TITLE OF THE PROJECT

Solid State Physics IV

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Student's name

Student's sciper number

Date

Report structure

Scientific Question:

How simple is aluminium: can its electronic properties be modelled with a classical Drude model or an independent electron approximation?

Abstract

Introduction

1. Description of the model and theoretical framework
2. Crystalline and electronic structure

Main report

1. General description of the experiment
2. Data and Analysis
3. Discussion

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Abstract

The Drude model provides a conceptionally straightforward and simple formalism for the description of the motion of electrons in a solid. Its main hypothesis is that electrons behave as free charge carriers that undergo a scattering mechanism. Density functional theory (DFT) provides a description of a solid based on the concepts developed after the discovery of quantum mechanics, and can be regarded as an ab-initio description. Its main approximation is very similar to that of the Drude model, and it consists of considering the electrons as free carriers, neglecting their mutual interaction. In this report, we start from the optical data obtained experimentally from a sample of aluminum and analyse them with both a simple Drude model and a DFT approach. We compare our results with the literature with the aim of describing the metallicity of the solid.

Introduction

We seek to understand if the Drude model of metals is sufficient to explain the metallic behaviour of aluminium. Although this model is widely used, it has some significant shortcomings when used to predict the properties of certain materials. In the Drude model, each ion donates one or more of its electrons to a common thermal gas. In Drude's original description, the electrons in the gas are free to move about this crystal and occasionally collide with the ions, but otherwise all other interactions between the electrons and other electrons are neglected. Thus, the electrons quickly settle into a state of thermal equilibrium, with properties determined by their number density and temperature (which is the same temperature as the underlying metal). The number density is determined by the valency of the metal. In the case of aluminium, the valency is 3, and so each atom donates 3 of its 27 electrons to the electron gas.

The Drude model was developed in 1900 and has retained remarkable success in its prediction of AC and DC electrical conductivity of metals, heat conductivity, the Hall effect, and magnetoresistance. The model successfully predicts that metals that conduct heat very well, such as copper, will also be very good electrical conductors, while metals such as Pb who are poor heat conductors are also poor electrical conductors. A general formula for the number density n of a metal in the Drude model with valency z, density ρ, and relative atomic mass M_r is given by

$$n = \frac{z\rho N_A}{M_r \times 10^{-3}\ kg\ mol^{-1}} \tag{1}$$

where N_A is Avagadro's number. The number density for electrons can be used to calculate the average spacing between them. This is given by

$$d = \left(\frac{N}{V}\right)^{-1/3} = n^{-1/3} \tag{2}$$

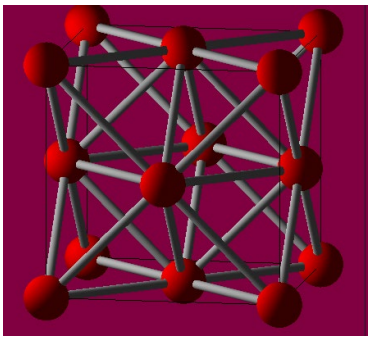
where N is the total number of electrons and V is the volume of the metal. For aluminium, this spacing is 0.2 nm, which is surprisingly close to the lattice parameter. Today, we know that this is a mere coincidence.. The potential energy between these electrons due to Coulomb repulsion is

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{d} = 7\ eV. \tag{3}$$

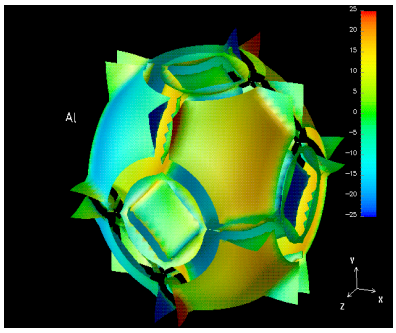
This is a very high energy, and suggests that the Drude model is unrealistic in its treatment of electrons. However, the key ingredient of the Drude model was to assume that conduction band electrons can be viewed as free particles undergoing a scattering mechanism with one well defined characteristic rate. This, we will see, remains valid and combining it with the quantum Fermi-Dirac statistics, in 1927, Sommerfield developed it into the commonly known free electron model, or the Drude-Sommerfield model. Applying the restriction that electrons in a material must follow Fermi-Dirac statistics, one can see that electrons will quickly fill the energy levels up to around 7 eV. We will examine whether or not this model is applicable for the simple metal aluminium.

In this report, we compare the results of the Drude model to the behaviour of aluminium in two ways. First, we fit the reflectivity of aluminium with a combination of Lorentz oscillators using the program RefFit, and use this fit to generate a prediction for the conductivity of the material. Next, we compare this conductivity to that of the literature, and compute the effective number of carriers involved in conduction from our model. Finally, we use density functional theory to calculate the bands of fcc aluminium and compare these band occupation numbers to the valency model used in the Drude model.

The crystalline structure of Al is face cubic centered (fcc), given in Fig. 1(a), and belongs to the point group m3m. In its irreducible representation, the unit cell of Al contains one atom.



(a)



(b)

Figure 1. *(a): FCC structure of Al. The red balls represent Al atoms [1]. (b) Fermi surface of Al [2].*

Experiment

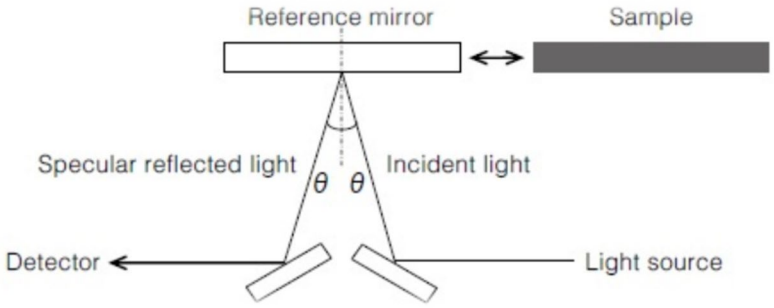


Figure 2. *Specular reflectance from a thin film sample [3].*

The optical constants of an Al single crystal were obtained by measuring the reflectivity of an optically polished flat sample by means of a Fourier transform spectrometer. The experimental schematic is shown in figure 2.

In Fig. 3, we plot the reflectivity spectrum together with a Drude Lorentz model. The fitting process for this fit was

completed using a Levenberg-Marquart fitting algorithm as implemented by the RefFit software [5]. The data are given by the black squares while the model is plotted in red. In this plot, the plasma edge of the material is visible at 120000 $\boldsymbol{cm^{-1}}$, representative of the light-induced collective oscilations of the conduction band electrons, and a low-energy absorption feature at 10000 $\boldsymbol{cm^{-1}}$.

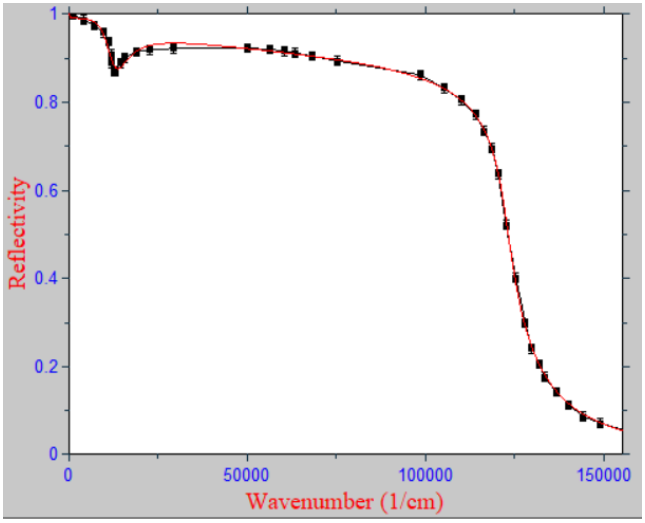


Figure 3. *Spectral dependence of the reflectivity of aluminium [4].*

To retrieve the optical conductivity, we model the optical reflectivity with a sum of Drude-Lorentz oscillators and calculate the dielectric function by applying the formula:

$$\boldsymbol{R(\omega)} = \left|\frac{\mathbf{1}-\sqrt{\boldsymbol{\varepsilon}}}{\mathbf{1}+\sqrt{\boldsymbol{\varepsilon}}}\right|^{\mathbf{2}} \qquad (4)$$

where

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \ . \qquad (5)$$

The intraband contribution to the optical properties can be described phenomenologically to within experimental error with a Drude-like model dielectric function for the electron gas:

$$\epsilon_{Drude} \sim \epsilon_0 \ - \ [\omega_p^2/\omega \ (\omega + \tfrac{i}{\tau})], \qquad (6)$$

where the contribution to the dielectric function from core interband transitions has been included in ϵ_0, which is almost constant (~1.035) throughout the region of conduction electron absorption. Here ω_p is the plasma frequency for intraband transitions and τ the intraband relaxation time. The dielectric function as calculated using our fit to optical spectra is plotted in Figure 4.

Next, the optical conductivity σ(ω) is related to ε(ω) by

$\sigma(\omega) = 2\pi i \frac{\omega}{z}(1-\varepsilon)$ where $\sigma = \sigma_1 + i\sigma_2$ and $\sigma_1 = \frac{\omega\varepsilon_2}{4}$, $\sigma_2 = \frac{\omega}{4\pi}(1-\varepsilon_1)$.

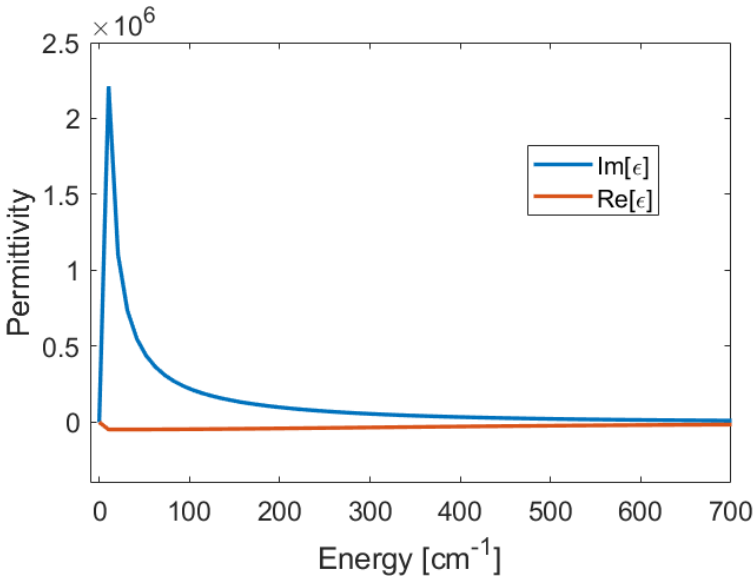


Figure 4. *Dielectric function: the real (plotted in red) and the imaginary part (plotted in blue) calculated with Reffit [5].*

Comparison between the Drude model and the independent electron model with LDA approximation

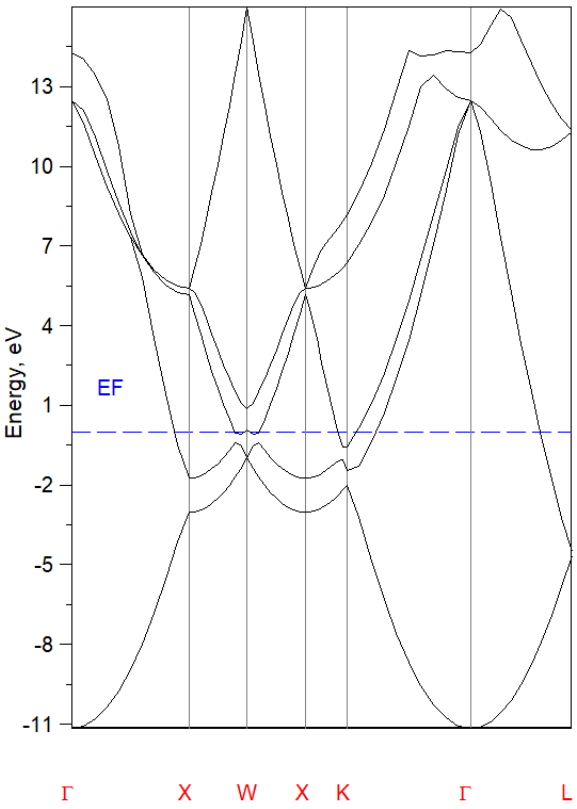


Figure 5. *The band structure of aluminium.*

We observe that a simple Drude-Lorentz model fits the optical spectrum of aluminium very well, in particular the low-energy part of the spectrum. From this, we deduce that the electrons in Al can be very well described by a Drude like model and behave mostly as independent particles that undergo only one scattering mechanism.

To quantitatively evaluate this idea, we perform a band structure calculation using open source software LMTart. This software uses the local density approximation to perform density functional theory calculations using linear muffin-tin orbitals as a basis for representing first-order corrections to the one electron wavefunctions [6]. In Figure 6 we plot the bands. We can clearly see that just below the Fermi level we have one completely filled band and two partially filled ones, for a total of three orbitals contributing to the low-energy optical spectrum, consistent with Drude's original count. With one Al atom per unit cell contributing 3 valence electrons, we expect to fill one and a half bands.

Next we calculate some optical properties from band structure using Fermi's golden rule. The real part of the optical conductivity is calculated from [7] using

$$\sigma_1(\omega) = \frac{2\pi e^2}{3m^2\omega}\sum\int\frac{d^3k}{(2\pi)^3}|\langle lk|p|nk\rangle|^2 \times f_l(k)[1-f_n(k)]\delta[E_n(k)-E_l(k)-\frac{h}{2\pi}\omega]\,. \qquad (7)$$

According to this calculation (plotted together with the conductivity from the Drude model and data from Ref [4]), we can see that there is similar behavior in the two models. The qualitative agreement confirms our idea that from looking at the bands we can determine that the conduction band is made of electrons from s-p hybridized orbitals in the number of 3 total.

We now use the optical conductivity from both the Drude model and density functional theory to make estimates on the effective number of carriers in each model using the formula [8]:

$$N_{eff}(20\ eV) = \frac{m_e}{2\pi^2 e^2}\int_0^{20eV}\omega\epsilon_2(\omega')d\omega' \qquad (8)$$

which is related to the effective number density of electrons participating in the absorption up to an energy of 20 eV (which should be the contribution from the electrons involved in the conduction band).

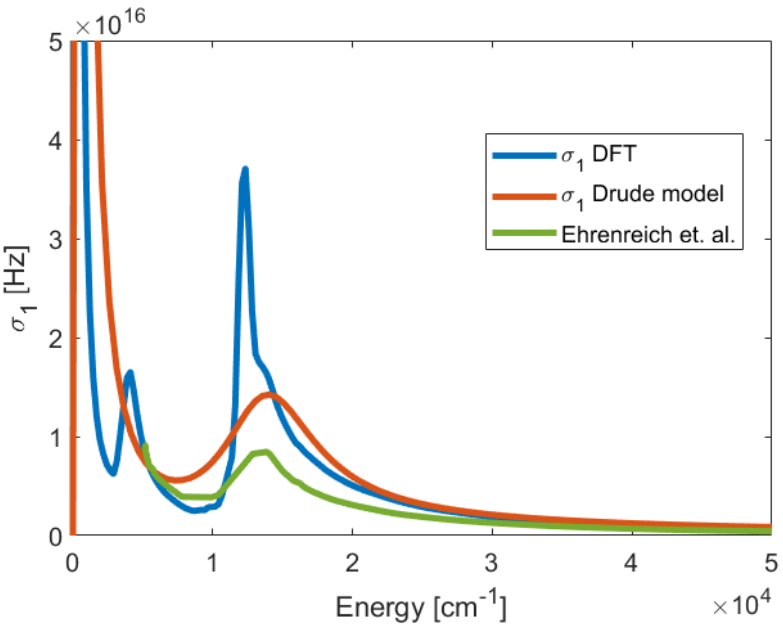


Figure 6. *Comparison between conductivity computed from the Drude model, DFT and Ehrenreich et. al .*

Using the data from Fig. 4 in the Drude model we calculate the number of electrons involved, N_{eff} (x number of electrons in a kg of Al) = 3.41. Next, we integrate the area under the conductivity from the DFT model (plotted in blue in Fig. 6) and we get a value for N_{eff} of 2.64. Since we expect there to be 3 charge carriers in the conduction band, we see that both models come fairly close to approximating the number of carriers well. To compare our calculation of N_{eff} to the literature we consider Ref [9], which extracts the N_{eff} from another optical conductivity data set, and finds the number of carriers to be 3.11. The overestimation of N_{eff} from our Drude model could be due to small differences in the data set and uncertainty in the exact location of the plasma frequency, or because the Lorentz-Drude fitting we used slightly overestimates the conductivity as compared to the data of Ehrenreich *et. al.* (see figure 6). For the band theory calculation, the errors can be due to numerical inaccuracy in the low frequency data of the LDA calculations which would require a much more powerful computer to be precise.

Conclusion

Aluminium is a simple metal in which electrons can be considered as free particles undergoing a scattering mechanism as described by the Drude model. The material is also well described by an independent electron model where correllations are treated as perturbations as in density functional theory. The optical properties of the system computed from both the Drude model and DFT confirm this scenario and allow us to estimate the number of carriers in the conduction band. Our calculations show that the number of carriers is close to 3 for both the DFT and the Drude modelling, and we confirm this value with references to the literature.

Works Cited

[1]: The crystalline structure was obtained using MStudio program: http://mindlab.physics.ucdavis.edu/MaterialResearch/MINDLab/index_general.htm

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