-matrix of the system:

$$\frac{d\sigma}{d\Omega}(\vec{k} \to \vec{k}') = \frac{16\pi^4 m^2}{\hbar^4} \left|T(\vec{k},\vec{k}')\right|^2 \qquad (3.17)$$

The many-ion T-matrix is expanded in terms of single-ion t-matrices and the free-electron Green function G_0:

$$T = \sum_n t_n + \sum_{n,m}{}' t_n G_0 t_m + \dots \qquad (3.18)$$

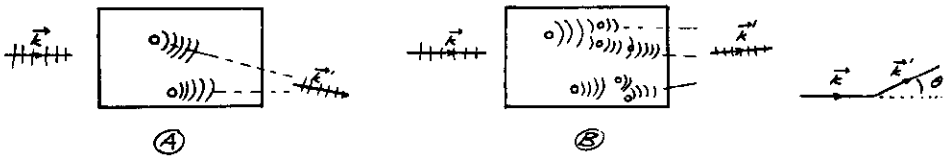


Fig. 5: A) Single-site scattering: only wavelets scattered from one ion are superposed.
B) Multiple scattering: scattered wavelets are allowed to scatter again from other ions.

If we neglect multiple scattering (restriction to case A in Fig. 5) we obtain

$$\frac{d\sigma}{d\Omega} = \sum_{n,m} e^{i\vec{q}\cdot(\vec{R}_n - \vec{R}_m)} \left|t(q,E)\right|^2 \qquad (3.19)$$

a result which has the same structure as (3.11). The single-site t-matrix, which replaces the pseudopotential in the previous formulae, depends on $E = \frac{\hbar^2 k^2}{2m}$ and on the momentum transfer $q = 2k \sin\frac{\theta}{2}$. For spherical potentials it can be expressed by the phase-shifts δ_ℓ:

$$t(q,E) = -\frac{2\pi\hbar^3}{\Omega_0 m\sqrt{2mE}} \sum_\ell (2\ell+1) P_\ell(\cos\theta) \sin\delta_\ell(E)\, e^{i\delta_\ell(E)} \qquad (3.20)$$

(P_ℓ = Legendre polynomial).
The final results for ρ and Q have the same form as (3.12–14), but $\hat{V}(q)$ is replaced by $t(q,E)$ in (3.14) and by $t(q,E_F)$ in (3.12), E_F being the Fermi energy.

For simplicity we have omitted spin indices in these formulae. It is, however, straightforward to include exchange scattering in this approach. The term $\sum_n J(\vec{r}-\vec{R}_n)\vec{\sigma}\cdot\vec{S}_n$ acts like a random magnetic field on the electron spin. The t-matrix is then really a 2×2 matrix in spin-space and (3.17) reads, in the single-site approximation:

$$\overline{\frac{d\sigma}{d\Omega}} = \frac{16\pi^4 m^2}{\hbar^4}\,\frac{1}{2}\sum_{ss'}\sum_{nm} t^{(n)}_{ss'}\,t^{(m)*}_{s's} \qquad (3.21)$$

The spin $\vec{S}_n$ of an individual ion sets an orientation in space, such that the most general form of t is [13]:

$$t^{(n)}_{ss'} = a\,\delta_{ss'} + b\,\vec{\sigma}_{ss'}\cdot\vec{S}_n \,. \qquad (3.22)$$

The coefficients a and b are best evaluated in the representation where the total spin $\vec{J}=\vec{\sigma}+\vec{S}_n$ is diagonal. There are then two scattering amplitudes t_J for $J = S\pm 1/2$, each given by a series like (3.20) where the phase-shifts depend on J. The relation to (3.22) is found by

$$b = \frac{2}{2S+1}\left(t_+ - t_-\right)\ ,\quad a = \frac{1}{2S+1}\left[(S+1)t_+ - S t_-\right] \qquad (3.23)$$

where S is the quantum number of the ionic spin and $t_\pm = t_J$ for $J = S\pm 1/2$. Inserting (3.22) into (3.21) yields, instead of (3.19):

$$\overline{\frac{d\sigma}{d\Omega}} = \frac{1}{2}\sum_{ss'}\sum_{nm} e^{i\vec{q}\cdot(\vec{R}_n-\vec{R}_m)}\left(a^*\delta_{ss'} + b^*\vec{\sigma}_{ss'}\cdot\vec{S}_n\right)\left(a\,\delta_{ss'} + b\,\vec{\sigma}_{s's}\cdot\vec{S}_m\right) \qquad (3.24)$$

Besides the usual (positional) structure factor for the ions we have to introduce spin correlation functions

$$\langle \vec{S}_n\cdot\vec{S}_m\rangle = \begin{cases} S(S+1) & n=m \\ S(S+1)\,\frac{1}{3}\,\hat{M}\left(|\vec{R}_n-\vec{R}_n|\right) & n\neq m \end{cases} \qquad (3.25)$$

We have assumed that the spin-spin correlation function depends only on the distance of the ions.

The final result for the resistivity is (compare with (3.12)):

$$\rho = \frac{3\pi\Omega_0 m^2}{4e^2\hbar^3 k_F^6}\int_0^{2k_F} dq\, q^3\left[S(q)R_1(q) + (1+M(q))\left(R_2(q)-R_1(q)\right)\right] \qquad (3.26)$$

Here $M(q)$ is the Fourier transform of the product $\hat{M}(r)g(r)$, and

$$R_1(q) = \left|\sum_J \frac{2J+1}{2(2S+1)}\,t_J\right|^2 \qquad (3.27a)$$

$$R_2(q) = \sum_J \frac{2J+1}{2(2S+1)}\,|t_J|^2 \qquad (3.27b)$$

are "coherent" and "incoherent" averages of the t_J's.

In principle it would be straightforward to include some "multiple scattering terms" from (3.18) into this formalisme. However, they would involve higher order ionic correlation functions, which are generally unknown and have to be approximated in some way. A favorite choice is the "quasi crystalline" approximation which amounts to factorizing successively the higher order ionic correlation function, such that the result is again of the form (3.12), but the quantity which replaces $\hat{V}(q)$ is now a structure dependent t-matrix [11].

The Hall coefficient is also easily evaluated in the framework of a relaxation time approximation to the collision operator (which was exact in our previous analysis!). Including the Lorentz force the transport equation reads:

$$-e\left(\vec{E}+\vec{v}\times\vec{B}\right)\frac{\partial f}{\partial \vec{k}} = -\frac{\varphi}{\tau} \qquad (3.28)$$

In a typical Hall geometry $\vec{B}=(0,0,B)$, $\vec{E}=(E_x,E_y,0)$ and $\vec{j}=(j_x,0,0)$. The result for the Hall coefficient for small B is

$$R_H \equiv \frac{E_y}{Bj_x} = \frac{3}{8\pi|e|}\,\frac{\int_0^\infty dk\, k\,\tau^2(k)\,v^2(k)\,\frac{dN_0}{dk}}{\left(\int_0^\infty dk\, k^2\tau(k)\,v(k)\,\frac{dN_0}{dk}\right)^2} \qquad (3.29)$$

At low T: $\frac{dN_0}{dk}=-\delta(k-k_F)$. Due to the isotropy of the system the relaxation time then drops out of (3.29), and we are left with the free electron value

$$R_H = -\frac{3}{8\pi|e|k_F^3} = -\frac{1}{n_c|e|} \qquad (3.30)$$

Thus the Hall coefficient would be a direct indicator of the density n_c of conduction electrons (see section IV). Unfortunately the measured values of R_H often do not seem to give the "right" values of n_c and are even positive in many instances. For magnetic materials this can be due to the "extraordinary" contribution to the Hall field E_y, measured by R_2:

$$E_y = (R_1B + R_2M)j_x \qquad (3.31)$$

and due to the (permanent or field induced) magnetic moment M. If M is "induced" by B, then $M=\chi B$ and the total Hall coefficient

$$R_H \equiv \frac{E_y}{Bj_x} = R_1 + R_2\chi \qquad (3.32)$$

contains the magnetic susceptibility χ. Other special features of disordered metals, such as electron life times, non-monotonic dispersion or multi band electron structure (see the end of section II) might also yield deviations from (3.30) – introducing, for instance, hole-like conduction – but these possibilities have not been checked in detail up to now.

3.2) "Linear response" approach

We have to calculate $\langle\vec{j}(\vec{r})\rangle_t$, the expectation value of (3.1), as an average over a density operator ρ whose time evolution includes the external field:

$$i\frac{\partial\rho}{\partial t} = \left[H_e - e\sum_i \vec{E}(t)\cdot\vec{r}_i\,,\,\rho\right] \qquad (3.33)$$

Splitting ρ into $\rho_{eq}\propto e^{-\beta H_e}$ and a deviation linear in $\vec{E}$ we find for an isotropic system:

$$\langle\vec{j}\rangle_\omega = \sigma(\omega)\,\vec{E}(\omega). \qquad (3.34)$$

The frequency dependent conductivity

$$\sigma(\omega) = \int_0^\infty dt\, e^{-i\omega t}\int_0^\beta d\lambda\,\langle\vec{j}(0)\cdot\vec{j}(t+i\lambda)\rangle_{eq} \qquad (3.35)$$

is given by an equilibrium current correlation function. Eq. (3.35) – called "Kubo formula" for σ – is again exact for weak fields. The difficulty lies in evaluating this correlation function for a disordered system. Since (2.9) treats the electrons as independent the two-electron correlation function

$$\langle\vec{j}(0)\cdot\vec{j}(t)\rangle = \sum_{\vec{k}\vec{k}'}\vec{v}(\vec{k})\cdot\vec{v}(\vec{k}')\,\langle a^+_{\vec{k}}a_{\vec{k}}\,a^+_{\vec{k}'}(t)\,a_{\vec{k}'}(t)\rangle \qquad (3.36)$$

immediately factorizes into a product of two one-electron correlation functions. Taking the configurational average over an ionic ensemble yields translationally invariant correlation functions, but the average of (3.36) is not equal to the product of the averages of the corresponding one-electron functions. Let us mention two approaches to the evaluation of (3.36):

(a) Derive a rigorous "Bethe-Salpeter" equation for (3.36), which involves the average one-electron functions and a kernel ("vertex part") [14]. In the limit where the life-time of an "average plane wave state" near the Fermi surface is long, one can arrive at the same results for ρ as our eq's. (3.12, 19, 26), by solving the Bethe-Salpeter equation (which is actually equivalent to a linearized transport equation). This is reassuring, since it justifies the "scattering approach" of subsection 3.1 from a different point of view.

(b) The "coherent potential approximation" (CPA), which has proven to be very useful for evaluating equilibrium properties of disordered systems [15] is used to calculate (3.36). However, this approach has mainly been limited to disordered crystalline alloys, since it is not easy to incorporate the structure factor of a topologically disordered system like a liquid metal. Moreover, even for weak scattering potentials the so-called "vertex-corrections" yielding the $\cos\theta$-term in (3.7) are usually missing [16].

Let us finally mention that there exist more sophisticated approaches, trying to go beyond the single-site t-matrix result [17] using heavy "many-body machinery". However, the formal results seem to be too complicated in most cases to be amenable to numerical calculations. In section V we will address ourselves specifically to the problem of "strong scattering" in disordered metals and present some new ideas which have been put forward recently.

IV) Application to liquid metals

Our results for the resistivity ρ and the thermopower Q for disordered metals, which can be found in the "scattering approach" of section III ("diffraction model") can be summarized as follows

$$\rho = \frac{3\pi\Omega_0 m^2}{4e^2\hbar^3 k_F^6}\, I\,, \qquad I = \int_0^{2k_F} dq\, q^3 S(q)\, A(q,E_F) \tag{4.1}$$

$$Q = -\frac{\pi^2 k_B^2 T}{3|e|\,E_F}\left[3 - \frac{1}{I}\left(8k_F^4 S(2k_F)\,A(2k_F,E_F) + \int_0^{2k_F} dq\, q^3 S(q)\,\frac{\partial A(q,E_F)}{\partial \ln E_F}\right)\right] \tag{4.2}$$

where

$$A(q,E_F) = \begin{cases} |\hat{V}(q)|^2 & \text{for simple metals} \\ |t(q,E_F)|^2 & \text{for TM, RE} \end{cases} \tag{4.3}$$

and spin disorder scattering has been left out for the moment.

Before reporting on concrete calculations let us focus on the T-dependence of these quantities. Besides the explicit T-factor in Q the main T-dependence comes from the structure factor, as shown in Fig. 2. The temperature coefficient (TC) of the resistivity, for example,

$$\alpha \equiv \frac{1}{\rho}\frac{d\rho}{dT} \tag{4.4}$$

sensitively depends on the value of $2k_F$, see Fig. 6:

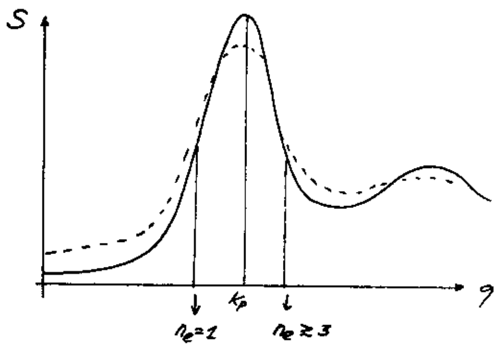


Fig. 6: $S(q)$ at 2 temperatures and three different positions of $2k_F$.

Since the factor q^3 in I gives most weight to the q-region just below $2k_F$, we expect

$$\alpha > 0 \quad \text{if} \quad 2k_F < k_p \quad \text{or} \quad 2k_F > k_p$$
$$\alpha < 0 \quad \text{if} \quad 2k_F \approx k_p \qquad (4.5)$$

Negative α's (which are exceptional for metallic conductivity from a "crystalline point of view") can therefore be expected for liquid metals when the number of conducting electrons per ion (n_e) is about 1.6 to 2, using the relation $k_F^3 = 3\pi^2 n_e/\Omega_0$. Then the most important momentum transfer ($2k_F$) for electronic backscattering coincides with the most important wave vector in the ionic structure. At higher T the ionic structure becomes more blurred which decreases the scattering probability. (4.5) is an important test for the validity of the diffraction model.

Let us now discuss some applications of (4.1-3) to various classes of liquid metals:

(a) Simple metals

Here n_e is taken to be the valence of the ions, and k_F and E_F are found in the quasi-free electron model. Many calculations of ρ and Q have been published using various pseudopotentials and structure factors (experimental and hard sphere model). On the whole the agreement with experiment is reasonable, but one has to admit that the results depend rather sensitively on the choice of $\hat{V}$ and $S(q)$. For pure metals α is usually positive, except, e.g., for Zn, where $2k_F \approx k_p$.

Rather than drawing conclusions from the comparison of one theoretical result with one experimental data point it is usually more informative to check general trends of $\rho(x,T)$ for alloys (binary, say) of concentration x.

To this end the "alloy generalization" of (4.1-3), discussed in section III, has to be used. The most sophisticated calculations are done by constructing pseudopotentials from first principles for each concentration (thus allowing for charge transfer). Screening is done by the best available $\varepsilon(q)$. The partial structure factors are taken from experiment wherever available or modelled by hard spheres, whereby packing fractions etc. are determined from thermodynamics using first principle ionic pair potentials (for details see Ref. [3] or original papers like [18]).

The T-dependence (4.5) can be checked very nicely on such alloys (whereby we will denote by k_p the position of the main peak of the total structure factor for simplicity)

(i) Components of equal valence (e.g. alloys of alkalis)

Here $2k_F$ does not change appreciably with concentration x. Thus $\alpha > 0$ for all x, if $\alpha > 0$ for both pure components. The behavior of ρ as a function of x is usually parabolic for monovalent and rather linear for polyvalent alloys, which is easily understood (see section 707 of [3]):

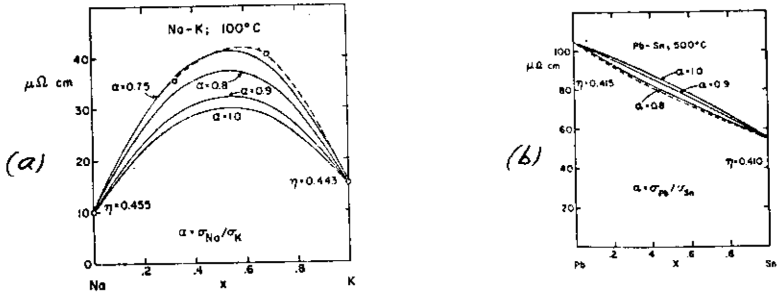


Fig. 7 : Resistivity for (a) Na-K alloy
(b) Pb-Sn alloy

(from [30])

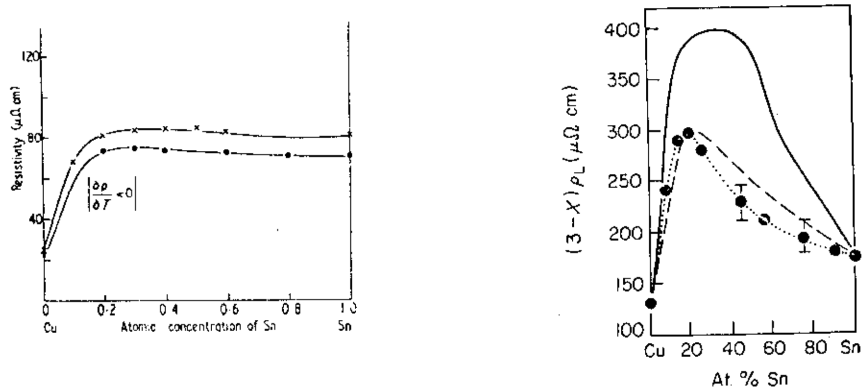
α = ratio of hard-sphere diameters

(ii) Components of different valence (e.g. Noble metal-polyvalent)

Here $2k_F$ changes with x. For an example like Cu-Sn (see Fig. 8) n_e goes from 1 (Cu) to 4 (Sn). There is an intermediate x-range where $2k_F$ crosses k_p. Here $\alpha < 0$ as expected, and moreover ρ itself has a rather high value, which is understood from (4.1) and Fig. 6: for $2k_F < k_p$ the integral I increases strongly with $2k_F$ (and thus with x), for $2k_F > k_p$ I still grows slowly, but the prefactor k_F^{-6} tends to suppress ρ again. This correlation between $\alpha < 0$ and high ρ-values will be discussed in section V.

The thermopower is somewhat more delicate to predict, since – according to (4.2) – it depends sensitively on the precise value of S and $\hat{V}$ at $2k_F$. Nevertheless in many cases the x-dependence is well reproduced (see Fig. 8), specially if the values of $S_{\alpha\beta}(2k_F)$ can be taken from experiment.

Fig. 8: Resistivity (a) and thermopower (b) of liquid CuSn.



(a)

From [19]

× theory

• experiment

(b)

From [3]

• experiments

(b) Strong scatterers (specially TM, RE and some alkaline earths)

In these systems the equilibrium electronic structure is already quite different from free-electron like. A thorough transport theory should therefore be based on a good approach to what we called "average band structure" in section II, e.g. by summing up sufficient terms of (3.18). In the absence of a systematic attempt in this direction the following simplified concept has been used:

Once the atomic muffin-tin potential is calculated energy dependent phase shifts $\delta_\ell(E)$ for $\ell = 0,1,2,3$ are evaluated. What we need in (4.1-3) is the various δ_ℓ near E_F – giving the scattering probability of a conduction electron near the Fermi surface – and $2k_F$, the maximum momentum transfer. The "Bristol group" (see, e.g., [19]) proceeded as follows:

(i) The bottom energy E_B of the lowest conduction band (see Fig. 3), which is usually free electron like, is evaluated by a Wigner-Seitz condition.

(ii) E_F is taken from solid band structure data.

(iii) k_F is determined by n_e, using the free-electron relation

$$k_F^3 = 3\pi^2 n_e / \Omega_0 \qquad (4.6)$$

(iv) An effective mass determined by $E_F = E_B + \frac{\hbar^2 k_F^2}{2m^*}$ is then introduced into (4.1-3).

This amounts in some sense to choosing, out of the complicated band structure of the type of Fig. 3, one free-electron like band (call it "s-p band") which starts at E_B and intersects the Fermi energy at a wave vector k_F. Its shape is determined such that the usual free-electron relations remain valid for a given n_e. Other bands (mostly d-like), which also intersect E_F, are neglected. This may be justified by invoking the lower mobility of d-electrons and has found some corroboration in first principle calculations of ρ for crystalline metals [20]. The crucial quantity is then n_e. For the alkaline earths an obvious and simple choice is $n_e = 2$ (valence). Calculations of ρ and Q for Ca, Sr, Ba done in this way have yielded reasonable agreement with experiment [21]. The high ρ-value of $306\,\mu\Omega\,cm$ of Ba is explained by large phase shifts, especially for $l=2$. Cs, under pressure, also acquires important d phase-shifts, leading to high resistivity [22].

For late TM, n_e is on the order of 1 or somewhat smaller. This "choice" is supported by two main pieces of evidence:

(i) Hall constant: For Ni, $R_H < 0$ and consistent with such a value of n_e. Co has $R_H > 0$. However, the extraordinary part can be subtracted by plotting R_H versus χ, according to (3.32). The remaining "normal" part corresponds to $n_e = 0.5$ [23].

(ii) Systematic studies of ρ for alloys of TM with monovalent and polyvalent metals have confirmed $n_e \leq 1$: $\alpha > 0$ for all x in the first case, whereas there is a region of x where $\alpha < 0$ in the second (e.g. FeGe...), namely when $2k_F = k_p$. This shows that late TM behave like monovalent as far as electrical transport is concerned.

The strong variation of ρ through the late TM is a consequence of $\delta_2(E_F)$ going through a resonance. At resonance $\delta_2 = \pi/2$, leading to a large value of t. Whereas the T-dependence of ρ is mainly governed by $S(q)$, the pressure dependence is also strongly influenced by the phase-shifts, changing due to density variations. Thus the resistivity of liquid Fe is predicted to decrease substantially at pressures that may be found in the interior of the earth [22].

More recently it has been suggested [24] that a consistent theory should also provide information about n_e and E_F, using the same type of approximation as for the calculation of ρ; and moreover the only relation between these quantities consistent with the free-electron boundary conditions in evaluating phase shifts is

$$E_F = \frac{\hbar^2 k_F^2}{2m} \qquad k_F^{\,3} = 3\pi^2 n_e / \Omega_0 \qquad (4.7)$$

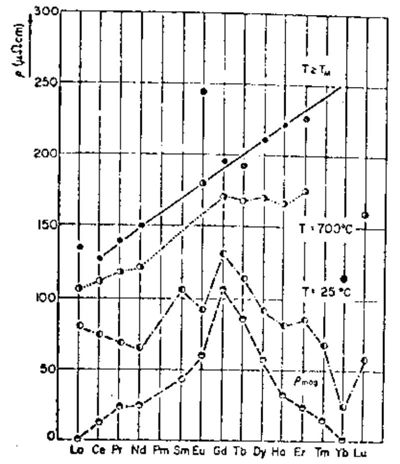
Imposing a reasonable value for E_F in (4.7) would, however, lead to $n_e \approx 1.2$ for Fe, e.g., and ρ would be much too high, owing to the relatively large $2k_F$-value in the Ziman integral (4.1) [24]. Actually, requiring (4.7) may be too stringent, since even in a KKR band structure calculation free electron boundary conditions are used for calculating $\delta_\ell(E)$.

In the rare earth series the elements Eu and Yb behave as divalent in the solid state. Their resistivities have been calculated by choosing $n_e = 2$. Their strongly different ρ-values, see Fig. 9, can be understood from the difference in the muffin-tin potentials. Since $2k_F \approx k_p$ the negative α is easily reproduced [25].

Fig. 9:

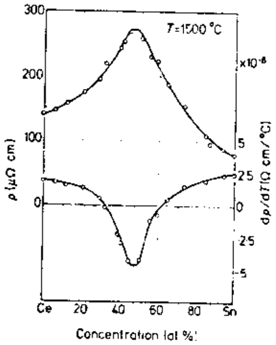
Resistivity of the RE series, at various temperatures.

(from [23])



For the remaining lanthanides, which have 3 s-d electrons in the outer shells, $n_e = 3$ has yielded reasonable ρ-values [26], but it is inconsistent with the temperature coefficients of alloys: $\alpha > 0$ for alloys of RE with monovalent metals, but $\alpha < 0$ in some domain for alloys with polyvalent metals, see Fig. 10.

Fig. 10
Resistivity ρ and temperature coefficient α for liquid Ce-Sn
(from [23])



In a different approach to the trivalent RE [27], the criticism of Ref. [24] has been "taken seriously":

(i) From the phase-shifts the total integrated density of states (containing the first scattering correction to the free electron value N_{FE}):

$$N(E) = N_{FE}(E) + \frac{2}{\pi} \sum_{\ell} (2\ell+1)\, \delta_\ell(E) \qquad (4.8)$$

is used to find E_F by putting $N(E_F) = 3$ (= valence).

(ii) The partial s-p integrated density of states

$$N_{sp}(E) = \frac{2}{\pi} \sum_{\ell=0}^{1} (2\ell+1)\, \delta_\ell(E) + N_{FE}(E) \qquad (4.9)$$

yields the number of effectively current carrying electrons:

$$n_e = N_{sp}(E_F) \quad \text{and} \quad k_F^3 = 3\pi^2 n_e / \Omega_0 . \qquad (4.10)$$

This choice of k_F is, in general, not consistent with the requirement (4.7) and yields too high values for ρ.

(iii) $E_B = E_F - \frac{\hbar^2 k_F^2}{2m}$ is the bottom of the conduction band. $E_B \neq 0$ is a sign that the ionic potentials change sufficiently the electron structure such that "incoming" electrons have an approximate dispersion relation

$$E(k) = E_B + \frac{\hbar^2 k^2}{2m} \qquad (4.11)$$

rather than simply $\hbar^2 k^2/(2m)$. In order to take this effect of the medium outside a muffin-tin into account the single-ion potential was then given the value E_B outside the ionic spheres (rather than zero). Thus the modified "consistency relation"

$$E_F - E_B = \frac{\hbar^2 k_F^2}{2m} \qquad (4.12)$$

was fulfilled for the scattered electrons at the Fermi surface [27]. The calculated ρ-values were then in good agreement with experiment. Moreover the trend of ρ and of α through the series was traced back to a systematic variation of n_e, going from about 0.6 for La to about 1.3 for Lu. This is in good agreement with the number of s-p-like Bloch states in crystalline band structure calculations [28]. For Lu it leads to $2k_F \leq k_p$, which explains the slightly negative α in that case. Thus, a consistent picture of ρ and α for RE and their alloys has been achieved on the basis of (4.1). It is interested to note that incorporating multiple scattering effects into the calculation of ρ for transition metals [11], as discussed in section III, has also produced a reduction of ρ in many cases, like the above mentioned incorporation of an effective medium into the ionic potential.

For Gd the effect of s-f exchange scattering has also been investigated [29]. The exchange function $J(r)$

in eq. (2.10) was taken from solid state band structure calculations. The main result is that the total resistivity of Gd is only about 5 to 10 percent higher than without s-f scattering, which is consistent with the rather monotonic behavior of ρ through the RE series, without showing any higher values for the magnetic elements in the liquid state. At room temperature ρ has its maximum at Gd, which was previously explained by spin-disorder scattering. It is still not clear why the situation changes so drastically between the solid at ambient T and the liquid phase.

$\underline{V}$) Beyond weak (single-site) scattering

In this final section we briefly sketch some "new ideas", how to calculate transport coefficients when the electron-ion interaction is strong. Most of these approaches can equally be applied to liquid and to solid disordered metals, such as random alloys or metallic glasses.

In order to illustrate that even our single-site t-matrix approach is questionable in many cases we estimate the mean free path $\bar{\ell} \equiv v_F \bar{\tau}$ of a conduction electron with Fermi velocity, $\bar{\tau}$ being a mean relaxation time entering the "kinetic formula" $\rho = m/(ne^2\bar{\tau})$ with $n = n_e/\Omega_0$. We find typically $\bar{\ell} \approx 250/\rho$, given in Å, when ρ is inserted in $\mu\Omega$cm. Thus the mean free path becomes as short as an average interionic distance d, when ρ is bigger than about 100 to 200 $\mu\Omega$cm. It is clear that under these circumstances the neglect of multiple scattering is hard to justify. [On the other hand one should be a bit cautious about the statement "$\bar{\ell} < d$ makes no sense", since the scattering potential is, of course, non-zero also "between ions"].

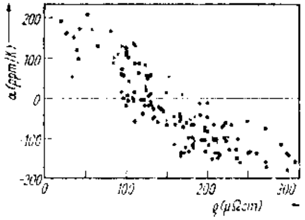
Thus there are two main problems with high resistivity, disordered metals:

(i) A "sound" theoretical approach should go beyond single-site scattering. Such methods are not yet readily available for concrete calculations.

(ii) The fact that many different materials, liquid or solid, show negative α calls for a "universal" explanaiton. More precisely there seems to be a correlation between $\alpha < 0$ and high ρ-values, which is often referred to as "Mooij's rule", although Mooij [31] had originally observed it for disordered transition metal alloys only. Fig. 11, where the data of many such alloys are compiled, shows that $\alpha < 0$ typically when $\rho > \rho_c \approx 150\ \mu\Omega$cm.

Fig. 11

"Mooij's rule":
Correlation between $\alpha \equiv \frac{1}{\rho}\frac{d\rho}{dT}$
and ρ for various
transition metal alloys
(from [31])



Let us disregard the above formal criticism (i) and review the success and failure of the "diffraction model" of section $\underline{III}$ concerning (ii):

(a) The ρ-values calculated this way are "reasonable" and often allow to understand the "basic trends". The price to pay is a possibly "inconsistent" $k_F \leftrightarrow E_F$ relation or the use of an ad hoc renormalization of the electron-ion potential (see RE calculations) in order to "save" the $k_F \leftrightarrow E_F$ relation. Moreover the inclusion of some multiple scattering [11] seems to improve the results more or less systematically.

(b) Many negative α – for pure metals like Ba, Eu, Yb, Lu or for heterovalent alloy series – can be understood consistently on the basis of the structure factor and the number of conduction electrons, which are two very general features of a disordered metal. There are also correlations between ρ and Q: the second term in the bracket of (4.2) is expected to be important when $2k_F \simeq k_p$ (and if the energy variation of the third term is small). Thus the condition (4.5) for $\alpha < 0$ would yield $Q > 0$. This is indeed observed, for example in glassy BeTiZr [32].

(c) In some sense Mooij's rule is also predicted: if in an alloy, like Ce-Sn in Fig. 10 and many others, the resistivity has a high value in the intermediate concentration range, this is also typically the domain where $\alpha < 0$. On the other hand exceptions from this rule, like liquid Eu and Yb, which have both $\alpha < 0$ but very different ρ-values (Fig. 9), can also be understood (see section $\underline{\text{IV}}$).

(d) There are, however, counter-examples, such as the alloy $Gd_{67}Co_{33}$ [8] which has a pronounced negative α, both in the liquid and glassy phase, but according to our "rules" (section $\underline{\text{IV}}$) for the number of conduction electrons $2k_F$ is expected to lie below k_p. Thus, either α is negative against the rules (4.5) or there is sufficient "rearrangement" of the electron structure in the alloy, such that n_e is not the weighted sum of the values for pure Gd and Co.

In the remainder of this section we shall present very briefly some recent developments towards a more rigorous transport theory (Other models, like Mott's "s-d scattering" [33] or "tunnelling models" for low T [34] will not be considered here).

① Precursor effects of "localization"

It is well known that strong disorder in a system described by (2.9) can lead to the existence of localized eigenstates (Anderson localization) [35]. In a one-band model density of states $D(E)$ and mobility $\sigma(E)$ are thought to have the behavior of Fig. 12:

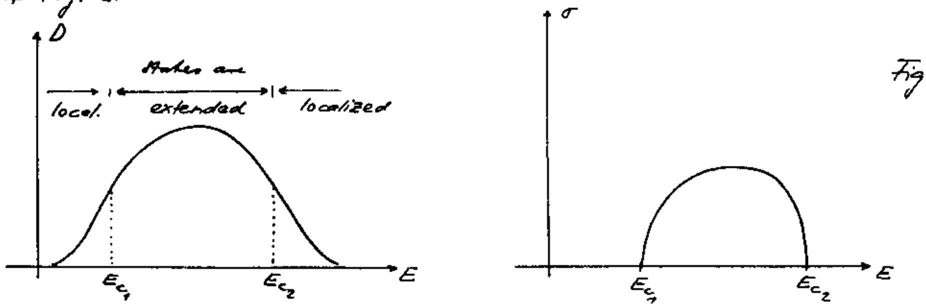


Fig. 12

If E_F lies in the region of localized states ($E_F < E_{c_1}$ or $> E_{c_2}$) the $T=0$ conductivity of the system vanishes. If E_F is between the mobility edges E_{c_i} the conductivity is metallic like in our liquid and amorphous metals or in disordered alloys. At $T>0$ the conductivity will be finite even in the first case, due to two mechanisms:

(i) electrons are thermally activated into extended states (respectively: holes are created in such states). This leads to thermally activated transport like in crystalline semiconductors.

(ii) Interaction with phonons allow the electron to hop from one localized state to another (thermally activated hopping).

In a disordered metal we may see "precursors" of these effects even though the states at E_F are extended, if E_F is close enough to E_{c_1}, say. Both effects can then be visible:

(i) The conductivity $\sigma(T)$ can be calculated as

$$\sigma(T) = \int_{E_{c_1}}^{E_{c_2}} dE \, \sigma(E) \left[4T \cosh^2\left(\frac{E-E_F}{2k_BT}\right)\right] \qquad (5.1)$$

If $\sigma(E)$ varies strongly near E_F this may yield appreciable T-dependence of σ, especially $\alpha > 0$.

(ii) Although the eigenstates near E_F are in principle extended, there "shape" is very different from a plane wave with a constant amplitude. The probability density $|\psi|^2$ will be large in some regions only, which are linked by "bottlenecks" of small amplitude, see Fig. 3:

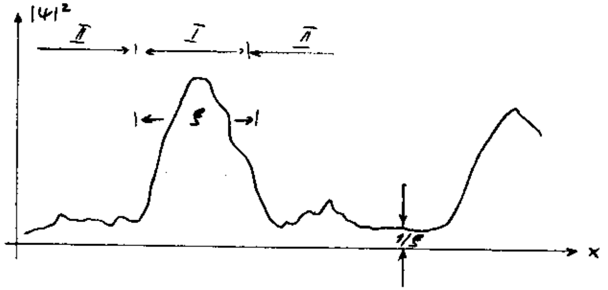


Fig. 13: electronic wave function in strongly disordered system.

If the electron is in region I electron-phonon collisions tend to attenuate the electrical current, contributing to a finite resistivity, whereas in regions of type II, phonons may "help" the electron to get through the bottleneck, thereby effectively decreasing ρ.

② Scaling theory

Various authors have developed a scaling formalism to describe localization [36]. Imry has then incorporated the above mechanism (ii) into this scaling approach [37]. The main quantity is some correlation length ξ which diverges when the Anderson transition is approached by, for instance, shifting E_F through E_{c_1}. In the "localized phase" ($E_F < E_{c_1}$) ξ is the localization length, whereas in the "extended phase", ξ has the geometrical meaning shown in Fig. 13., caracterizing

the extent of regions I and the width of the bottlenecks [37]. At $T=0$ scaling yields

$$\sigma \propto \frac{e^2}{\hbar \xi} \qquad (5.2)$$

in the extended phase. At $T>0$ electron-phonon collisions introduce another length l_{ph}, the inelastic mean free path. If $l_{ph} > \xi$ there is a weak T-dependence like in "usual metals", whereas, if $l_{ph} < \xi$, (4.2) has to be replaced by

$$\sigma \propto \frac{e^2}{\hbar l_{ph}} \qquad (5.3)$$

which yields $\alpha < 0$.

③ Non-adiabatic treatment of electron-phonon interaction

Electron-ion interactions are usually treated in the "adiabatic approximation" [10]. However, Girvin and Jonson [38] have recently pointed out that, owing to strong disorder, the electronic self-energy may vary rapidly on an energy scale of the order of a phonon energy, which invalidates the adiabatic approximation. They have evaluated the Kubo expression (3.35) for a tight-binding model on a "Cayley tree" and found that Mooij's rule could be reproduced when the frequency dependence of the electron self-energy accounted for the energy transfer between electrons and phonons.

④ Self-consistent transport equations

This approach, elaborated by Götze and collaborators [39], is perhaps the most promising, since it covers the weak-scattering limit (Ziman theory), it produces localization for strong disorder and it seems to be amenable to numerical calculations and to various generalizations. The main idea is to derive a transport equation like (3.4) for linear response functions such as (3.36), but with a collision kernel W (see eq. (3.41)) which self-consistently depends on the two-electron correlation function (3.36). Götze achieved this goal by using Mori's projector technique for deriving equations of motion for dynamical correlation functions but other many-body techniques, such as Green functions, would also do. The key quantity is the electronic density response function

$$\Phi_{\vec{k}\vec{k}'}(\vec{q}z) \equiv (-i)\int_0^\infty dt\, e^{izt} \langle [f_{\vec{k}}(\vec{q}t), f^+_{\vec{k}'}(\vec{q})] \rangle \qquad (5.4)$$

with $$f_{\vec{k}}(\vec{q}) = a^+_{\vec{k}+\frac{1}{2}\vec{q}}\, a_{\vec{k}-\frac{1}{2}\vec{q}} \qquad (5.6)$$

(see eq. (3.2)). Φ satisfies a linear integral equation [since the electrons are non-interacting] which involves the random potential $\mathcal{U}$ of eq. (2.9). When this equation is averaged over ionic configurations, the average of products like $\langle \mathcal{U}\Phi \rangle$ can be expressed by a self-energy C:

$$\left(z - \vec{q}\cdot\frac{\vec{k}}{m}\right)\hat{\Phi}_{\vec{k}\vec{k}'}(\vec{q}z) + \sum_{\vec{k}''} C_{\vec{k}\vec{k}''}(\vec{q}z)\,\hat{\Phi}_{\vec{k}''\vec{k}'}(\vec{q},z) = \delta_{\vec{k}\vec{k}'}\left[N_0(\vec{k}+\tfrac{\vec{q}}{2}) - N_0(\vec{k}-\tfrac{\vec{q}}{2})\right] \qquad (5.6)$$

where $\hat{\Phi}$ is the averaged Φ and $N_0(\vec{k})$ the equilibrium electronic distribution function. To lowest order in $\mathcal{U}$, C is given by

$$C_{\vec{k}\vec{k}''}(\vec{q}z) = \sum_{\vec{p}} \langle |\mathcal{U}(\vec{q}-\vec{p})|^2 \rangle \left[H_{\vec{k}+\frac{\vec{q}-\vec{p}}{2},\, \vec{k}''+\frac{\vec{q}-\vec{p}}{2}}(\vec{p}z) + \ldots \right] \qquad (5.7)$$

The missing terms (..) involve the same function H – the solution of (5.6) with the right hand side put equal to $\delta_{\vec{k}\vec{k}'}$ – but with different arguments. The aim is now to solve the generalized collision equation (5.6) together with (5.7). This is conveniently done by "projecting" $\hat{\Phi}$ onto the two important hydrodynamic variables "density" $\hat{\rho}$ and "current" $\vec{j}$:

$$\hat{\rho}(\vec{q}z) = \sum_{\vec{k}\vec{k}'} \hat{\Phi}_{\vec{k}\vec{k}'}(\vec{q},z) \qquad j(\vec{q}z) \equiv \sum_{\vec{k}\vec{k}'} \frac{\vec{k}\cdot\vec{k}'}{m^2}\,\hat{\Phi}_{\vec{k}\vec{k}'}(\vec{q},z) \qquad (5.8)$$

and by evaluating the "current relaxation time" $\tau \equiv M^{-1}$ with

$$M = B \sum_{\vec{k}} \langle |\mathcal{U}(\vec{k})|^2 \rangle\, k^2 \hat{\rho}(\vec{k},0) \qquad (5.9)$$

B involving various constants. M is directly proportional to the resistivity of the system. Solving the linear transport equation (3.4) or (5.6) in a relaxation time approximation like (3.21) by taking into account, however, the conserved quantity "density", one finds that $\hat{\rho}(q,z)$ has a rather different behavior, depending on whether $\Omega\tau \ll 1$ or $\Omega\tau \gg 1$ ($z = \Omega + i\varepsilon$)

(i) $\Omega\tau \gg 1$ (few collisions):

$$\hat{\rho}(q,\Omega) \propto \left[\Omega^2\left(1 - \frac{i}{\Omega\tau}\right) - q^2 v_F^2\right]^{-1} \qquad (5.10)$$

This corresponds to wave-like propagation of density disturbances ("zero sound").

(ii) $\Omega\tau \ll 1$ (many collisions):

$$\hat{\rho}(q,\Omega) \propto \left[\Omega - i q^2 v_F^2 \tau\right]^{-1} \qquad (5.11)$$

This is a hydrodynamic mode of diffusive character.

Inserting a result like (5.10) into (5.9) in the weak scattering limit reproduces Ziman's results (3.7), (3.10) for the resistivity. For very strong scattering, however, inserting (5.11) into (5.9) yields a non-linear equation for M:

$$M = \alpha M + \beta M^{-1} + o(M^{-3}), \qquad (5.12)$$

α and β being related to $\langle |\mathcal{U}|^2 \rangle$. For large M the result is

$$M = \left(\frac{\beta}{1-\alpha}\right)^{1/2} \qquad (5.13)$$

i.e. M diverges, when $\alpha \to 1$. This corresponds to localization ($\sigma \to \infty$, $\rho \to \infty$) due to strong disorder. Thus, this theory allows to cover — in an approximate way — the whole range between weak and strong disorder scattering.

Here are some results, which can be obtained in this framework:

(i) For a given potential U, the resistivity ρ can be evaluated in a self-consistent way, going beyond second order perturbation theory. The results for ρ turn out to be higher than in second order (because the system tends towards "localization") by up to 30-40 % for systems like polyvalent liquid metals are alkaline earths.

(ii) By varying the Fermi energy the function $\sigma(E)$ needed in (5.1) can be evaluated. This has been used for calculating $\sigma(T)$ for alloys like $La_{1-x}Sr_xVO_3$ or Sb-doped Ge — systems which show a metal-insulator transition, which is probably due to disorder [40].

(iii) Including an additional term, describing randomness in the kinetic energy of the electrons, in (2.9), it has been shown [41] that an increase of the disorder can lead to a decrease of ρ, if the latter is relatively high. Such a behavior would be compatible with Mooij's rule, the increase in disorder then being due to higher temperatures.

It seems evident that these "new ideas" are promising new approaches to strongly disordered electron systems, but they definitely need more refining. More numerical calculations have to be done and the influence of electron-phonon, as well as electron-electron interactions has to be investigated.

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