
Analysis of Conductivity of Noble Metals Near Room Temperature

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Abstract

In the present paper an analysis of conductivity of noble metals near room temperature (~ 293 °K where °K is Degree Kelvin) is carried out. The extreme high conductivity of noble metals (specially Cu from cost point of view) make them suitable to find their use in connecting various circuit elements offering an extremely low resistance path of the connectors in the physics (Laboratory)/electric/electronic networks/circuits. Thus the importance of noble metals in physics (Laboratory)/electric/electronic engineering is obvious. Conductivity of noble metals near room temperature is analyzed and calculated here. The conductivity comes into picture due to limitation of current by collisions of conduction electrons with fixed ions undergoing coupled mass-vibrations at the temperature of the metal under consideration. The process of electron-ion collisions in the metal is described in terms of a collision frequency, using gas-kinetics. The collision frequency of an electron, with velocity corresponding to Fermi-energy, can be determined if effective collision cross-section of electron - ion collisions be known. In the present analysis, an expression for effective collision cross-section describing collisions of the electron with the ions undergoing thermal mass-vibrations is obtained. The effective collision cross-section is given by overall average of the resultant mean square value of amplitudes of the ion undergoing coupled mass-vibrations. Whence knowing the collision frequency, conductivity of the metal is obtained. Discrepancy of conductivities between theoretical and tabulated values from physical tables is attributed to anisotropic process of scattering of the electron at electron-ion collision. This analysis gives fairly well values of conductivities near room temperature for noble metals especially for gold, the ornamental metal. Purpose of this work is to illustrate in a simple manner how conductivity of the metal comes in picture by isotropic/anisotropic scattering of the electron at collisions with ions in the metal.

Keywords

Noble-metals, Electron, Ions, Collisions, Coupled-Mass-Vibration, Ions, Conductivity, Room-Temperature

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1. Introduction

In the present paper an analysis of conductivity of noble metals near room temperature (~ 293 °K where °K is Degree Kelvin) is carried out. The extreme high conductivity of noble metals (specially Cu from cost point of view) make them suitable to find their use in connecting various circuit elements offering an extremely low resistance path of the connectors in the physics (Laboratory)/electric/electronic

networks/circuits. Thus the importance of noble metals in physics (Laboratory)/electric/electronic engineering is obvious.

Reference to detailed theoretical calculations of the conductivity of metals is given in the review by a previous investigator who has given his results on the conductivity at 273 °K in his paper by Barden (1940) [1]. His results are shown below in Table 1.1:

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Table 1.1. Comparison of experimental and calculated conductivities for noble metals at 273 °K in mhos/m due to Bardeen.

Metal	Experimental Conductivity	Calculated Conductivity
Cu	6.4x10 ⁷	17.4x10 ⁷
Ag	6.6 x10 ⁷	14.3 x 10 ⁷
Au	4.9 x 10 ⁷	14.2 x 10 ⁷

Table 1.1 shows that calculated values of conductivities are too large, in the case of noble metals. Thus the assumptions in the theory are not best justified for noble metals, as indicated by Table 1.1. Here refer also to Justi etc 1948 [2], Weisskopf 1943 [3], Grüneisen 1933 [4], Blackman 1951 [5] and Klemens 1952 [6] for General Reference to electrical conductivity of metals.

In the present paper, an expression for conductivity of noble metals near room temperature is obtained in a different way as explained below.

Here the metal is regarded to consist of fixed ions (or the atoms devoid of one conduction electron each) in its volume at regular intervals on an average and a number of conduction electrons in the intervening space referred to as a free-electron gas. In calculations of conductivities of noble metals, attention is confined to homogeneous and isotropic media whose properties are the same in every part and in every direction. This rules out the consideration of directional properties of the crystalline media and only average values are treated. For the noble metal under consideration, it is assumed that there is one free conduction (valence) electron per atom. And further the number density of free electrons is equal to that of positive ions in the metal.

It is assumed that the ions undergo thermal mass-vibrations at temperature T of the metal under consideration. The fixed ions in the metals are elastically bound. Coupled mass-vibrational modes of the ions are associated with elastic waves in transverse and longitudinal modes of Debye type in the metal. On the other hand, conduction electrons in the metal follow Fermi-Dirac distribution of energy at temperature T of the metal. Such a system of ions and electrons in the metal is regarded to be in equilibrium at temperature T.

When a d.c. electric field is applied to the metal, conduction electrons in the metal acquire drift velocities limited by collisions of the electrons with the ions undergoing mass-vibrations. The collision phenomenon is described in terms of electron-ion collision frequency, using gas-kinetics. While dealing with the collision frequency, velocity of the electron corresponding to Fermi level is taken into account. The collision frequency can be determined by gas-kinetics, if effective collision cross-section of electron-ion collision in the metals is known. In the present analysis an expression for overall average of resultant mean square amplitudes of

coupled mass-vibrations of the ion is obtained and is regarded as the effective collision cross-section. Hence knowing the collision frequency, conductivity of the metal at temperature T can be obtained. Discrepancy of conductivities between theoretical value of this analysis and tabulated value from physical tables is attributed to anisotropic process of scattering of the electron at electron-ion collision.

2. Mass-Vibrations of the Fixed Ion in the Metal

The fixed ions in the metal are assumed to undergo harmonic mass-vibrations at temperature T of the metal.

In order to analyze the mass-vibrations of the ions consider that one of the ions be displaced from its equilibrium position, under thermal action. The displaced ion would carry out harmonic mass-vibrations about its equilibrium position and its potential energy would be the same as three one-dimensional harmonic mass-vibrator, one for each direction of motion perpendicular to each other.

Differential equation of motion of an ion undergoing thermal mass-vibrations at temperature T, say along x-axis at time t is given by,

$$M_i \frac{\partial^2 x}{\partial t^2} = -Ax \quad (1)$$

where x is displacement of the ion at time t, $\frac{\partial^2 x}{\partial t^2}$ is its acceleration, M_i is its mass and A is a constant of the harmonic motion.

If f is frequency of mass-vibration of the ion, then f is related to A by the following relationship, viz,

$$f = \frac{1}{2\pi} \left(\frac{A}{M_i} \right)^{1/2} \quad (2)$$

Now Ax in eqn. (1) gives restoring force maintaining mass-vibrations of the ion, so that potential energy V_{AI} of the ion at time t is given by:

$$V_{AI} = \int_0^x Ax \, dx = \frac{1}{2} Ax^2. \quad (3)$$

If x_0 be the r.m.s. value of amplitude of vibration of the ion, then average potential energy V_{AI} of the ion over a period of the vibration is given by,

$$V_{AI} = \frac{1}{2} Ax_0^2. \quad (4)$$

Using eqn. (2), eqn. (4) gives,

$$V_{AI} = 2\pi^2 f^2 M_i x_0^2. \quad (5)$$

Let probability density or weight factor $P(V_{AI})$ at temperature T to have value V_{AI} be given by Boltzmann factor, viz.,

$$P(V_{AI}) = \exp\left(-\frac{V_{AI}}{kT}\right), \quad (6)$$

where k is Boltzmann constant.

Average value of x_0^2 i.e. \bar{x}_0^2 over various values of x_0^2 for the ionic mass-vibrator with frequency f can be obtained by averaging all values of x_0^2 with the weight factor given by eqn. (6).

Thus,

$$\bar{x}_0^2 = \frac{\int_0^\infty x_0^2 P(V_{AI}) \partial x_0}{\int_0^\infty P(V_{AI}) \partial x_0}. \quad (7)$$

Using eqns. (5) and (6), eqn. (7) gives:

$$\bar{x}_0^2 = \frac{\int_0^\infty x_0^2 \left\{ \exp\left(-\frac{2\pi^2 f^2 M_i x_0^2}{kT}\right) \right\} \partial x_0}{\int_0^\infty \left\{ \exp\left(-\frac{2\pi^2 f^2 M_i x_0^2}{kT}\right) \right\} \partial x_0} \quad (8)$$

Solution of eqn. (8) gives,

$$\bar{x}_0^2 = \frac{kT}{(2\pi f)^2 M_i}. \quad (9)$$

Similar analysis can be carried out for the ionic mass-vibrator with frequency f along y - and z -axes, and corresponding values of \bar{y}_0^2 & \bar{z}_0^2 are given by

$$\bar{y}_0^2 = \frac{kT}{(2\pi f)^2 M_i}, \quad (10)$$

and,

$$\bar{z}_0^2 = \frac{kT}{(2\pi f)^2 M_i}. \quad (11)$$

If,

$$\bar{R}_0^2 = \bar{x}_0^2 + \bar{y}_0^2 + \bar{z}_0^2, \quad (12)$$

then eqn. (12) using eqns. (9) to (11) gives,

$$\bar{R}_0^2 = \frac{3kT}{(2\pi f)^2 M_i}. \quad (13)$$

Eqn. (13) gives square of resultant average of mean square value of the amplitudes of the ionic mass-vibrations, averaged in the way mentioned above.

Ions in the metal are elastically bound with respect to each other. These ions are assumed to undergo mass-vibrations at temperature T of the metal in presence of elastic waves existing in the metal, where the metal is regarded as a continuous medium so far as the propagation of elastic waves are concerned. Frequency of mass-vibrations of the ions is considered to be the same as that of elastic waves.

Considering the metal as a continuous medium for elastic waves, the number of modes of elastic waves per unit volume of the metal denoted by $Z_i(f) \partial f$ in the elastic wave frequency interval ∂f between f and $f + \partial f$ can be shown to be given by

(refer to Appendix A.1 of this paper):*

$$Z_i(f) \partial f = 4\pi f^2 \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \partial f, \quad (14)$$

where v_t denotes velocity of elastic wave in transverse mode and v_l denotes of elastic wave in longitudinal mode.

If n be the number density of ions in the metal, then there would be $3n$ modes of elastics waves per unit volume because there are $3n$ degrees of freedom per unit volume for mass-vibrations of the ions along three mutually perpendicular axes. This limits the maximum frequency of the wave. If minimum frequency be taken zero for all practical purposes and maximum be denoted by Debye frequency f_D of cut-off, then,

$$\int_0^{f_D} Z_i(f) \partial f = 3n, \quad (15)$$

meaning thereby coupled mass-vibrational modes of ions take place in the presence of elastic wave modes in the metal. And further, each of the ions has a band of frequency ranging 0 to f_D for all practical purposes, when linear dimensions of the metal are extremely large as compared to the inter-ionic distance(s).

Equation (15) using eqn. (14), gives that,

$$3n = \int_0^{f_D} 4\pi f^2 \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \partial f. \quad (16)$$

Assuming v_t and v_l to be independent of f , eqn. (16) gives,

$$f_D = \sqrt[3]{\frac{9n}{4\pi}} / \sqrt[3]{\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)}. \quad (17)$$

Coming to eqn. (14), $Z_i(f)$ is considered to denote a weight factor at frequency f for the elastic waves or the ionic mass-vibrator(s) in the metal, where,

$$Z_i(f) = 4\pi f^2 \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right). \quad (18)$$

Further, eqn. (13) gives value of \bar{R}_0^2 for the ionic mass-vibrator at frequency f . Overall average of \bar{R}_0^2 i.e. $\langle \bar{R}_0^2 \rangle$ of the ionic mass-vibrator is obtained by averaging the value of \bar{R}_0^2 with the weight factor $Z_i(f)$ given by eqn. (18), for all values of frequencies ranging 0 to f_D giving coupled ionic mass-vibrations. Hence $\langle \bar{R}_0^2 \rangle$ is given by,

$$\langle \bar{R}_0^2 \rangle = \frac{\int_0^{f_D} \bar{R}_0^2 Z_i(f) \partial f}{\int_0^{f_D} Z_i(f) \partial f}. \quad (19)$$

Using eqns. (13), (15) and (18), eqn. (19) gives,

$$\langle \bar{R}_0^2 \rangle = \frac{\int_0^{f_D} \frac{3kT}{(2\pi f)^2 M_i} 4\pi f^2 \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \partial f}{3n} \quad (20)$$

Assuming the elastic wave velocities to be independent of f

as before, solution of eqn. (20) using eqn. (17), gives:

$$\langle \bar{R}_0^2 \rangle = \sqrt[3]{9n/4\pi} \frac{k}{\pi p} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right)^{2/3} T, \quad (21)$$

where,

$$M_i n = \rho, \quad (22)$$

gives density of metal. Here n is ion density in the metal which is same as conduction electron density in the metal.

Equation (21) gives overall average of the resultant mean square value of the amplitudes of the coupled mass-vibrations of the ion in the metal.

3. Electron-Ion Collision Frequency in the Metal

In the metal free (conduction) electrons follow Fermi-Dirac distribution of energy at temperature T of the metal. Whereas the ions follow Boltzmann distribution of energy at the same temperature T . The electrons and the ions in the metal are considered to be in a kind of equilibrium (analogous to thermal equilibrium), in order to derive an expression for electron-ion collision frequency using methods of gas-kinetics. Here the ions undergoing coupled mass-vibrations are fixed in the metal and the electrons move about in the interior of the metal colliding with the ions at temperature T of the metal.

If n is ion density in the metal, Q_0 is effective collision cross-section for electron - ion collisions and v_0 is appropriate velocity corresponding to Fermi energy of the electron coming into the picture of collisions, then using gas-kinetics,

$$g_0 = nQ_0v_0, \quad (23)$$

where g_0 is electron-ion collision frequency.

An expression for g_0 can be obtained as follows:

Consider the free electron-gas in the metal having unit volume. Further consider those electrons whose momenta lie between p and $p + \partial p$. Then phase volume between momenta p and $p + \partial p$ is given by,

$$V_p = \frac{4\pi}{3} [(p + \partial p)^3 - p^3] = 4\pi p^2 \partial p, \quad (24)$$

where ∂p is small. If volume of an elementary cell in phase-space be h^3 which follows from Heisenberg's uncertainty principle, where h is Planck constant, then total number of quantum states per unit volume of the metal between momenta p and $p + \partial p$, is given by,

$$\partial s' = \frac{4\pi p^2 \partial p}{h^3}. \quad (25)$$

If spin degeneracy parameter for electrons be 2, which follows from Pauli's exclusion principle, then eq. (25) gives,

$$\partial s = 2 \partial s' = \frac{8\pi p^2 \partial p}{h^3}, \quad (26)$$

where ∂s is total number of quantum states per unit volume of the metal between momenta p and $p + \partial p$, considering spin degeneracy parameter for electrons. Further momentum p of an electron of free electron-gas is related to its energy E by the relationship,

$$\frac{p^2}{2m_e} = E, \quad (27)$$

where m_e is mass of an electron. Using eqn. (27), eqn. (26) gives,

$$\partial s = (8\pi/h^3) \sqrt{2m_e E} m_e \partial E. \quad (28)$$

Integrating eqn. (28) from $E = 0$ to $E = E_0$, where E_0 is the maximum energy of the electron in the electron-gas, total number of quantum states viz., s , is given by,

$$s = \int \partial s = \int_0^{E_0} (8\pi/h^3) \sqrt{2m_e E} m_e \partial E = \frac{8\pi}{3} \left(\frac{2m_e E_0}{h^2} \right)^{3/2} \quad (29)$$

If n be the number density of electrons in the metal, then n would practically occupy all the states given by eq. (29) i.e. then $s = n$. Thus substituting $s = n$ in eqn. (29), eqn. (29) gives,

$$n = \frac{8\pi}{3} \left(\frac{2m_e E_0}{h^2} \right)^{3/2}, \quad (30)$$

where value of E_0 using eqn. (30) is given by,

$$E_0 = \frac{h^2}{2m_e} \left(\frac{3n}{8\pi} \right)^{2/3}. \quad (31)$$

In eqn. (31), E_0 gives Fermi energy of the electrons in the metal. Although E_0 of eqn.(31) gives Fermi energy of the metal at $T = 0^0K$, still eqn.(31) represents the value of Fermi energy at Temperature T of the metal when T lies near room temperature ($\sim 293^0K$) such that $kT \ll E_0$ which is a well-known result. Here k is Boltzmann Constant. (Max Born 1963, pp284-285) [7].

If v_0 is the velocity of an electron of the free electron-gas, corresponding to E_0 then,

$$\frac{1}{2} m_e v_0^2 = E_0, \quad (32)$$

which gives,

$$v_0 = \left(\frac{h}{m_e} \right)^{1/3} \sqrt[3]{3n/8\pi}, \quad (33)$$

using eqn. (31). It is this velocity v_0 of the electron in free electron-gas denoted by eqn. (33), which is considered to come into the picture of electron-ion collision frequency

defined by eqn. (23).

Further in this analysis Q_o in eqn. (23) which is effective cross-section of electron - ion collisions, is considered to be given by $\langle \bar{R}_o^2 \rangle$ which is overall average of the resultant mean square value of the amplitudes of the coupled mass-vibrations of an ion in the metal at temperature T. Thus using eqn. (21),

$$Q_o = \langle \bar{R}_o^2 \rangle = \sqrt[3]{9n/4\pi} \frac{k}{\pi\rho} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right)^{2/3} T. \quad (34)$$

Finally the following expression for electron-ion collision frequency g_o in the metal at temperature T is obtained using eqns. (33) and (34), in eqn. (23),

$$g_o = \left[\sqrt[3]{6} (kh/\pi\rho m_e) \left\{ \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) (3n^{5/2}/8\pi) \right\}^{2/3} \right] T, \quad (35)$$

where n is electron or ion density in the metal.

4. Conductivity of the Metal

Assume that each free (conduction) electron in the metal starts with zero initial velocity after each collision with ions in presence of a d.c. electric field E_x applied, say parallel to x-axis, in the metal. Because of the field E_x , the electron experiences an electric force eE_x where e is charge of an electron. This force imparts to the electron an acceleration of value f_{ex} given by,

$$f_{ex} = \frac{e}{m_e} E_x. \quad (36)$$

Let X be the average distance travelled by the electron along x axis in time $1/g_o$ which is the time that elapses before next collision, in presence of the acceleration f_{ex} . Here g_o is given by eqn. (35). Then X is given by,

$$X = \frac{1}{2} f_{ex} \left(\frac{1}{g_o} \right)^2 = \frac{1}{2} \left(\frac{e}{m_e} E_x \right) \left(\frac{1}{g_o} \right)^2. \quad (37)$$

If U_x is the average drift velocity of the electron in presence of E_x , then,

$$U_x = \frac{X}{\left(\frac{1}{g_o} \right)} = \frac{eE_x}{m_e(2g_o)}. \quad (38)$$

In the present analysis, it is assumed that average velocity given by eqn. (38) remains the same before and after scattering of the electron by an obstacle in form of an ion in the metal at electron-ion collision. This is illustrated with reference to fig.1 (a) and (b)

With references to Fig. 1(a), $\theta = \pi/2$ is the angle of scattering of the electron on collision with the ion. Fig. 1(b) shows that as a result of scattering process, the velocity of the electron along x-axis remains unaltered retaining its original value of

U_x as given by eqn. (38). This situation explained with references to Fig. 1(a) and (b) is referred to as the case of isotropic scattering of the electron at electron-ion collision which is characterized by $\theta = \pi/2$.

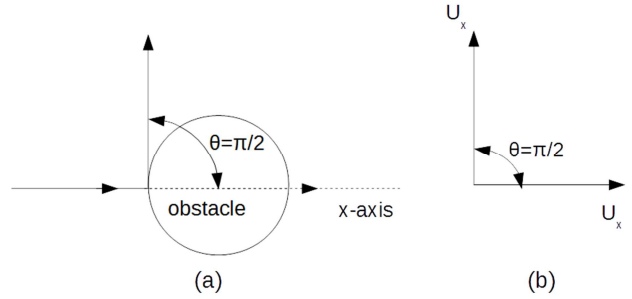


Fig. 1. Isotropic scattering of an electron by an obstacle in the metal.

Now it is possible to define an average drift current density J_x due to n electrons per unit volume in the metal by the following relationship, viz.,

$$J_x = neU_x \quad (39)$$

Using eqn. (38), eqn. (39) gives,

$$J_x = \frac{ne^2}{m_e(2g_o)} E_x. \quad (40)$$

Hence conductivity σ_o of the metal is given by,

$$\sigma_o = \frac{J_x}{E_x} = \frac{ne^2}{m_e(2g_o)} \quad (41)$$

In eqn. (41), $1/2g_o$ has dimensions of time and it is denoted by τ_o , so that,

$$\tau_o = 1/2g_o. \quad (42)$$

Here τ_o is referred to as a relaxation time of electron-ion collision process in the metal. The value of τ_o is further given by,

$$\tau_o = 1/2g_o = \frac{1}{2nQ_o v_o}, \quad (43)$$

where g_o is defined by eqn. (23). Substituting the value of g_o as given by eqn. (35) in eqn. (43), eqn. (43) gives,

$$\tau_o = 1/\left[\sqrt[3]{48} (kh/\pi\rho m_e) \left\{ \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) (3n^{5/2}/8\pi) \right\}^{2/3} T \right]. \quad (44)$$

Equation (44) gives relaxation time of electron-ion collision process at temperature T of the metal.

In terms of the relaxation time given by eqn. (42), eqns. (38) and (41) give,

$$U_x = \frac{e}{m_e} \tau_o E_x, \quad (45)$$

and,

$$\sigma_o = \frac{ne^2\tau_o}{m_e} \tag{46}$$

$$n = \frac{\rho N_A}{M_A} \tag{50}$$

Now mobility of an electron is defined as the average drift velocity acquired by the electron per unit electric field and is denoted by k_{eo} . Thus using eqn. (45), the value of k_{eo} is given by,

$$k_{eo} = \frac{U_x}{E_x} = \frac{e}{m_e} \tau_o \tag{47}$$

Substituting the value of τ_o as given by eqn. (44) in eqn. (47), eqn. (47) gives that,

$$k_{eo} = \left(\frac{e}{m_e}\right) \frac{1}{\left[\sqrt[3]{48} \cdot (kh/\pi\rho m_e) \cdot \left\{\left(\frac{2}{v_t^2} + \frac{1}{v_l^2}\right) (3n^{5/2}/8\pi)\right\}^{2/3} T\right]} \tag{48}$$

Eqn. (48) gives mobility k_{eo} of an electron in the metal at temperature T.

Further from eqns. (41) and (35) or (44) and (46), the value of σ_o is given (Nandedkar 1983) [8] by,

$$\sigma_o = \left(\frac{ne^2}{m_e}\right) \frac{1}{\left[\sqrt[3]{48} \cdot (kh/\pi\rho m_e) \cdot \left\{\left(\frac{2}{v_t^2} + \frac{1}{v_l^2}\right) (3n^{5/2}/8\pi)\right\}^{2/3} T\right]} \tag{49}$$

Eqn. (49) gives conductivity at temperature T of the metal.

5. Theoretical Data

If N_A is Avogadro's number, M_A is atomic weight of the noble metal, then electron or ion density in case of noble metal is given by,

where ρ is the density of the metal.

The elastic wave velocities viz. v_t (the transverse wave velocity) and v_l (the longitudinal wave velocity), neglecting crystalline structure of the metal, on an average can be shown to be given by (refer to Appendix A.2 of this paper

$$v_t = \left(\frac{\eta}{\rho}\right)^{1/2} \tag{51}$$

and,

$$v_l = \sqrt{q(1 - \sigma')/\rho(1 + \sigma')(1 - 2\sigma')} \tag{52}$$

where η is modulus of rigidity, q is Young module and σ' is Poisson ration for the metal.

Table 5.1 gives physical constants of noble metals, viz., atomic weight M_A and density ρ from Clark (1970, pp.53-55) [9]; Young modulus q , modulus of rigidity η and Poisson's ration σ' from Lindsay (1962, table on pp.314) [10].

Column 7 of Table 5.1 gives value of electron or ion density n as calculated from eqn. (50). Column 8 and 9 of the table give values of transverse elastic wave velocity v_t and longitudinal elastic wave velocity v_l in the metal as calculated from eqns. (51) and (52) respectively.

Table 5.1 gives room temperature (~ 293 °K) values for various parameters in the case of noble metals. In the present analysis when temperature T of the metal is near room temperature, then variations of various parameters given in Table 5.1 with respect to temperature of the metal are neglected and all these parameters are treated a constants.

Table 5.1. Room Temperature (~ 293 °K) values of physical constants of noble metals.

Metal	M_A	$\rho \times 10^{-3}$	$q \times 10^{-10}$	$\eta \times 10^{-10}$	σ'	$n \times 10^{-28}$	$v_t \times 10^{-3}$	$v_l \times 10^{-3}$
	(Kgm-at)	(kg/m ³)	(Nw/m ²)	(Nw/m ²)		(m ⁻³)	(m/sc)	(m/sc)
Cu	63.54	8.93	12.0	4.3	0.40	8.464(8)	2.194(4)	5.366(1)
Ag	107.87	10.5	7.5	2.7	0.39	5.862(8)	1.603(6)	3.774(7)
Au	196.97	19.3	8.0	3.0	0.34	5.901(6)	1.246(8)	2.525(9)

6. Numeric Analysis

Equations (34) and (35) show that, effective collision cross-section Q_o and electron-ion collision frequency g_o are both

proportional to temperature T of the metal; whereas eqns. (44), (48) and (49) indicate that electron-ion relaxation time τ_o , electron mobility k_{eo} and conductivity σ_o of the metal, all are inversely proportional to T.

Table 6.1. Values of Q_o , g_o , τ_o , k_{eo} , σ_o and σ_t for metals at T = 293 °K.

Metal	$Q_o \times 10^{22}$	$g_o \times 10^{-13}$	$\tau_o \times 10^{14}$	$k_{eo} \times 10^3$	$\sigma_o \times 10^{-7}$	$\sigma_t \times 10^{-7}$
	(m ²)	(sc ⁻¹)	(sc)	(m ² /V/sc)	(mhos/m)	(mhos/m)
Cu	1.909(4)	2.541(6)	1.967(3)	3.460(7)	4.692(9)	5.842(2)
Ag	2.697(6)	2.200(4)	2.272(3)	3.997(2)	3.754(3)	6.207(3)
Au	2.467(1)	2.030(1)	2.462(9)	4.332(5)	4.096(1)	4.104(0)

In the present analysis T is temperature of the metal near room temperature (~ 293 °K). Near room temperature physical constants of noble metals given in table 5.1 are independent of temperature T of the metal. Further this analysis assumes that it is possible to define collision frequency g_o by eqn. (35) or relaxation time τ_o by eqn. (44), when temperature T of the metal is near room temperature. This analysis also assumes that although all electrons take part in conduction mechanism only the electron-ion collision frequency or the relaxation time of the electrons with velocity v_o of eqn. (33) corresponding to Fermi energy E_o as given by eqn. (31) occurs in the conductivity.

Table 5.1 is used to get the values of Q_o , g_o , τ_o , k_{e_o} , and σ_o of noble metals when temperature T of the metal is 293 °K, using various equations of the present analysis. These calculated values are given in Table 6.1. Last column of table 6.1 gives value of conductivity of the metal σ_t at $T = 293$ °K as calculated from the data given in physical tables from Clark (1970, pp.56) [9].

Table 6.1 shows that in the case of noble metals at $T = 293$ °K (i) order of collision cross-section Q_o is 11^{-22} m², (ii) order of electron-ion collision frequency g_o is 10^{13} sc⁻¹, (iii) order of electron-ion relaxation time τ_o is 10^{-14} sc, (iv) order of electronic mobility k_{e_o} is 10^{-3} m²/V/sc and (v) order of conductivity σ_o is 10^7 mhos/m.

Comparing last two columns of table 6.1, it is seen that agreement between the two values of conductivities viz., σ_o (as obtained by present analysis) and σ_t (as calculated from data given in the physical tables) is best for Au and successively differs in case of Cu and Ag respectively. The discrepancy between the two values of conductivities is attributed to anisotropic scattering of the electron at electron-ion collision, as described below:

In the present analysis it is assumed that average velocity of the electron given by eqn. (38) viz.,

$$U_x = \frac{eE_x}{m_e(2g_o)},$$

remains the same before and after scattering of the electron by an obstacle in the form of an ion in the metal at electron-ion collision.

The case of isotropic scattering having scattering angle $\theta = \pi/2$ is already illustrated in Fig. 1 (a) and (b).

Next consider case of the scattering when $\theta \neq \pi/2$ and is referred to as the case of anisotropic scattering. Here θ is an arbitrary angle chosen other than $\frac{\pi}{2}$.

Now another case of the scattering when $\theta \neq \pi/2$, is

illustrated in Fig. 2(a) and (b), and is referred to as case of anisotropic scattering. Here θ is an arbitrary angle chosen other than $\pi/2$.

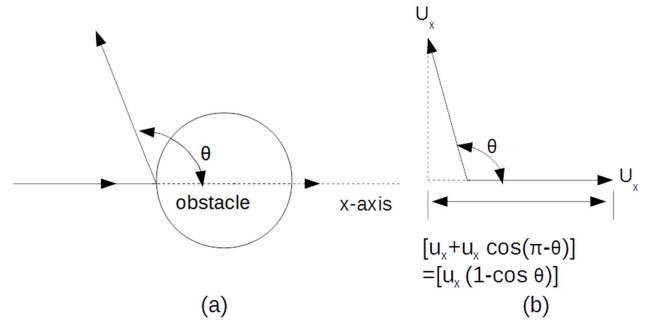


Fig. 2. Anisotropic scattering of an electron by an obstacle in the metal.

With reference to Fig. 2(a), let θ be angle of scattering of the electron on collision with the ion. Fig. 2(b) shows that as a result of the scattering process, the velocity U_x as given by eqn. (38) is changed to $U_x (1 - \cos \theta)$. When U_x changes to $U_x (1 - \cos \theta)$, then let g be defined as modified collision frequency. Under these circumstances, eqn. (38) is modified as follows,

$$U_x(1 - \cos \theta) = \frac{eE_x}{m_e(2g)}, \quad (53)$$

which gives,

$$U_x = \frac{eE_x}{m_e\{2g(1 - \cos \theta)\}}. \quad (54)$$

If with reference to eqn. (54), U_x is to remain same before and after scattering in comparison with eqn. (38), then comparison of the two expressions gives,

$$\frac{g_o}{g} = 1 - \cos \theta; \quad (55)$$

here g_o corresponds to collision frequency for isotropic case (i.e. $\theta = \pi/2$) and g corresponds to collision frequency for anisotropic case i.e. ($\theta \neq \pi/2$). In terms of relaxation times [refer to eqn. (42)],

$$\tau_o = \frac{1}{2g_o} \quad (56)$$

and,

$$\tau = \frac{1}{2g} \quad (57)$$

for isotropic and anisotropic case of the scattering respectively. Eqn. (56) is same as eqn. (42). Using eqns. (56) and (57), eqn. (55) gives,

$$\frac{\tau}{\tau_o} = 1 - \cos \theta. \quad (58)$$

In the present analysis, θ is an arbitrary angle of scattering

chosen. The above analysis holds good when θ lies in general between 0 to π . When $0 < \theta < \pi/2$, then this is considered to be a case of forward anisotropic scattering. Whereas, when $\pi/2 < \theta < \pi$, then this is considered to be a case of reverse anisotropic scattering. And $\theta = \pi/2$, gives the case of isotropic scattering.

If σ_o of present analyses corresponds to g_o or τ_o , and σ_t from data in physical tables corresponds to g or τ , then eqn. (55) or (58) gives,

$$\frac{\sigma_t}{\sigma_o} = 1 - \cos \theta, \tag{59}$$

since the conductivity is inversely proportional to the collision frequency or directly proportional to the relaxation time for a given electron density in the metal. Using eqn. (59), θ is given by,

$$\theta = \cos^{-1} \left(1 - \frac{\sigma_t}{\sigma_o} \right). \tag{60}$$

Value of θ can be calculated from the values of σ_t and σ_o . And the values of θ for noble metals at 293 °K are given in table 6.2, using last two columns of table 6.1. Table 6.2 shows that the values of θ for the metals analyzed in the present paper, lie in 2nd quadrant, θ being greater than $\pi/2$. So this is a case of reverse anisotropic scattering of the electron at electron-ion collision, with reference to the model of conductivity of noble metals of the present analysis.

Table 6.2. Values of scattering angle θ and relaxation Time τ for noble metals at $T = 293$ °K.

Metal	σ_t (mhos/m)	σ_o (mhos/m)	θ (degrees)	τ (sc)
Cu	$5.842(2) \times 10^7$	$4.692(9) \times 10^7$	$1.041(8) \times 10^2$	$2.449(2) \times 10^{-14}$
Ag	$6.207(3) \times 10^7$	$3.754(3) \times 10^7$	$1.308(0) \times 10^2$	$3.757(1) \times 10^{-14}$
Au	$4.104(0) \times 10^7$	$4.096(1) \times 10^7$	$9.011(1) \times 10^1$	$2.467(7) \times 10^{-14}$

In the present analysis, when θ lies in second quadrant i.e., $180 > \theta$ (Degrees) $> 90^\circ$ (Table 6.2), then eqn. (61) or (62) gives

$$\tau > \tau_o, \tag{63}$$

or,

$$g < g_o. \tag{64}$$

Although data taken from various physical tables in this analysis give representative average values, still it is sufficient to use them to illustrate the principals involved in connection with various results analyzed in this paper.

In the present analysis, average electronic drift current density in presence of a d.c. electric field in the metal is limited due to its finite conductivity, and d.c. energy and hence power associated with normal component of average electronic drift velocity (refer to Figs. 1 and 2) with respect to the direction of the d.c. electric field parallel to x-axis is

Further, the present analysis for conductivity shows that, the expression for conductivity of the metal given by eqn. (46) or eqn. (41) viz.,

$$\sigma_o = \frac{ne^2}{m_e} \tau_o,$$

or,

$$\sigma_o = \frac{ne^2}{m_e(2g_o)},$$

respectively, for the case of isotropic collisions, is to be modified by replacing τ_o by τ or g_o by g given by eqn. (58) or (55) i.e. by,

$$\tau = \tau_o(1 - \cos \theta), \tag{61}$$

or,

$$g = \frac{g_o}{(1 - \cos \theta)}, \tag{62}$$

to get corresponding value of the conductivity considering anisotropic scattering of the electron at electron-ion collision. This model assumes that θ is a constant for a given metal.

Values of $\tau = 1/2g$, for various values of θ given in Table 6.2, are shown in last column of Table 6.2 for noble metals at $T = 293$ °K.

scattered over randomly at electron-ion collisions, thereby increasing temperature of the metal accounting for Ohmic (heat) losses at the temperature T of the metal which here represents an average temperature of the metal attained in presence of these heat losses over the surroundings in equilibrium conditions.

7. Conclusions

Comparing last two columns of table 6.1, it is seen that agreement between the two values of conductivities viz., σ_o (as obtained by present analysis) and σ_t (as calculated from data given in the physical tables) is best for Au and successively differs in case of Cu and Ag respectively. The discrepancy between the two values of conductivities is attributed to anisotropic scattering of the election at electron-ion collision, as already described.

Value of θ (the scattering angle) is calculated from the values

of σ_t and σ_0 . And the values of θ for noble metals at 293 °K are given in table 6.2, using last two columns of table 6.1. Table 6.2 shows that the values of θ for the metals analyzed in the present paper, lie in 2nd quadrant, θ being greater than $\pi/2$. So this is a case of reverse anisotropic scattering of the electron at electron-ion collision, with reference to the model of conductivity of noble metals of the present analysis. Only metal gold practically undergoes isotropic scattering for electron-ion interactions in the metal, as $\theta \sim 90$ degrees.

Appendix

A.1. Modes of Elastic Waves Per Unit Volume of the Metal

Consider the metal in the form of a solid cube of length L . The elastic waves exist in the metal with nodes at the walls of the cube. Thus a length in the cube contains integral number of half wave-lengths. Considering all three mutually perpendicular axes, the wave-length λ of the elastic wave satisfies the following relationships, viz.,

$$L_x = n_x \frac{\lambda}{2} \dots (a); L_y = n_y \frac{\lambda}{2} \dots (b); L_z = n_z \frac{\lambda}{2} \dots (c) \quad (1.1)$$

where n_x , n_y and n_z are integers along the x-axis, y-axis and z-axis, respectively.

Equation (1.1) gives,

$$n_x^2 + n_y^2 + n_z^2 = \frac{4L^2}{\lambda^2}, \quad (1.2)$$

where

$$L = (L_x^2 + L_y^2 + L_z^2)^{1/2}. \quad (1.3)$$

Equation (1.2) represents a sphere in integral space of radius $2L/\lambda$. If v be the velocity of elastic wave, then $v = f\lambda$, where f is the frequency of the elastic wave. Thus, the radius of the sphere in integral space is given by, $2L/\lambda$.

The number of modes of elastic waves $Z_i'(f) \partial f$ with frequencies of the elastic waves between f and $f + \partial f$, considering the metal as a continuous medium, can be obtained by finding the volume of the annular space of thickness between $(2L/v)f$ and $(2L/v)(f + \partial f)$. From eqn. (1.2), it is clear that the length L of the cube contains integral number of half wavelengths. Moreover the integers (n_x , n_y , n_z) are considered as a set of modes of elastic waves in the integral space. The number of modes of elastic waves between the annular space is, therefore, equal to the volume of the shell given by,

$$4\pi (n_x^2 + n_y^2 + n_z^2) \partial \sqrt{(n_x^2 + n_y^2 + n_z^2)} = 4\pi \left(\frac{2Lf}{v}\right)^2 \partial \left(\frac{2Lf}{v}\right) = (4\pi f^2 / v^3)(2L)^3 \partial f \quad (1.4)$$

The number of modes of elastic waves, corresponding to positive values of integers (n_x , n_y , n_z) of the integral space would be 1/8th of those given by eqn. (1.4), viz.,

$$Z_i'(f) \partial f = \left(\frac{4\pi Vf^2}{v^3}\right) \partial f, \quad (1.5)$$

where $V = L^3$ is the volume of the metal under consideration. Thus the number of modes of elastic waves per unit volume of the metal in frequency interval between f and $f + \partial f$, using eqn. (1.5), is given by,

$$Z_i''(f) \partial f = (4\pi f^2 / v^3) \partial f. \quad (1.6)$$

In the above treatment only one possible mode of elastic waves has been considered. Actually three independent modes of elastic waves are to be considered. Two corresponding to a transverse elastic wave with velocity v_t and one corresponding to a longitudinal elastic wave with velocity v_l . Then considering the presence of both waves, eqn. (1.6) is modified to the one given by following expression, viz.,

$$Z_i(f) \partial f = 4\pi f^2 \left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right) \partial f. \quad (1.7)$$

The above mentioned expression given by eqn. (1.7) is used in the present analysis for the modes of elastic waves per unit volume of the metal, viz., eqn. (14) of the present paper. Further $Z_i(f)$ in eqn. (1.7), i.e.

$$Z_i(f) = 4\pi f^2 \left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right), \quad (1.8)$$

also gives the weight factor at frequency f for the elastic waves or the ionic mass-vibrator in the metal with reference to eqn. (18) of the present analysis. Here it is assumed that the fixed ions in the metal are elastically bound with respect to each other. These ions are considered to undergo mass-vibrations at temperature T of the metal in presence of the elastic waves, where frequency of mass-vibrations of the ions is assumed to be the same as that of elastic waves.

The above mentioned analysis holds good when length L of the cube is extremely large as compared to inter-ionic distance, viz. $2R_{os}$, where $R_{os} = (3/4\pi)^{1/3} n^{-1/3}$ and here n is ion density in the metal. The order of $2R_{os}$ for noble metals under considerations, using Table 5.1 is seen to be about 3×10^{-10} m. Although the present analysis is carried out for a metallic cube, the same results apply to any shape and size of the metal under consideration, provided the linear dimensions of the metal are extremely large as compared to the inter-ionic distances. In short, the metal is of macroscopic dimensions of conventional sizes.

A.2. Elastic Wave Velocities in the Metal

In the presence of elastic waves associated with fixed ions elastically bound with respect to each other in the metal and undergoing coupled mass-vibrations as analyzed in Secn. 2 of this paper, here it is assumed that the metal is thrown into vibrations as a whole considering it to be a continuous medium. Whence expressions, for transverse elastic wave velocity v_t and for longitudinal elastic wave velocity v_l in terms of average elastic constants of the metal can be obtained as follows:

A.2.1. Transverse Elastic Wave Velocity, v_t

The transverse (elastic) wave propagation in the metal is associated with the vibrations (of fixed ions in the metal, which are elastically bound with respect to each other) normal to the direction of wave propagation.

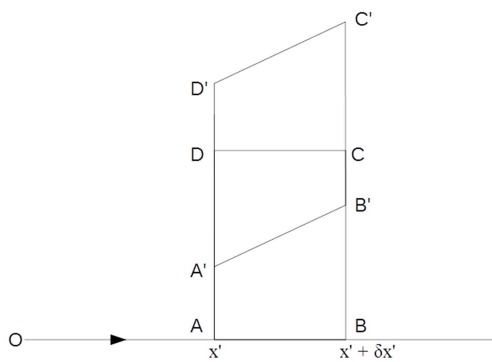


Fig. 2.1. Propagation of transverse elastic wave in the metal.

Let Ox' be the direction of wave propagation in the metal, in this case (Fig. 2.1). Consider a slice of metal $ABCD$ of thickness $\delta x'$, normal to Ox' . When the wave passes along, let every fixed ion in the plane AD undergoes the same lateral displacement in the plane of the figure, so that A goes to A' and D to D' . Let $AA' = DD' = y'$. Similarly, let every fixed ion in the plane BC undergo a lateral displacement $y' + \delta y'$. In this case, $BB' = CC' = y' + \delta y'$. In such circumstances the slice undergoes shearing in the y' -direction. The angle of shear is the relative displacement $\delta y'$ divided by the thickness $\delta x'$, that is given by $\frac{\delta y'}{\delta x'}$ for small values of the angle of shear. Thus the tangential force producing this shear at x' is $A_s \eta (\partial y' / \partial x')$ which acts in direction $D'A'$. Here A_s is area of cross-section of the slice normal to x' -direction and η is the modulus of rigidity of the metal. Similarly a tangential force producing a shear at $x' + \delta x'$ is given by,

$$A_s \eta \left(\frac{\partial y'}{\partial x'} \right) + A_s \partial / \partial x' \{ (\eta (\partial y' / \partial x') \delta x') \},$$

which acts in a direction $B'C'$. The net force tending to displace the slice in the y' -direction is the difference: $A_s \eta$

$\left(\frac{\partial^2 y'}{\partial x'^2} \right) \delta x'$. Further the volume of the slice is $A_s \delta x'$. And hence its mass is $\rho A_s \delta x'$, where ρ is the density of the metal. Thus the acceleration $\frac{\partial^2 y'}{\partial t^2}$ of the slice at any time t , is satisfied by the following relationship, viz.,

$$\rho A_s \delta x' \left(\frac{\partial^2 y'}{\partial t^2} \right) = A_s \eta \left(\frac{\partial^2 y'}{\partial x'^2} \right) \delta x', \quad (2.1.1)$$

which gives:

$$\left(\frac{\partial^2 y'}{\partial t^2} \right) = (\eta / \rho) \left(\frac{\partial^2 y'}{\partial x'^2} \right), \quad (2.1.2)$$

which is wave-equation with velocity of transverse elastic wave propagation in the metal given by,

$$v_t = \left(\frac{\eta}{\rho} \right)^{1/2}. \quad (2.1.3)$$

This value of v_t given by eqn. (2.1.3) is used in the present analysis, viz., the expression given by eqn. (51).

A.2.2. Longitudinal Elastic Wave Velocity, v_l

The longitudinal (elastic) wave propagation in the metal is associated with the vibrations (of fixed ions in the metal, which are elastically bound with respect to each other) in the direction of wave propagation.

If $e_{x'}$ be the strain in the metal in Ox' -direction which is the direction of wave propagation, then in this case,

$$e_{x'} = (1/q) [P_{x'} - \sigma'(P_{y'} + P_{z'})], \quad (2.2.1)$$

$$0 = (1/q) [P_{y'} - \sigma'(P_{z'} + P_{x'})], \quad (2.2.2)$$

$$0 = (1/q) [P_{z'} - \sigma'(P_{x'} + P_{y'})], \quad (2.2.3)$$

where strains in Oy' - and Oz' -directions normal to the direction of wave propagation are zero. $P_{x'}$, $P_{y'}$ and $P_{z'}$ are the stresses developed in the metal along the three axes of coordinates. q is young modulus and σ' is Poission ratio of the metal.

Solution of eqns. (2.2.1) to (2.2.3) gives,

$$\frac{P_{x'}}{e_{x'}} = q' = \frac{q(1-\sigma')}{(1+\sigma')+(1-2\sigma')}. \quad (2.2.4)$$

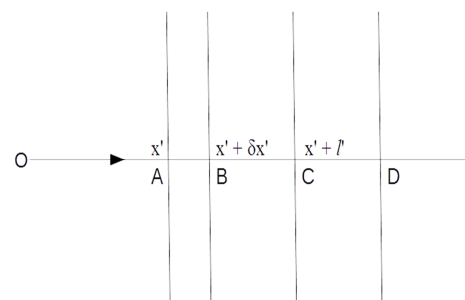


Fig. 2.2. Propagation of longitudinal elastic wave in the metal.

Eqn. (2.2.4) gives the relationship between stress and strain along Ox'-direction, when the longitudinal wave propagates through the metal. Here q' gives modulus of elongation.

Now consider the forces on a slice of metal AB of thickness $\delta x'$ (see Fig. 2.2) which is displaced along Ox'-direction to CD, so that each fixed ion in slice AB moves to slice CD longitudinally. Longitudinal strain at C for the slice is $(\partial l' / \partial x')$. This force on the slice at C is $A_s q' (\partial l' / \partial x')$, towards O along x'-direction. Here A_s is area of cross-section of the slice normal to x'-direction and q' is elongation modulus of the metal given by eqn. (2.2.4). Similarly force at D on the slice is,

$$A_s q' (\partial l' / \partial x') + A_s q' \partial / \partial x' (\partial l' / \partial x') \delta x',$$

which acts away from O along x'-direction. The net force tending to displace the slice in x'-direction is the difference: $A_s q' (\partial^2 l' / \partial x'^2) \delta x'$. Further the volume of the slice is $A_s \delta x'$ and hence its mass is $\rho A_s \delta x'$, where ρ is density of the metal. The acceleration $\partial^2 l' / \partial t^2$ of the slice at any time t, is satisfied by the following relationship, viz.,

$$\rho A_s \delta x' (\partial^2 l' / \partial t^2) = A_s q' (\partial^2 l' / \partial x'^2) \delta x' \quad (2.2.5)$$

which gives,

$$\left(\partial^2 l' / \partial t^2 \right) = (q' / \rho) \left(\partial^2 l' / \partial x'^2 \right). \quad (2.2.6)$$

Using eqn. (2.2.4), eqn. (2.2.6) gives,

$$\left(\partial^2 l' / \partial t^2 \right) = [q(1 - \sigma') / \rho(1 + \sigma')(1 - 2\sigma')] \left(\partial^2 l' / \partial x'^2 \right), \quad (2.2.7)$$

which is wave equation with velocity of longitudinal elastic wave propagation in the metal given by,

$$v_l = \left[\frac{q(1 - \sigma')}{\rho(1 + \sigma')(1 - 2\sigma')} \right]^{1/2}. \quad (2.2.8)$$

This value of v_l given by eqn. (2.2.8) is used in the present analysis, viz., the expression given by eqn. (52).

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