# The effective density of randomly moving electrons and related characteristics of materials with degenerate electron gas

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# The effective density of randomly moving electrons and related characteristics of materials with degenerate electron gas

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Interpretation of the conductivity of metals, of superconductors in the normal state and of semiconductors with highly degenerate electron gas remains a significant issue if consideration is based on the classical statistics. This study is addressed to the characterization of the effective density of randomly moving electrons and to the evaluation of carrier diffusion coefficient, mobility, and other parameters by generalization of the widely published experimental results. The generalized expressions have been derived for various kinetic parameters attributed to the non-degenerate and degenerate electron gas, by analyzing a random motion of the single type carriers in homogeneous materials. The values of the most important kinetic parameters for different metals are also systematized and discussed. It has been proved that Einstein's relation between the diffusion coefficient and the drift mobility of electrons is held for any level of degeneracy if the effective density of randomly moving carriers is properly taken into account.  [http://dx.doi.org/10.1063/1.4871757]

## I. INTRODUCTION

The experimental results on the heat capacity of electrons in the metals now are traditionally explained[1–8] on the basis of Fermi-Dirac statistics. It had been established that electrons with energy well below the Fermi level can not change their energy $E$ (either through scattering or due to external fields) as all the upper states are occupied, – the Fermi distribution function leads to $f(E) = 1$. Thus, only a small part of electrons, which energy is close to the Fermi level, are able to move randomly. However, the total density of electrons in the conduction band $n$ is traditionally employed[1–8] for evaluation of the electrical conductivity $\sigma$ of the metals and of the superconductors in the normal state[9–13] by using expression $\sigma = e^2 n\tau/m^*$. Here, $e$ is the electrical charge of electron, $\tau$ is the averaged relaxation time of electron, $m^*$ is the effective mass of electron. Such an expression of the electrical conductivity is doubtful if a rigorous consideration is performed by using Fermi statistics. Usage of the total density $n$ instead of the effective density of the randomly moving carriers leads to a quantity $e\tau/m^*$, which could not be ascribed as the drift mobility of carriers. On the other hand, it is well established that the thermal noise, which appears due to the random motion of electrons, is adequately described by the real part of the conductance, using the Nyquist's formula.[14,15] The widely published[1–8] results on the electron heat capacity and on the thermal noise of metals unambiguously show that only a part of free electrons, those with energy close to the Fermi level, determines the parameters of the kinetic phenomena, – because only these electrons are able to change their energy under scattering and due to an influence of the external fields. Thus, the adequate evaluation of the effective density $n_{\text{eff}}$ of the randomly moving electrons should be performed. Additionally, the proper

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estimation of the parameters of the diffusion coefficient $D$, of the drift mobility $\mu_{\text{drift}}$ of randomly moving charge carriers, of Fermi energy $E_{\text{F}}$, and of electron velocity $v_{\text{F}}$ at Fermi level is inevitable. The mentioned problems are very important in solid state physics for relevant understanding and description of kinetic phenomena.

This study is addressed to characterization of the effective density of randomly moving electrons and to the evaluation of their diffusion coefficient, mobility, and other parameters by generalization of the widely published experimental results. The generalized expressions have been derived for various kinetic parameters attributed to the both non-degenerate and degenerate electron gas, by analyzing a random motion of a single type carriers in homogeneous materials. The values of the most important kinetic parameters for different metals are also systematized and discussed. It has been proved that Einstein relation between the diffusion coefficient and the drift mobility of electrons is held for any level of degeneracy if the effective density of randomly moving carriers is properly taken into account.

## II. THE EFFECTIVE DENSITY OF RANDOMLY MOVING ELECTRONS

The Fermi distribution function for electrons routinely is expressed as

$$f(E) = \frac{1}{1 + \exp(E - \eta)/kT}. \tag{1}$$

It specifies a probability that a level with the energy $E$ is occupied by an electron. Here, $E$ is the electron energy, $\eta$ is the chemical potential, $k$ is he Boltzmann's constant, and $T$ is the absolute temperature. The total density of electrons $n$ in the conduction band is then represented by an integral over the density $g(E)$ of states in the conduction band as

$$n = \int_0^\infty g(E) f(E) \mathrm{d}E. \tag{2}$$

It can be directly deduced from the Fermi-Dirac statistics that the effective density of electrons $n_{\text{eff}}$ is exceptionally determined by the electrons participating in random motion. Thus, the electrical conductivity depends not only on the density of electrons $g(E)$ and the Fermi distribution function $f(E)$, but it also depends on the probability $f_1(E) = 1 - f(\text{E})$ that any electron with the definite energy $E$ at a given temperature $T$ can be scattered, and, thereby, it can leave the definite energy level.[16–18] The effective density of randomly moving electrons can then be rewritten as

$$n_{\text{eff}} = \int_0^\infty g(E) f(E) \cdot [1 - f(E)] \mathrm{d}E = kT \int_0^\infty g(E) \left( -\frac{\partial f(E)}{\partial E} \right) \mathrm{d}E. \tag{3}$$

The term $(-\partial f(E)/\partial E)$ in the latter expression (Eq. (3)) can be understood as the probability density of the randomly moving electrons in metals and other materials with highly degenerate electron gas. Such a definition of the probability density, expressed as

$$p(E) = -\frac{\partial f(E)}{\partial E} = f(E)[1 - f(E)]/kT, \tag{4}$$

meets the requirements of the probability theory.[18] It should be emphasized that for metals the total density of electrons $n$ is the integral parameter – the fixed quantity, while the effective density of randomly moving electrons $n_{\text{eff}}$ is a stochastic variable. Thus, there are two parameters to characterize the free electron gas in metals and other materials with highly degenerate materials, namely, the total density of the free electron in conduction band and the density of randomly moving electrons.

For the materials with a non-degenerate electron gas, a value of the probability function $f_1(E) = 1 - f(E) \approx 1$, because of $f(E) \ll 1$. Therefore, all the electrons in the conduction band of density

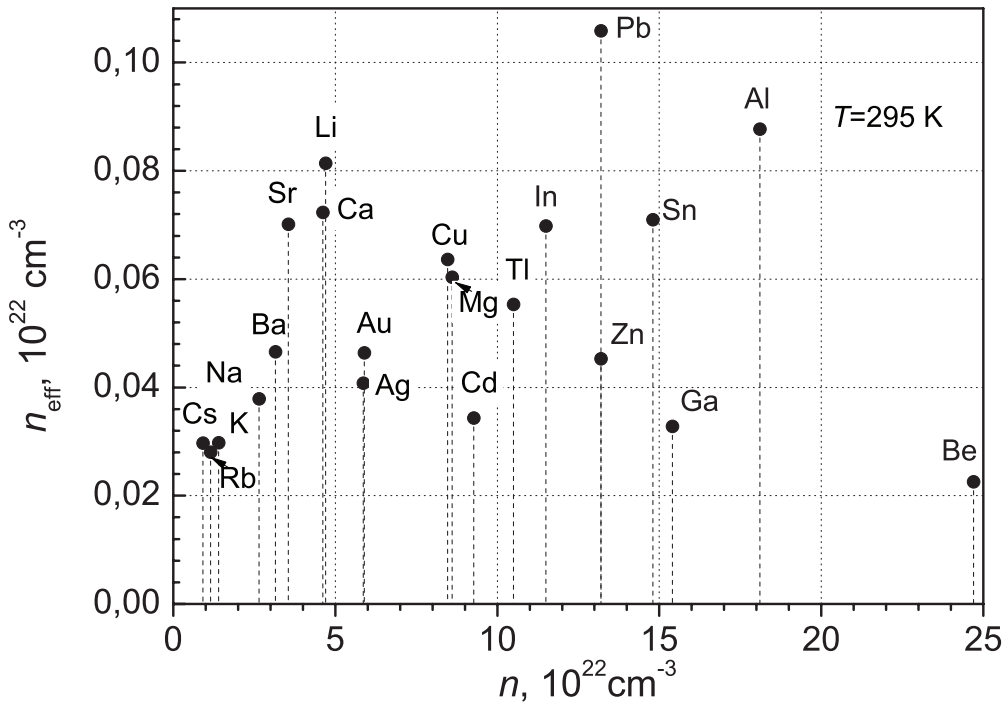


FIG. 1. Relation between the effective density $n_{\text{eff}}$ of the randomly moving electrons and the total density $n$ of electrons for different metals. The values of the total density of electrons for different metals and of the electron heat capacity for calculation of $n_{\text{eff}}$ are taken from literature.[5,6]

$n$ participate within the random motion and determine the electrical conductivity, i.e.:

$$n_{\text{eff}} = n = \int_0^\infty g(E) f(E) \mathrm{d}E; \tag{5}$$

$$\sigma = e n_{\text{eff}} \mu_{\text{drift}} = e n \mu_{\text{drift}} = \frac{e^2 n \tau}{m_0}, \tag{6}$$

Here, $\mu_{drift}$ is the drift mobility of the randomly moving electrons. In such a case, the classical statistics is applicable.

In the case of a high degree of degeneracy, a dependence of the product function $f(E)[1 - f(E)]$ on the energy has a sharp maximum at the energy $E$ value which represents the chemical potential $\eta$. Then, Eq. (3) can be expressed as:

$$n_{\text{eff}} = g(\eta) kT \approx g(E_F) kT \ll n. \tag{7}$$

Here, $g(E_{\text{F}})$ denotes the density of states at $E = E_{\text{F}}$, and $n_{\text{eff}}$ is proportional to the temperature $T$.

The density of states at the Fermi energy $g(E_{\text{F}})$ can separately be obtained from the experimental results on the electronic heat capacity for metals:[5–7]

$$c_V = \gamma T = \frac{\pi^2}{3} g(E_{\text{F}}) k^2 T = \frac{\pi^2}{3} k n_{\text{eff}}, \tag{8}$$

A comparison of the calculated at $T = 295$ K values of an effective density $n_{\text{eff}}$ of randomly moving electrons with those of the total density $n$ of electrons for different metals is presented in Fig. 1. It can be inferred from Fig. 1 that no clear tendency between the density of randomly moving electrons and the total their density can be resolved for different metals. It can also be deduced from Fig. 1 that a part of $n_{\text{eff}}$ within a total density $n$ of electrons comprises less than a few percents of the $n$ value.

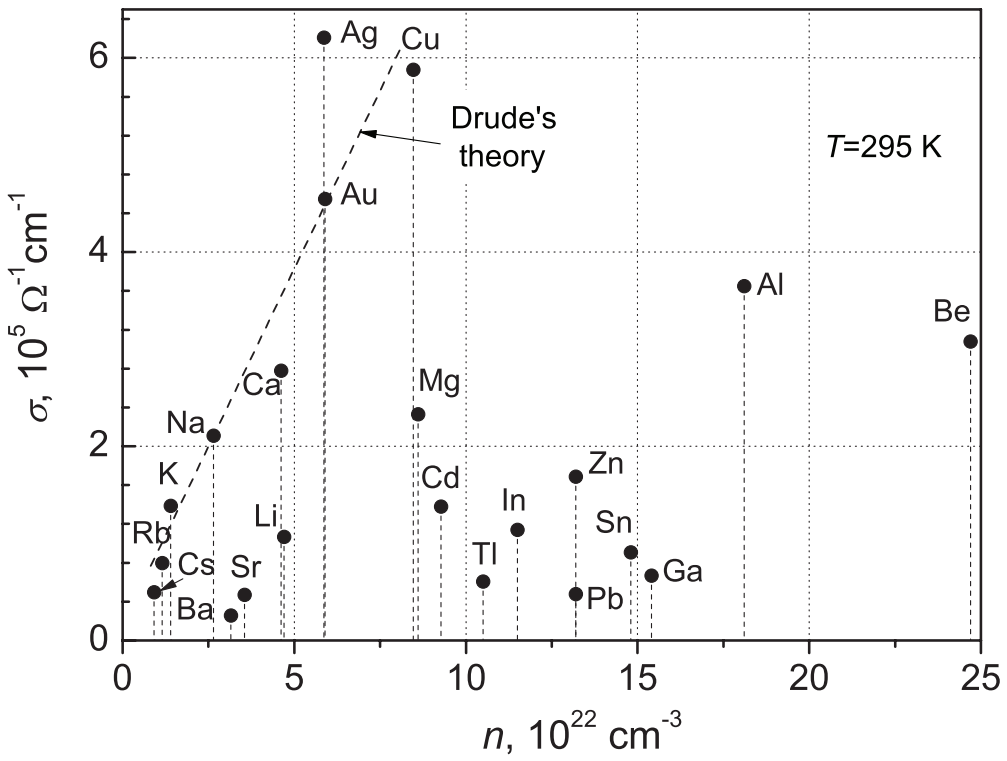


FIG. 2. The experimental data of the electrical conductivity dependence on the total density of electrons for different metals. The dash line represents the conductivity values calculated by using Drude's theory. The values of the experimentally measured electrical conductivity are taken from Ref. 6.

## III. ELECTRICAL CONDUCTIVITY AND RELATED PARAMETERS

According to the Drude's model,[1–8] the electrical conductivity of the metals is described by Eq. (6), where $n$ is the total density of valence electrons. Evaluation of the electrical conductivity for the alkali and noble metals, performed using Drude's model, leads to conductivity values which are close to experimental data (Fig. 2). But, it can be seen from Fig. 1 that the effective density of randomly moving electrons is considerably less (by about two orders of magnitude) than the total carrier density. Complementarily, values of the drift mobility of electrons (it will be shown later) exceed (again by about two orders of magnitude) those values calculated by using the classical expression $\mu_{drift} = e\tau/m_0$. Thus, the conductivity values, estimated using Drude's model (Eq. (6)), fit rather well the experimental data (Fig. 2), especially for several alkali and noble metals, due to mutual compensation (within a product $n\mu_{\text{drift}}$) of the errors in the inconsistent evaluations of $n$ and $\mu_{\text{drift}}$. However, evaluations of the electrical conductivity for the multivalent metals (Fig. 2) by using Drude's model (Eq. (6)) lead to the unacceptable inconsistency between the calculated and experimental results (Fig. 2).

The electric conductivity $\sigma$ of the material and the diffusion coefficient $D$ of carriers are commonly related by a generalized expression:[19,20]

$$\sigma = e^2 D \left(\frac{\partial n}{\partial \eta}\right)_T . \tag{9}$$

Further, the electric conductivity $\sigma$ can be expressed and related to $D$ by calculating of the derivative $\partial n/\partial \eta$ (respective to the chemical potential $\eta$) as follows:[18]

$$\sigma = e^2 D \int_0^\infty g(E) \frac{\partial\{[1+\exp(E-\eta)/kT]^{-1}\}}{\partial \eta} dE = \frac{e^2 D}{kT} \int_0^\infty g(E) f(E)[1-f(E)]\mathrm{d}E = \frac{e^2 D}{kT} n_{\text{eff}}. \tag{10}$$

Here, $n_{\text{eff}}$ is the effective density of randomly moving charge carriers (see Eq. (3)). This expression is valid for all materials with a single type of charge carriers at any degeneracy degree. This equation (Eq. (10)) unambiguously shows that the electric conductivity for all metals is determined by the effective density of randomly moving charge carriers, – not by the total free electron density in the conduction band. The total density of the conduction band electrons in determination of electrical conductivity can be employed only for materials with a non-degenerate electron gas. The electrical conductivity can alternatively be represented as

$$\sigma = en_{\text{eff}}\mu_{\text{drift}} = \frac{e^2 D}{kT} n_{\text{eff}}. \tag{11}$$

Here, $\mu_{\text{drift}}$ is the drift mobility of randomly moving charge carriers in homogeneous materials with a single type of charge carriers (electrons or holes). From the generalized relation (Eq. (11)), the Einstein's relation is consequently obtained

$$\frac{D}{\mu_{\text{drift}}} = \frac{kT}{e}. \tag{12}$$

This expression is valid for both the degenerate and non-degenerate electron gas in homogeneous materials with the single type carriers (either electrons or holes), which are able to randomly move.

The diffusion coefficient of the randomly moving carriers in materials with highly degenerate electron gas can be expressed (by using equations (Eq. (7)) and (Eq. (11))) as

$$D = \sigma/(e^2 g(E_{\text{F}})). \tag{13}$$

Thus, the diffusion coefficient $D$ and drift mobility $\mu_{\text{drift}}$ ((Eq. (12)), for randomly moving carriers) can be related by combining of the independently obtained experimental results on the conductivity and the electron heat capacity measurements in materials with highly degenerate electron gas.

The diffusion coefficient can also be expressed through a product of the average of the square of carrier velocity and of the average of the carrier relaxation time:

$$D = \frac{1}{3}\langle v^2\rangle\langle\tau\rangle. \tag{14}$$

This relation for the highly degenerate electron gas is represented as[18]

$$D = \frac{1}{3}\frac{\int_0^\infty g(E)v^2\tau f(E)[1-f(E)]\mathrm{d}E}{\int_0^\infty g(E)f(E)[1-f(E)]\mathrm{d}E} = \frac{1}{3}v_{\text{F}}^2\tau_{\text{F}}, \tag{15}$$

i.e. the diffusion coefficient is determined by velocity (its square function) and free pass time of randomly moving charge carriers at the Fermi level. It can be obtained, using Eqs. (7), (11) and (15), the alternative expression for conductivity

$$\sigma = \frac{1}{3}e^2 g(E_{\text{F}})v_{\text{F}}^2\tau_{\text{F}}. \tag{16}$$

This expression is well-known for metals, and it is commonly obtained by solving of the kinetic equation.[2,3]

The drift mobility can be expressed (by combining Eqs. (12) and (14)) as

$$\mu_{\text{drift}} = \frac{e\langle v^2\rangle\langle\tau\rangle}{3kT}. \tag{17}$$

The expression for the drift mobility can be represented (by including the effective mass $m^*$ of charge carriers into Eq. (17)) in the generalized form as:

$$\mu_{\text{drift}} = \frac{e\langle\tau\rangle}{m^*}\cdot\frac{(1/2)m^*\langle v^2\rangle}{(3/2)kT} = \frac{e\langle\tau\rangle}{m^*}\cdot\frac{\langle E\rangle}{(3/2)kT} = \alpha_\varepsilon\frac{e\langle\tau\rangle}{m^*}. \tag{18}$$

Here, $\langle E\rangle = (1/2)m^*\langle v^2\rangle$ is the average kinetic energy of the randomly moving carriers. Thus, this equation (Eq. (18)) represents the expression for the drift mobility of randomly moving charge carriers in homogeneous materials, containing the single type of the charge carriers (either electrons

or holes). This fundamental expression Eq. (18) is applicable for materials with both non-degenerate and degenerate carrier gas, including metals. The energy ratio factor (within Eq. (18))

$$\alpha_\varepsilon = \frac{\langle E \rangle}{(3/2)kT}, \tag{19}$$

shows a ratio between the average kinetic energy $\langle E \rangle$ of the randomly moving carriers and the classical thermal energy $(3/2)kT$. For the materials with a non-degenerate electron gas, the value of this factor equals a unity $\alpha_\varepsilon = 1$. Then, an expression for the drift mobility is transformed to

$$\mu_{\text{drift}} = \frac{e\langle \tau \rangle}{m^*}. \tag{20}$$

The latter expression corresponds to a classical case. However, the energy ratio factor evaluated for the highly de semiconductors, metals and superconductors in the normal state, leads to values

$$\alpha_\varepsilon = \frac{2}{3}\frac{E_{\text{F}}}{kT} \gg 1. \tag{21}$$

Thereby, the drift mobility values of the randomly moving carriers at room temperature are hundred times larger than those estimated by using the classical expression (Eq. (20)) for metals.

The generalized expression for the conductivity is expressed, using Eqs. (11) and (18), as follows:

$$\sigma = en_{\text{eff}}\mu_{\text{drift}} = en_{\text{eff}}\frac{e\langle \tau \rangle}{m^*} \cdot \frac{\langle E \rangle}{(3/2)kT}. \tag{22}$$

This Eq. (22) transforms to Eq. (6) for the non-degenerate material (classical case) with $\alpha_\varepsilon = 1$ and $n_{\text{eff}} = n$. However, the specified expression, Eq. (16), should be applied for the highly degenerate semiconductors and metals using $n_{\text{eff}} = g(E_{\text{F}})kT$). Surprisingly, it can be inferred from Eqs. (18) and (22) that the drift mobility of randomly moving electrons and the conductivity of metals do not depend on the effective mass of the electrons.

According to the results of the investigations on the proportionality of a resistivity to temperature $T$, the relaxation time ascribed to randomly moving carriers at Fermi level (for a mentioned temperature range) is expressed as[21]

$$\tau_{\text{F}} = \hbar/(kT). \tag{23}$$

Here $\hbar = h/2\pi$ is the Plank's constant. This expression is valid and generalized for all the homogeneous metals and the highly degenerate semiconductors. The inherent value of $\tau_{\text{F}} \approx 2.59\ 10^{-14}$ s is then obtained at $T = 295$ K.

The velocity of electrons at the Fermi level $v_{\text{F}}$ and the Fermi energy $E_{\text{F}}$ (assuming that an effective mass of an electron is equal to a mass $m_0$ of free electron, i. e. $E_{\text{F}} = m_0 v_{\text{F}}^2/2$) can be evaluated by employing Eqs. (13), (15) and (23). The simulated values of $E_{\text{F}}$ for different metals are presented in Fig. 3. A spherical (Sommerfeld's free electron theory)[5,15] Fermi surface approach is usually exploited in the traditional evaluations of the Fermi energy. This leads to the expression:[5,15]

$$E_{\text{F}} = \left(\hbar^2/2m^*\right)(3\pi^2 n)^{2/3}. \tag{24}$$

A profile of the Fermi surface can be rather complicated[9,22] for many metals and superconductors in normal state. Thereby, no simple function (an analytical approximation) can be obtained to definitely relate the total density of charge carriers $n$ and the Fermi energy $E_{\text{F}}$ (see Fig. 3).

## IV. EVALUATION OF CONDUCTIVITY COMPONENTS

The drift mobility and the diffusion coefficient for the randomly moving electrons at any degree of degeneracy can be represented as:

$$\mu_{\text{drift}} = \sigma/(en_{\text{eff}}) = 1/(e\rho n_{\text{eff}}); \tag{25}$$

$$D = \frac{\sigma kT}{e^2 n_{\text{eff}}} = \frac{kT}{e^2 \rho n_{\text{eff}}}. \tag{26}$$

Here, the parameter $n_{\text{eff}}$ is defined by Eq. (3).

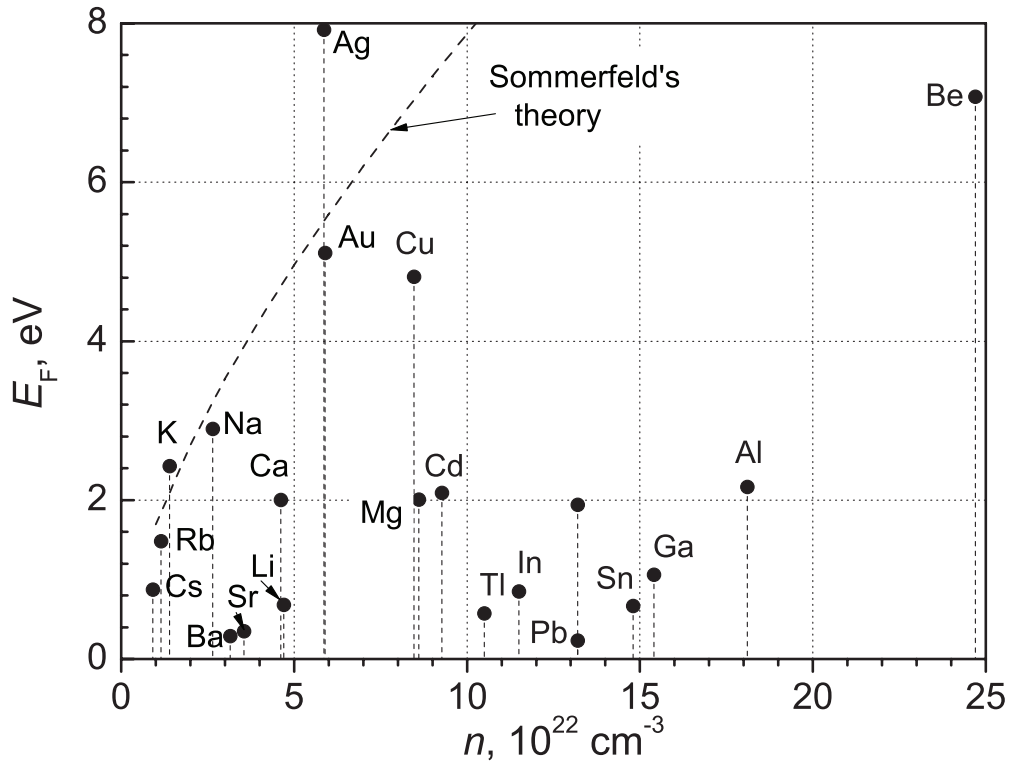


FIG. 3. Relation between the Fermi energy and the total density of the conduction band electrons for different metals. The dash line represents the simulated (using Eq. (24)) Fermi energy dependence on the total density of the conduction band electrons predicted by the Sommerfeld's free electron theory (Eq. (24)).[5]

It is possible to evaluate the electron diffusion coefficient (Eq. (13)) in highly degenerate materials by combining of the experimental results of the conductivity and the electron heat capacity. The relationships between the drift mobility, the Fermi energy and the diffusion coefficient of randomly moving electrons for different metals are presented in Fig. 4. It can be deduced from this figure (Fig. 4) that the changes of these parameters for different metals are strongly correlated. The rather precise linear fit has simultaneously been obtained for the both $\mu_{drift-D}$ and the $E_F - D$ sets. The linearity of the $\mu_{drift-D}$ set proves validity of the Einstein's relation, Eq. (12). The linear $D - E_F$ set represents the relation:

$$\frac{E_F}{D} = \frac{3}{2}\frac{m_0}{\hbar}kT. \tag{27}$$

The significant relation among the set of parameters $\mu_{drift} - D - E_F$ can be obtained from Eqs. (12) and (27). It is expressed as

$$\frac{\mu_{drift}}{D} \cdot \frac{E_F}{D} = \frac{3}{2}\frac{em_0}{\hbar} \approx 2.07 \cdot 10^{-15}\left[\frac{kg}{Vs}\right], \tag{28}$$

and this is valid within a temperature range, where resistivity of metals has a linear dependence on temperature.

The Einstein's relation Eq. (12) can alternatively be obtained by using a Nyquist's theorem for the thermal noise. The spectral density of the current fluctuations $S_{i0}$ for low frequencies $f$ ($f \ll 1/(2\pi\tau)$, here $\tau$ is the relaxation time of carriers) can be presented as[14,18,23]

$$S_{i0} = 4kT\frac{1}{R} = 4kT\sigma\frac{A}{L} = 4e^2 n_{eff} D\frac{A}{L}. \tag{29}$$

Here $R$ is the resistance of the sample of material under test; $A$ is the area of the sample cross-section, and $L$ is the length of a sample, respectively. This relation is applicable for all the homogeneous

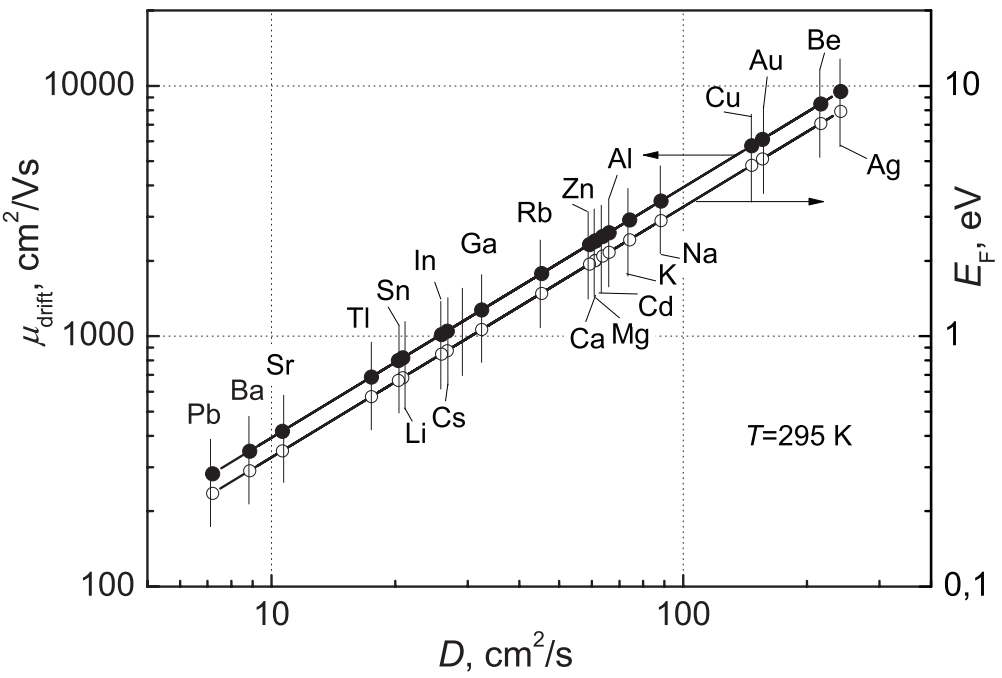


FIG. 4. Relations between the drift mobility, the Fermi energy and the diffusion coefficient of randomly moving electrons for different metals at $T = 295$ K. Solid dots are used for $\mu_{\text{drift}}$, and open dots – for $E_F$. Short vertical lines only show the dependence of dots for definite metal.

materials in equilibrium. Both equalities in Eq. (29) can also be obtained from the general Kubo's formula for conductivity:[15,18]

$$\sigma_x = \frac{1}{kT}\int_0^\infty \langle j_x(t+\tau_1)\cdot j_x(t)\rangle \mathrm{d}\tau_1, \tag{30}$$

The conductivity in Kubo's formula (Eq. (30)) is defined by the autocorrelation function $k_{jx}(\tau_1) = \langle j_x(t+\tau_1)\cdot j_x(t)\rangle$ of the current density $j_x(t)$ fluctuations on time $t$. For the steady-state processes, the autocorrelation function depends only on time difference $\tau_1$.

To conclude the discussion, a set of the main expressions can be summarized as:

$$\frac{\mu_{\text{drift}}}{D} = \frac{e}{kT}; \tag{12′}$$

$$\sigma = e^2 D g(E_F); \tag{13′}$$

$$\tau_F \approx \hbar/kT; \tag{23′}$$

$$\frac{E_F}{D} = \frac{3}{2}\frac{m_0}{\hbar}kT; \tag{27′}$$

$$\frac{\mu_{\text{drift}}}{D}\cdot\frac{E_F}{D} = \frac{3}{2}\frac{em_0}{\hbar} \approx 2.07\cdot 10^{-15}\left[\frac{\text{kg}}{\text{Vs}}\right]. \tag{28′}$$

These expressions are valid and applicable for metals in the temperature range, where the resistivity exhibits a linear dependence on temperature. The presented analysis unambiguously shows that the Einstein's relation ascribed to a single type of charge carriers within a homogeneous material is always held under equilibrium conditions and for weak electric fields. This result is independent neither of non-parabolicity of conduction band nor of the mechanisms of electron scattering. Such the conclusion is relevant because the Eq. (29) is always valid.

## V. SUMMARY

This study has been addressed to improvement of the interpretation of the charge transport properties in metals and degenerate semiconductors. It has been shown that the erroneous values of parameters might be extracted if classical statistics is applied for the evaluation of transport characteristics for such materials. The generalized expressions have been derived for electrical conductivity (Eq. (22)), for drift mobility (Eq. (18)) of the randomly moving carriers in materials containing a single type of charge carriers (either electrons or holes). These derivations have been obtained on the ground of the detail analysis of the effective density of randomly moving carriers (Eq. (3)) in homogeneous materials. It has been shown that the derived expressions are valid for any degree of degeneracy of the electron gas. The obtained expressions are applicable for extraction of the transport parameters in various experimental situations, – for non-degenerate semiconductors, degenerate semiconductors, metals and superconductors in normal state. The fundamental relations generalized over parameter sets for various metals (Eqs. (27) and (28)) have been obtained. It has been shown that Einstein's relation between the diffusion coefficient and the drift mobility of randomly moving carriers is valid also for materials containing highly degenerate electron gas, including metals.

## ACKNOWLEDGMENTS

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