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Free Electron Characteristic Peculiarities Caused by Lattice Vibrations in Metals

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Abstract

It is shown that the traditional explanation of the free electron properties, such as mean free electron path, drift mobility, and the relaxation time, by lattice vibrations, is not valid for real free randomly moving (RM) electrons in materials with degenerate electron gas. It is shown that the effective density of the free RM electrons in elemental metals is completely determined by density-of-states at the Fermi surface and by absolute temperature. The study has shown that the lattice vibrations excite not only the free RM electrons but also produce the same number of weakly screened ions (so-named electronic defects), which cause the scattering of the free RM electrons and related electron kinetic characteristics.

Keywords

Metals, Free Randomly Moving (RM) Electron Density, Density-of-States (DOS) Probability Density, Electronic Defects, Lattice Vibration

1. Introduction

Electron transport in metals during the last century was explained on the presumption that all valence electrons are free, and can freely move, and can be scattered, but this proposition contradicts the Fermi-Dirac statistics [1] [2] [3]. In order to obtain the correct order of the conductivity and correct temperature variation, it was necessary to assume that the mean free electron path is of order a few hundred interatomic distances, and which steeply increases at low temperatures.

According to quantum mechanics, the free electrons as Bloch waves can freely move in the ideal periodic lattice of the metal with the periodic distribution of the potential energy without any scattering by lattice ions [4] [5] [6]. It means that the scattering of the free randomly moving (RM) electrons can be only in the spots where there are distortions of the periodicity of the potential energy of the ideal lattice structure. The distortions of the periodic potential distribution in real metals are caused by the presence of impurities, interstitials, vacancies, dislocations, limits of the grains, and by the surface of the tested samples that create a resistance to current flow. The electron mean free path due to the named defects almost does not depend on temperature, and their dominance appears at very low temperatures, and it causes the residual resistivity of the metal. But in a very wide temperature range, the resistivity depends on temperature as T at a temperature above the Debye's temperature, and at a temperature below the Debye's temperature it usually changes as T^{-5} [7], and it is considered that such resistivity dependence is caused by the lattice vibrations [8] [9] [10] [11] [12]. Such a model cannot explain why the real electron mean free path is about one or two orders larger than the interatomic distance. So, the lattice vibrations play another role, and another model is needed to explain this role. This work is a sequel to the work [1], in which the metal properties have been investigated in temperature range over the Debye temperature. In this work, the basic metallic properties in all temperature ranges and what peculiar roles the lattice atom vibrations play are presented.

2. Presentation Details and Analysis

2.1. The Effective Density of Free RM Electrons in Elemental Metals

According to quantum mechanics, the electrons in ideal periodicity material are arranged in energy bands according to the Bloch waves, and each primitive cell exactly contributes only one independent value of the wave vector to each energy band [4] [8] [13]. It does not depend on the atom or electron masses. The energy of the valence electron in metal is smaller than in an isolated atom. This decrease in the energy of the valence electrons causes the binding energy between atoms in metals [5] [13] [14]. The valence electron wave functions due to interaction with neighbor atom ions substantially overlap [8] [13] [14] but these electrons remain associated with the native ions. So, the valence electron charge cloud density is concentrated around the parent ions. The thermal vibrations of the lattice atoms stimulate the excitation of a small part of valence electrons, whose energy is close to the Fermi level energy, to leave the native atoms, and produce the Brownian motion in the metal. Therefore, the term of the free electrons can be used only for randomly moving electrons, which the effective density is described as [1] [2]:

$$n_{\text{eff}}=\int_0^\infty g(E)\,f(E)\left[1-f(E)\right]\mathrm{d}E=kT\int_0^\infty g(E)\left[-\partial f(E)/\partial E\right]\mathrm{d}E\,, \qquad (1)$$

where the member $f(E)\left[1-f(E)\right]$ describes the probability that at a given temperature T electron is in the energy level E, and also it has the capability to leave this energy level. The Equation (1) is valid for all homogeneous materials with degenerate and non-degenerate electron gas. From this equation also follows that the term

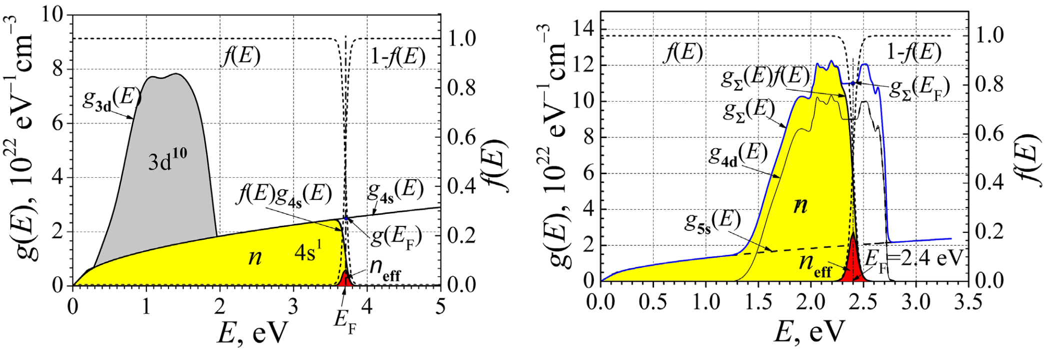
$$p(E) = \left(-\partial f(E)/\partial\eta\right) = f(E)\left[1 - f(E)\right]/kT \tag{2}$$

is the probability density function which means that an electron having the energy E can randomly move and change its energy due to scattering or due to electric field influence; η is the chemical potential. The other part of valence electrons ($n - n_{\text{eff}}$) cannot change its energy or be scattered by lattice atom vibrations because the lattice atom vibration energy is too small to excite them into free energy levels near the Fermi level. Moreover, these electrons cannot change their energy because all neighbor energy levels are occupied, and energy variance of those electrons is equal to zero. Thus, that part of electrons is localized, and moves around the native ions. It is important to point that free RM electrons in equilibrium conditions do not interact with those ($n - n_{\text{eff}}$) electrons, because the latter due to Pauli exchange principle cannot change their energy. That part of valence electrons can only be excited by high energy photons as in the photoemission experiment.

Taking into consideration [12] [15], a schematic hypothetical illustration of density-of-states (DOS) of s-states and d-states distributions on energy for noble (a) and transition (b) group metals at room temperature are presented in **Figure 1**.

In the case of the noble metals (**Figure 1(A)**), the *s*-band is half-filled, but there is also a complex set of *d*-band that occupy the region lying a few electronvolts lower from the Fermi level energy [4] [15]. The yellow area below the curve $g_s(E)f(E)$ of the *s*-band represents the total density of the valence electrons in the conduction band; the red area corresponds to the area evaluated by Equation (1) and represents the effective density of the RM electrons for $E_F = 3.5$ eV at $T = 295$ K. It is seen that *d*-band does not influence the density of the RM electrons, but they can influence some optic and other properties of noble metals [4].

In transition metals, the *d*-band lies high up in conduction band and extends through the Fermi level energy. Considering that *d*-band is not completely filled,



(A) (B)

Figure 1. Schematic hypothetical illustration of function $g(E)$ and $g(E)f(E)$ dependences on energy (A) for noble and (B) for transition group metals at room temperature. The yellow area represents the total density n of the valence electrons in the conduction band, and the red area represents the effective density n_{eff} of the free RM electrons; $g_\Sigma(E) = g_{5s}(E) + g_{4d}(E)$.

a particular part of *d*-electrons, which energy is close to the Fermi level energy, can be excited, can randomly move, and can take part in the conductivity, as it does *s*-band electrons near the Fermi level energy. The total effective density of the RM electrons is equal to $n_{\text{eff}} = g_{\Sigma}(E_{\text{F}})kT = \left[g_{\text{s}}(E_{\text{F}}) + g_{\text{d}}(E_{\text{F}})\right]kT$, where $g_{\Sigma}(E_{\text{F}})$ is the total DOS at the Fermi surface, which is obtained from the electronic heat measurement results. A schematic illustration of the DOS distribution on energy for transition metals is shown in Figure 1(B). From the comparison of Figure 1(A) and Figure 1(B), it is seen that the effective density of RM electrons in transition group metals due to the contribution of the *d*-band electrons is larger than that of the noble metals [4] [15]. There rises a question, why the conductivity of transition metals is lower than that of the noble metals, though the effective density of the RM electrons in transition metals is many times larger? As it will be shown later, it is due to many times the smaller diffusion coefficient of the free RM electrons in transition group metals.

The thermal vibrations of the lattice atoms not only excite the free RM electrons, but at the same time produce the same number of electronic defects: the local distortion spots of the potential periodicity. In Figure 2(A), there is presented a schematic illustration of the location of atoms in a two-dimensional lattice of metal: the valence electron waves partially overlap with ones of the neighbor atoms, but the valence electrons do not leave the native ions, and move in the field of a central force of the native ions [5]. If a particular atom excites a free RM electron, as it is shown in Figure 2(A) in (b) row, it produces a distortion of the potential $U(x)$ periodicity, as is schematically shown in Figure 2(B) in (b) case.

The mean free path of the free RM electrons is about two orders larger than the distance between atoms. On the other hand, the atoms which generate free RM electrons produce the same number of ionic spots which are not completely screened by electrons. Considering that the density of the free RM electrons $n_{\text{eff}} = g(E_{\text{F}})kT$, it means that on average the effective density of atoms N_{eff}

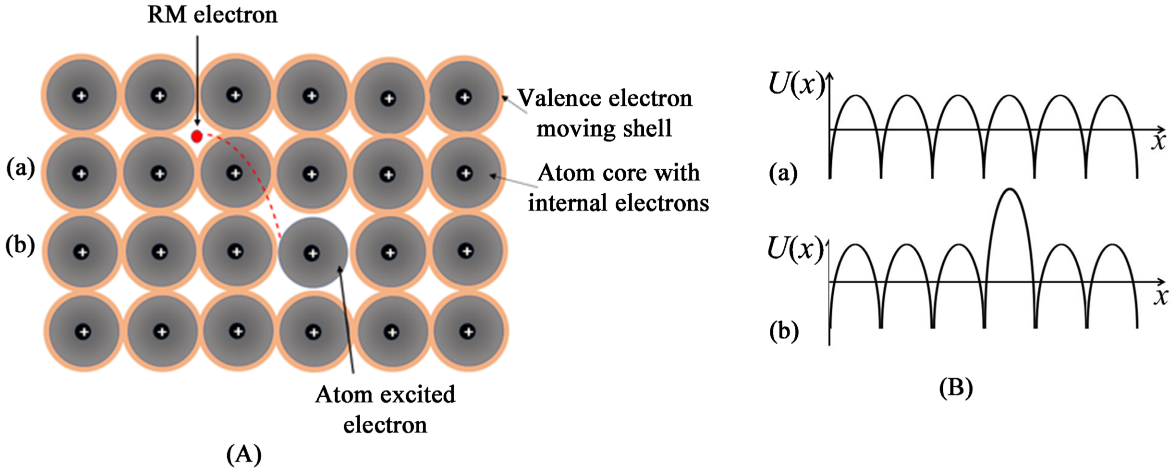


Figure 2. Schematic illustration of a two-dimensional pattern of metal atoms (A), and the potential $U(x)$ distribution (B). In row (b) one atom excites the RM electron, and it produces the distortion of the potential periodicity.

which can generate free RM electrons, and create the same density of distortion spots of the potential (or charge density) distribution periodicity. Thus, such distortion spots or electronic defects can be estimated as [16] [17] [18]:

$$N_{\text{eff}} = n_{\text{eff}} = g\left(E_{\text{F}}\right)kT\ . \tag{3}$$

The other part of atoms ($N - N_{\text{eff}}$) has not sufficient vibration (phonon) energy to generate free RM electrons near to Fermi level energy. There we want to point that the thermal vibrations of lattice atoms play another role, then it has been described in [4] [6] [7] [9] [10] [13]. The thermal vibrations of the lattice atoms stimulate the excitation of the free RM electrons, and at the same time produce the same density of electronic defects, *i.e.* the local distortion spots of the potential periodicity.

2.2. Transport Characteristics of the Free RM Electrons in Elemental Metals

As it is shown in [1] [2] [3] [17] [18] [19], the general expression of conductivity of homogeneous material can be expressed in the following way:

$$\sigma = q^2 n_{\text{eff}} D/kT = q n_{\text{eff}} \mu_{\text{drift}} \tag{4}$$

where D is the diffusion coefficient, and μ_{drift} is the drift mobility of the free RM electrons. From this expression follows that Einstein relation between diffusion coefficient and drift mobility $D/\mu_{\text{drift}} = kT/q$ is valid for one type of free RM charge carriers (electrons or holes) at any degree of degeneracy of the electron gas.

In case of metals, the resistivity ρ of the elemental metal can be described as:

$$\rho = 1/\sigma = 1/\left[q^2 g\left(E_F\right)D\right]. \tag{5}$$

The resistivity ρ, and diffusion coefficient D of the free RM electrons dependence on temperature for three elemental metals are presented in **Figure 3**. The

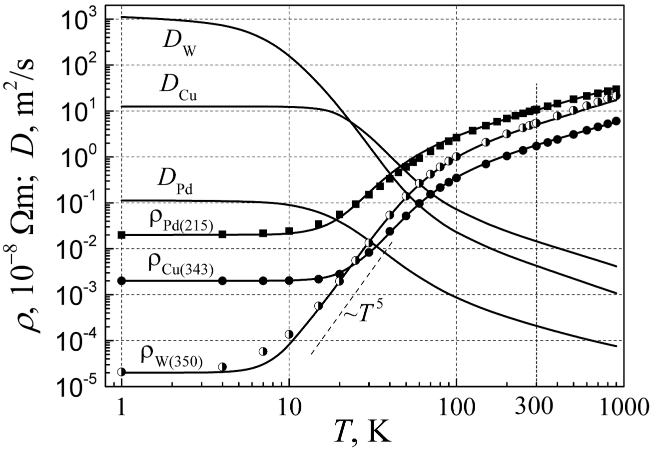


Figure 3. Diffusion coefficient D of RM electrons (calculated by Equation (5)) and resistivity ρ dependences on temperature for three elemental metals: Cu, Pd, and W. The dots are the experimental resistivity results [20]; the solid lines are the calculation data by Equation (9); the number near the chemical sign is the Debye temperature Θ in K used for calculations.

diffusion coefficient has been calculated by Equation (5) with known resistivity and DOS values [20]. For illustration of these temperature dependences, there are taken representative metals with different DOS at Fermi surface:

- Cu for noble group with $g(E_F)_{Cu} = 2.50 \times 10^{22}\ \text{eV}^{-1} \cdot \text{cm}^{-3}$
- W for transition group with $g(E_F)_W = 3.48 \times 10^{22}\ \text{eV}^{-1} \cdot \text{cm}^{-3}$;
- Pd for transition group with very high DOS $g(E_F)_{Pd} = 27.1 \times 10^{22}\ \text{eV}^{-1} \cdot \text{cm}^{-3}$.

Though the density of the free RM electrons n_{eff} of palladium is many times larger than that of the copper (**Figure 4**), but the resistivity of Pd is many times higher than that of Cu (**Figure 3**). It is due to that diffusion coefficient of the free RM electrons in Pd is many times smaller than in Cu (**Figure 3**).

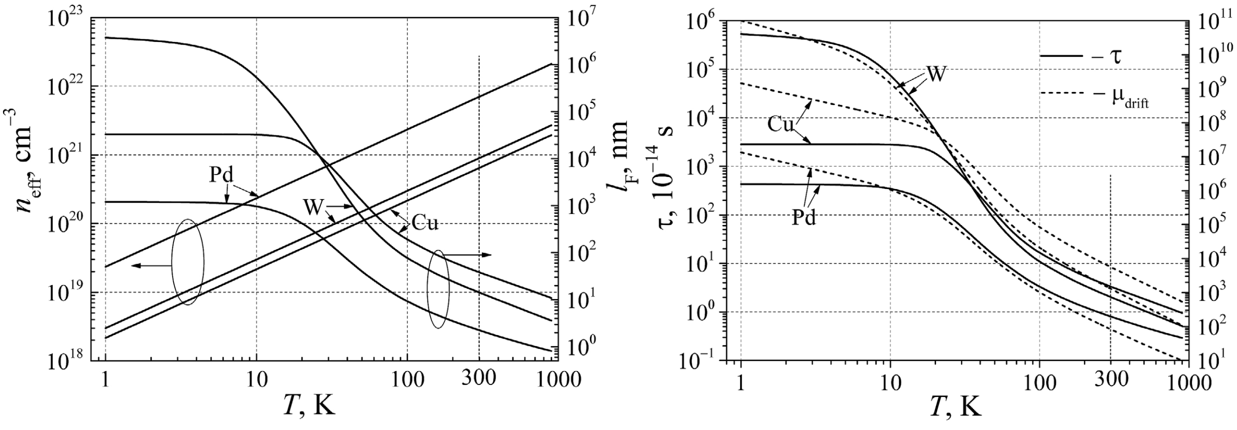
Considering Equation (3), the electron mean free path l_F in elemental metals now can be expressed as:

$$l_F = 1/(s_{eff} N_{eff}) = 1/[s_{eff}\, g(E_F)\, kT], \tag{6}$$

where s_{eff} is the effective scattering cross-section. The electron mean free path is caused by the free RM electrons scattering by electronic defects, which density increases with temperature increasing. It is seen that at temperatures above the Debye temperature Θ the effective scattering cross-section does not depend on temperature, and can be estimated from Equation (6) at $T = T_0 = 295$ K with known mean free path at room temperature [21]. The electron mean free path dependences on temperature for three elemental metals Cu, W and Pd are presented in **Figure 4(A)**. It is seen that at very low temperatures ($T < 10$ K), the electron mean free path of the wolfram is many times higher than that of copper, and analogically the resistivity of wolfram is many times smaller than that of copper (**Figure 3**). This important wolfram resistivity property can be used at cryogenic temperatures.

The average relaxation time of the free RM electrons can be estimated as:

$$\tau_F = 1/(s_{eff} N_{eff} v_F) = 1/[s_{eff}\, g(E_F)\, v_F kT]. \tag{7}$$



(A) (B)

Figure 4. (A) The effective density n_{eff}, and the mean free electron path l_F, and (B) the effective relaxation time τ, and the drift mobility μ_{drift} of the free RM electrons dependences on temperature for three elemental metals Cu, Pd and W.

Though the average scattering cross-section at temperatures above the Debye temperature does not depend on temperature, but considering that during scattering each electron absorbs or excites one phonon, in the general case, the scattering cross-section depends on the ratio of the exchange of the thermal energies between the free RM electrons and the electronic defects:

$$s_{\text{eff}} = s_{\text{eff}\,0}\eta_{ph}\left(T/\Theta\right), \tag{8}$$

where $s_{\text{eff}0}$ is the average RM electron scattering cross-section at room temperature, and $\eta_{ph}\left(T/\Theta\right)$ is the phonon mediation factor estimated as the ratio between average thermal energies of the phonon to the free RM electron, which causes the free RM electrons scattering by electronic defects [16] [17] [18]:

$$\eta_{ph} = \left(T/\Theta\right)^4 \int_0^{\Theta/T} \frac{4x^5\text{d}x}{\left(\text{e}^x - 1\right)\left(1 - \text{e}^{-x}\right)}. \tag{9}$$

This factor at temperatures above the Debye temperature is approximately equal to 1, and so in this temperature range, the effective scattering cross-section does not depend on temperature.

The average relaxation time and drift mobility of the free RM electrons dependences on temperature are presented in **Figure 4(B)**. Therefore, the electrical resistivity of the elemental metals in the overall temperature range can be described as [16] [17] [18]:

$$\rho\left(T\right) = \rho_0 + \rho\left(T_0\right)\cdot\left(T/T_0\right)\cdot\eta_{ph}\left(T/\Theta\right), \tag{10}$$

where $\rho\left(T_0\right) = 1\Big/\left[q^2 g\left(E_{\text{F}}\right)D\left(T_0\right)\right]$ is the resistivity at room temperature T_0 = 295 K, ρ_0 is the residual resistivity due to various impurities, and structural defects of the lattice. The electrical resistivity dependences on temperature for three elemental metals Cu, Pd, and W are presented in **Figure 3**. The small differences of the calculation data from experimental results can be explained by the fact that Debye temperature Θ is not constant and depends on temperature. The calculation has been carried out with constant Θ. It is shown that electron transport properties can be explained on the common model with randomly moving electrons, accounting for the peculiar role of the lattice atom vibrations, and it is valid for all elemental metals.

This model follows one other important property of the free RM electron scattering. The current density $\boldsymbol{j}$ is described as

$$\boldsymbol{j} = \sigma\boldsymbol{E} = qn_{\text{eff}}\boldsymbol{v}_{\text{drift}} = qn_{\text{eff}}\mu_{\text{drift}}\boldsymbol{E}, \tag{11}$$

where $\boldsymbol{E}$ is the electric field strength, $\boldsymbol{v}_{\text{drift}}$ is the drift velocity of the free RM electrons, μ_{drift} is their drift mobility, which can be described as [1] [2] [3]:

$$\mu_{\text{drift}} = \frac{qD}{kT} = \frac{q\langle\tau\rangle}{m^*}\frac{\langle E\rangle}{(3/2)kT} = \alpha_\varepsilon\frac{q\langle\tau\rangle}{m^*}, \tag{12}$$

where

$$\alpha_\varepsilon = \langle E\rangle\Big/\left[(3/2)kT\right] \tag{13}$$

is the multiplier showing how many times the free RM electron energy is larger than the classical energy (3/2*)kT*; the brackets < … > means the statistical averaging. Then the drift velocity can be expressed as

$$\boldsymbol{v}_{\text{drift}} = \mu_{\text{drift}}\boldsymbol{E} = \alpha_\varepsilon \frac{q\langle\tau\rangle}{m^*}\boldsymbol{E} = \frac{\langle\tau\rangle}{m^*}\boldsymbol{F}_{\text{eff}}, \tag{14}$$

where $\boldsymbol{F}_{\text{eff}} = \alpha_\varepsilon q\boldsymbol{E}$ is the effective force of the electrical field acting to free RM electron inside of the metal, *i.e.* the force acting to the free electron in metal is α_ε times larger than in the free space. The average energy change of the free RM electron due to electron scattering in metals is about 1.64 kT [21] which is about a few hundred smaller than the average electron energy E_F, it is limited by Fermi-Dirac statistics The change in momentum due to collision of the free electron with ion is equal to impulse. Considering that effective scattering force due to multiplier α_ε increases with temperature decreasing, the small energy changes due to free electron scattering causes the large free electron momentum changes. Thus, the free electron momentum direction in metals is completely indefinite after its every scattering at any temperature.

3. Conclusions

On the base of experimental data on electrical conductivity and electronic heat capacity of elemental metals, and considering that lattice atom vibrations excite the free RM electrons, and produce the same number of the electronic defects (not completely screened ions), the following conclusions are carried out:

- the effective free randomly moving (RM) electron density is described by Equation (1), and the probability density distribution of the free RM electrons on energy by Equation (2); these expressions are valid for all homogeneous materials with any degree of degeneracy of electron gas;
- the effective free RM electron density in elemental metals is proportional to density-of-states at the Fermi surface and absolute temperature ($n_{\text{eff}} = g(E_F)kT$);
- the effective density of the electronic defects in elemental metals is $N_{\text{eff}} = g(E_F)kT$, which causes the scattering of the free RM electrons;
- the free RM electron scattering cross-section at temperatures above the Debye temperature does not depend on temperature; the phonon mediation factor accounting for the free RM electron scattering by electronic defections is described by Equation (9);
- the resistivity of the elemental metals in the overall temperature range can be described by Equation (10).

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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