Effect of Particle Size on the Electrical Conductivity of Metallic Particles

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Abstract - Development of nanomaterial research has provided tremendous changes in technological advances. However, theories that have been used for this (bulk material) is not appropriate to explain the behavior of materials in nanometer size. Therefore, in this paper we explain the phenomenon of nanometer size effect of the metal to its electrical conductivity. Theory approach is used to derive the mathematical relationship between the nanometer scale of metal and the electrical conductivity. Electrical conductivity curve to the particle size is obtained from the results of mathematical formulation has been solved by simple calculation. Based on this curve, we obtained a decrease in the electrical conductivity as the size of nanoparticles decreases. These results were validated with experimental results from several sources that show the similar trends between the model and experimental results.

Keyword: electrical conductivity, metal, nanoparticles

1. Introduction

Electrical conductivity is one of the important characteristics of the metal for application in various fields. This characteristic is unique and different for each metal. Recently, development of nanomaterials research including nanoparticle metal has provided tremendous changes in sciences and technology. The study of nanoparticle metals show different properties compared to bulk metal. The Bulk metal has some properties such as the ability to be formed, has specific electrical conductivity and thermal conductivity [1]. However, there are changes in metal properties when their size are reduced to nanometer scale such as the transition to be a semiconductor, changing the super paramagnetic property to be ferromagnetic, a shift of absorption (Plasmon Absorption) and the utilization of nanometer-size metal in material applications of thermo electric [1-8].

The bulk metal has a specific electrical conductivity depending on its temperature. This behavior is not valid when the size of metal is reduced to the nanometer scale. Metal nanoparticle has varies electrical conductivity depending on the size. Based on this variation, the metal can be used for different application by controlling its size. However, the existing theories are irrelevant to explain the behavior of electrical conductivity in nanometer scale. So, some modification and correction are required on the existing theories. In addition, very few references that discuss specifically about the electrical conductivity of metal in nanometer scale. Therefore, in this paper we will discuss the electrical conductivity of metal in nanometer scale.

The electrical conductivity is associated with electron mobility. So, in order to obtain the relationship between electrical conductivity and size of the metal nanoparticle, mathematical approach was performed based on the behavior of electron in metals. We used simple calculation method to solve the mathematical approach result. The final result is the relationship curve between electrical conductivity and particle size. These results then validated with experimental data from several sources that aimed to determine the accuracy of the mathematical approach that used. In this paper we use experimental data in the form of the thermal conductivity of metal. We know that thermal conductivity and electrical conductivity have a linear relationship based on Wiedemann-Franz ratio, with k / σ is proportional to the absolute temperature ($k/\sigma = L \cdot T$), where k is thermal conductivity ($\text{watt}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), σ is electrical conductivity ($\text{ohm}^{-1}\cdot\text{m}^{-1}$) and L is Lorentz number (2.3×10^{-8} $\text{watt}\cdot\text{ohm}\cdot\text{K}^{-2}$). From this relationship, for the same temperature, electrical and thermal conductivity will be proportional. On nanometer scale, thermal conductivity tends to decrease with decreasing size [9].

2. Theoretical Approach of Metal Electrical Conductivity

The electrical conductivity is associated with electron mobility in metal and also closely related to the mean free path. To derive the mathematical equation of metal electrical conductivity, we described the behavior of electrons in metal. We can illustrate the position of the electron as shown in Fig. 1. An electron is located at a distance of **r** from the center of particle. When electron obtained energy from the outside, the electrons can move freely and collide with other nucleus. The electron is assumed can move in all directions with the same probability. In bulk metal, the electron will be scatters having traveled as long as λ (mean free path). Because the presence of particle boundary, in some direction the electron will be scattered after traveling shorter than λ.

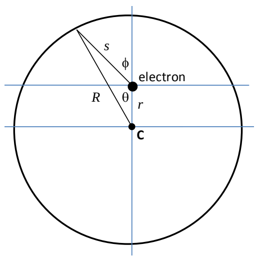

Fig. 1 The illustration of location of the electron.

Based on Fig. 1, we can obtain some mathematical expression based on Pythagoras law and cosines law. The distance s of electron from a point in the particle surface making an angle ϕ with the axis satisfies

$$s^2 = R^2 + r^2 - 2Rr\cos\theta \quad (1)$$

$$R\cos\theta = r + s\cos\phi . \quad (2)$$

with substituting Eq. (2) into Eq. (1), we got

$$s^2 = R^2 - r^2 - 2rs\cos\phi . \quad (3)$$

When the distance (s) of electron from the surface is equal to the mean free path (λ) or $s = \lambda$, we define as the critical angle (ϕ_c). So, from Eq. (3) we obtained

$$\cos\phi_c = \frac{R^2 - r^2 - \lambda^2}{2r\lambda} \quad (4)$$

Electron traveling at an angle of less that critical angle will be scattering after traveling shorter than the mean free path but electron traveling at angles of larger than the critical angle will be scattering after traveling as long as λ. From this situation we can estimate the average mean free path experienced by electron located at a distance r from the particle center as

$$\lambda(r) = \int_0^{\phi_c} s\left(\frac{1}{2}\sin\phi d\phi\right) + \int_{\phi_c}^{\pi} \lambda\left(\frac{1}{2}\sin\phi d\phi\right)$$

$$\frac{1}{2}\int_0^{\phi_c}\sqrt{R^2 - r^2 + r^2\cos^2\phi}\,\sin\phi d\phi =$$

$$\frac{\sqrt{R^2-r^2}}{2}\int_0^{\phi_c}\sqrt{1+\left(\frac{r^2}{R^2-r^2}\right)\cos^2\phi}\,\sin\phi d\phi \quad (5)$$

To simplify the eq.5, we define

$$\frac{r}{\sqrt{R^2-r^2}}\cos\phi = x \quad (6)$$

So that

$$-\frac{r}{\sqrt{R^2-r^2}}\sin\phi d\phi = dx \quad (7)$$

We remembered, when $\phi = 0$, then $x_0 = \frac{r}{\sqrt{R^2-r^2}}$ and when $\phi = \pi$, then $x_c = -\frac{r}{\sqrt{R^2-r^2}} = -x_0$. Therefore Eq. (5) takes the following form

$$\lambda_b(r) = \frac{\sqrt{R^2-r^2}}{2}\int_0^{\pi}\sqrt{1+\left(\frac{r^2}{R^2-r^2}\right)\cos^2\phi}\,\sin\phi d\phi$$

$$= \frac{\sqrt{R^2-r^2}}{2}\int_{x_0}^{-x_0}\sqrt{1+x^2}\left(-\frac{\sqrt{R^2-r^2}}{r}dx\right)$$

$$= -2\left(\frac{R^2-r^2}{2r}\right)\int_0^{-x_0}\sqrt{1+x^2}\,dx$$

$$= -\left(\frac{R^2-r^2}{2r}\right)\left[(-x_0)\sqrt{1+(x_0)^2} + \sinh^{-1}(-x_0)\right]$$

(8)

$$(-x_0)\sqrt{1+(-x_0)^2} = -\frac{r}{\sqrt{R^2-r^2}}\sqrt{1+\frac{r^2}{R^2-r^2}}$$

$$= -\frac{r}{\sqrt{R^2-r^2}}\sqrt{\frac{R^2-r^2+r^2}{R^2-r^2}}$$

$$= -\frac{rR}{R^2-r^2} \quad (9)$$

$$x_c\sqrt{1+x_c^2} = \frac{r\cos\phi_c}{\sqrt{R^2-r^2}}\sqrt{1+\frac{r^2}{R^2-r^2}\cos^2\phi_c}$$

$$= \frac{r\cos\phi_c}{R^2-r^2}\sqrt{R^2-r^2+r^2\cos^2\phi_c} \quad (10)$$

We define,

$$\sinh^{-1}(-x_0) = -\sinh^{-1}\frac{r}{\sqrt{R^2-r^2}} \quad (11)$$

$$\sinh^{-1}x_c = \sinh^{-1}\frac{r\cos\phi_c}{\sqrt{R^2-r^2}} \quad (12)$$

Then, we are substituting Eqs. (9-12) into Eq. (8) and we get

$$\lambda_b(r) = -\left(\frac{R^2-r^2}{2r}\right)\left[-\frac{rR}{R^2-r^2} - \sinh^{-1}\frac{r}{\sqrt{R^2-r^2}}\right]$$

$$= \left(\frac{R^2-r^2}{2r}\right)\left[\frac{rR}{R^2-r^2} + \sinh^{-1}\frac{r}{\sqrt{R^2-r^2}}\right]$$

$$= \frac{R}{2} + \left(\frac{R^2-r^2}{2r}\right)\sinh^{-1}\frac{r}{\sqrt{R^2-r^2}} . \quad (13)$$

Let us then determine the wave function of electron in the metallic sphere of radius R. For spherical symmetry potential, the general solution of Schrodinger equations satisfies

$$\Psi(r,\theta,\phi) = R(r)Y_{\ell m}(\theta,\phi) , \quad (13)$$

with $Y_{\ell m}(\theta,\phi)$ is the spherical harmonic function. The spherical harmonic function is the Eigen function of operator

$$\hat{\ell}^2 = -\frac{1}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right], \quad (13)$$

that satisfies

$$\hat{\ell}^2 Y_{\ell m}(\theta,\phi) = \ell(\ell+1)Y_{\ell m}(\theta,\phi) . \quad (13)$$

Schrodinger equation for this case:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi) \quad (17)$$

We approximate the potential inside the sphere is zero and the potential outside is infinity. The solution for wave function inside the sphere is following

$$\left\{-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}\right\}R(r) = ER(r) \quad (18)$$

Equation (18) derived from the differential Schrodinger equation. To simplify the Eq. (18), we define

$$k^2 = \frac{2mE}{\hbar^2} \quad \text{and} \quad \rho = kr \tag{19}$$

$$\Re(\rho) = \sqrt{\rho}R(r) \tag{20}$$

The above equation takes the following form

$$\rho^2 \frac{d^2\Re(\rho)}{d\rho^2} + \rho \frac{d\Re(\rho)}{d\rho} + \left[\rho^2 - \left(\ell + \frac{1}{2}\right)^2\right]\Re(\rho) = 0 \tag{21}$$

The Eq. (21) is form of Bessel's equation. Solution for positive energy is the spherical Bessel function and the general solution for radial function of electron wave function becomes

$$R(r) = j_\ell(kr) = \sqrt{\frac{\pi}{2kr}} J_{\ell+1/2}(kr) \tag{22}$$

Since the potential outside the sphere is infinity, at r = R, the wave function must be zero. This is accommodated by

$$j_\ell(kR) = 0 \tag{23}$$

We are looking for spherical symmetric orbital ($\ell = 0$). In this case,

$$R(r) = \frac{\sin(kr)}{kr}. \tag{24}$$

When $r = R$, is given by $\sin(kR) = 0$ or, $k = \frac{n\pi}{R}$. We can define energy that related to wave function E_n,

$$E_n = \frac{\hbar^2 k^2}{2m} = n^2 \frac{\hbar^2 \pi^2}{2mR^2} = n^2 \frac{h^2}{8mR^2} \tag{25}$$

From previous explanation, the general solution for wave function becomes:

$$\Psi(r,\theta,\phi) = \Psi_n(r) = \frac{\sin(n\pi r/R)}{n\pi r/R} \tag{26}$$

The probability of obtaining particles at a distance between r and $r+dr$ from the center of the sphere can be defined as in Eq. (27)

$$\frac{|\Psi_n(r)|^2 4\pi r^2 dr}{\int_0^R |\Psi_n(r)|^2 4\pi r^2 dr} = \frac{|\Psi_n(r)|^2 r^2 dr}{\int_0^R |\Psi_n(r)|^2 r^2 dr} \tag{27}$$

We can write the averages mean free path of electron belongs to wave function $\Psi_n(r)$ as in Eq. (28).

$$\lambda_{b,n}(R) = \frac{\int_0^R \lambda_b(r) |\Psi_n(r)|^2 r^2 dr}{\int_0^R |\Psi_n(r)|^2 r^2 dr} \tag{28}$$

The thermal average of the mean free path

$$\langle \lambda(R) \rangle = \frac{\sum_{n=1} \frac{\lambda_n(R)}{\exp(E_n - E_F)/kT + 1}}{\sum_{n=1} \frac{1}{\exp(E_n - E_F)/kT + 1}} \tag{29}$$

where E_F is the Fermi energy of the metal, k is the Boltzmann constant, and T is the absolute temperature.

3. Results and Discussion

The main purpose of this letter is to obtain mathematical formulation for electrical conductivity of metal in nanometer scale. At the stages of the calculation, we are substituting Eq. (26) into Eq. (28)

$$\lambda_n(R) = \frac{\int_0^R \lambda_b(r) \left(\frac{\sin(n\pi r/R)}{n\pi r/R}\right)^2 r^2 dr}{\int_0^R \left(\frac{\sin(n\pi r/R)}{n\pi r/R}\right)^2 r^2 dr} \tag{30}$$

Substituting Eq. (13) into Eq. (28) will produce

$$\lambda_n(R) = \frac{\int_0^R \left\{\frac{R}{2} + \left(\frac{R^2 - r^2}{2r}\right)\sinh^{-1}\frac{r}{\sqrt{R^2 - r^2}}\right\}\sin^2\left(\frac{n\pi r}{R}\right)dr}{\int_0^R \sin^2\left(\frac{n\pi r}{R}\right)dr}$$

$$\lambda_n(R) = \frac{R}{2} + \frac{\lambda_0^2}{R}\int_0^R \left\{\left(\frac{(R/\lambda_0)^2 - (r/\lambda_0)^2}{(r/\lambda_0)}\right)\sinh^{-1}\frac{(r/\lambda_0)}{\sqrt{(R/\lambda_0)^2 - (r/\lambda_0)^2}}\right\}\sin^2\left(\frac{n\pi(r/\lambda_0)}{(R/\lambda_0)}\right)d(r/\lambda_0) \tag{31}$$

To get the solution of Eq. (31) easily, we define $r/\lambda_0 = x$ and $R/\lambda_0 = Y$. Then, we define the boundary integral for Eq. (31). When $r=0$, so $x=0$ and when $r=R$, so $x=Y$.

$$\lambda_{b,n}(R) = \frac{R}{2} + \frac{\lambda_0^2}{R}\int_0^Y \left\{\left(\frac{Y^2 - x^2}{x}\right)\sinh^{-1}\frac{x}{\sqrt{Y^2 - x^2}}\right\}\sin^2\left(\frac{n\pi x}{Y}\right)dx$$

$$\lambda_{b,n}(R) = \lambda_0\left[\frac{Y}{2} + \frac{1}{Y}\int_0^Y \left\{\left(\frac{Y^2 - x^2}{x}\right)\sinh^{-1}\frac{x}{\sqrt{Y^2 - x^2}}\right\}\sin^2\left(\frac{n\pi x}{Y}\right)dx\right]$$

$$\lambda_{b,n}(R) = \lambda_0 \omega_n\left(\frac{R}{\lambda_0}\right)$$

Then, we have,

$$\omega_n\left(\frac{R}{\lambda_0}\right) = \frac{Y}{2} + \frac{1}{Y}\int_0^Y \left\{\left(\frac{Y^2 - x^2}{x}\right)\sinh^{-1}\frac{x}{\sqrt{Y^2 - x^2}}\right\}\sin^2\left(\frac{n\pi x}{Y}\right)dx$$

when n = 1, we get

$$\lambda_{b,1}(R) = \lambda_0 \omega_1\left(\frac{R}{\lambda_0}\right)$$

And free mean path,

$$\lambda_{eff}(R) = \frac{\lambda_0}{1 + \frac{1}{\omega_1(R/\lambda_0)}}$$

From this relationship we have the expression for the size dependent electrical conductivity as Eq. (32)

$$\sigma(R) = \frac{\sigma(\infty)}{1 + \frac{1}{\omega_1(R/\lambda_0)}} \tag{32}$$

From this solution, we can explain the relationship of electrical conductivity of metal and nanoparticle size as shown in Fig. 2. We can see that the electrical conductivity decreases as the size of nanoparticles decreases. From this solution, we got a critical value for electrical conductivity. When electrical conductivity is less than critical value, the electrical conductivity is proportional to the nanoparticle size. When electrical conductivity is larger than critical value, the particle size increasing does not affect the electrical conductivity.

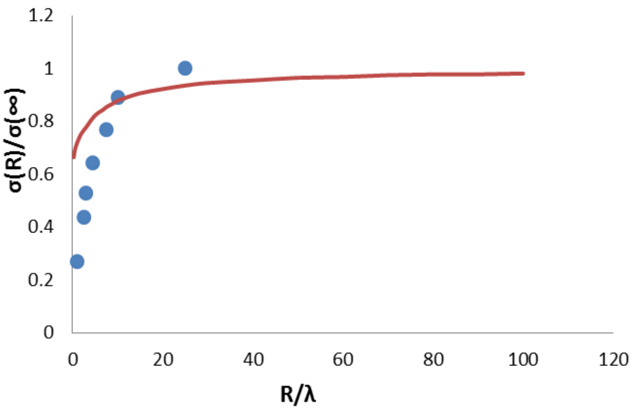

Fig. 2 The electrical conductivity of metallic particles. The solid line represent electrical conductivity of nanoparticle metal from our model and dashed line represent electrical conductivity of copper metal. Data point is copper thin film [9].

The experimental data was used to validate the developed model. According to Fig. 2, it has not been clearly observed the accuracy of the model due to the limited experimental data that was obtained. However, generally, similar tendency was observed in both experimental data and the developed model.

4. Conclusion

We have developed a model for electrical conductivity and using experiment date for validation. Based on model and experiment date, we obtained the electrical conductivity decreases as the size of nanoparticles decreases.

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