Theoretical study on the effects of polarons on the transport properties of anatase TiO₂

A Bupu* and M A Majidi
Department of Physics, Faculty of Mathematics and Natural Sciences (FMIPA), Universitas Indonesia, Depok, Indonesia 16424

*aziz.majidi@sci.ui.ac.id

Abstract. We present a theoretical study on the effects of electron-phonon interactions on the transport properties of anatase TiO₂. Temperature-dependent resistivity measurement on anatase TiO₂ thin film has shown that carrier concentrations and temperatures affect the resistivity of this material. At low carrier concentrations, a metal to insulator transition could be observed, while at high carrier concentrations this material only shows metal-like resistivity. In this study we aim to investigate the behaviour of temperature-dependent resistivity at various carrier concentrations as revealed in the experimental study. We hypothesize that electron-phonon interactions with intermediate coupling constant govern the transport properties of this material. We construct Holstein model Hamiltonian incorporating both conduction and valence bands of anatase TiO₂ within parabolic dispersion approximation. We solve the model within the Dynamical Mean Field Theory (DMFT). We calculate the density of states of the system and the corresponding inverse of the square of the density of states at the chemical potential, which is approximately proportional to the resistivity, as a function of temperature. Using carrier concentration values taken as in the experimental data, the calculations show that only insulating phase is found in the low carrier concentrations regime. Meanwhile, at high carrier concentrations, the results show metal-like properties, in agreement with the experimental data.

1. Introduction
Anatase TiO₂ has attracted considerable amount of interest of researchers due to its fascinating properties and potential applications. Besides its well-known role as photocatalyst [1,2], anatase TiO₂ has become a promising material for spintronics, optoelectronic devices, and as a transparent conducting oxides as well [3,4]. A stoichiometric anatase TiO₂ is an insulator with band gap of 3.2 eV. Its conduction band which mainly consists of Ti 3d orbitals is unoccupied. However, the presence of oxygen vacancies, the most common defect in this material, alters the electronic transport properties by adding excess electrons to the conduction band.

Several experimental works have been done in exploring the electronic transport properties of anatase TiO₂ [5-8]. DC conductivity measurements show that when the carrier density is on the order of $10^{17} - 10^{18}$ cm⁻³, a transition from insulator to metal is observed. Below ~60 K, resistivity falls with increasing temperature while above ~60 K resistivity increases as temperature goes higher. Recently, Yan et al. also measured the temperature-dependent resistivity of anatase TiO₂ at various carrier concentrations, ranging from $7 \times 10^{18}$ cm⁻³ up to $2 \times 10^{20}$ cm⁻³ [9]. In spite of the similar behaviour of the resistivity as function of temperature at low carrier concentrations, they found that
only metal-like transport properties are observed at high carrier density ($> 2 \times 10^{19}$ cm$^{-3}$). While those experimental works suggest that interactions between electrons and phonons play an important role in describing the temperature-dependent resistivity [7,9], the mechanism of the temperature dependence of transport properties of this material has not been clearly explained yet.

It has been a discourse from several experimental and theoretical studies that electrons in anatase TiO$_2$ are coupled with phonons, formed quasiparticles called polarons [10-14]. Previous studies reveal that the polarons in anatase TiO$_2$ can be classified as large polarons which have large radii up to several units lattice constant with intermediate values of coupling constant [15]. However, theoretical investigations on relating the presence of large polarons with the observed temperature-dependent resistivity are still scarce. In this work we hereby propose a theoretical study to investigate how electron-phonon interactions affect the transport properties of anatase TiO$_2$, as a function of temperature and carrier density, as observed in the experimental data of Yan et al [9]. Here, we use a simple model for the anatase TiO$_2$ incorporating excess of electrons. We use the Holstein model incorporating both valence and conduction bands in our Hamiltonian. Considering that large polarons are favoured in anatase TiO$_2$, we tune the electron-phonon interaction coupling constant, $g$, in the Hamiltonian such that the system exhibits the large polaronic behaviour. To obtain the dependence of resistivity on temperature and carrier concentration, we calculate the inverse of the square of density of states at the chemical potential, which is proportional to the resistivity, for various temperatures and carrier concentrations.

2. Model

As we aim to explore the effects of the electron-phonon interactions on the transport properties of anatase TiO$_2$, we choose two basis orbitals corresponding to the conduction and valence bands of anatase TiO$_2$. Using this basis set, we construct a Hamiltonian based on Holstein model that explicitly takes into account electron-phonon interactions as

$$ H = \sum_{k\lambda}(\epsilon_{\nu}(k)\alpha_{\nu k}^{\dagger}a_{\nu k} + \epsilon_{\sigma}(k)a_{\sigma k}^{\dagger}a_{\sigma k}) + \sum_{i} g(n_{\nu i} + n_{\sigma i})x_{i} $$

(1)

where $a_{\nu k}^{\dagger}(a_{\nu k})$ and $a_{\sigma k}^{\dagger}(a_{\sigma k})$ are the creation (annihilation) operators corresponding to the valence and conduction bands, respectively, $g$ is the electron-phonon coupling constant, $n_{\nu i}(n_{\sigma i})$ is the occupation number of electrons in the valence (conduction) band, $x_{i}$ is the displacement of the atoms. Here, $\epsilon_{\nu}(k) = -\frac{\hbar^{2}k^{2}}{2m_{\nu}}$ and $\epsilon_{\sigma}(k) = \frac{\hbar^{2}k^{2}}{2m_{\sigma}}$ are the energy dispersions of valence and conduction bands, respectively, with $E_{g} = 3.2$ eV being the energy gap of anatase TiO$_2$.

3. Method

We solve the Hamiltonian in equation (1) using Green’s function technique in the framework of the Dynamical Mean-Field Theory (DMFT). We first define the corresponding one-particle Green’s function through the Dyson equation, which is then coarse-grained over all $k$ points in the Brillouin zone as

$$ G_{\lambda}(z) = \Sigma_{k}(z - \epsilon_{\lambda}(k) - \Sigma(\lambda)(z))^{-1} $$

(2)

with $\lambda$ being an index denoting the valence or conduction band, $z$ is the complex frequency variable with $z = i\omega + \mu$ in Matsubara frequency domain, and $z = \omega + i0^{+}$ in real frequency domain, $\Sigma(z)$ is the self-energy. The DMFT algorithm requires that we initialize the chemical potential value, $\mu$, and self-energy with some guessed value. In this work, we transform the summation over $k$ into an integration over an energy-variable $\epsilon$ by taking the continuum limit of $k$ which yields
Here, \( \rho_{\theta \lambda}(\epsilon) \) is the bare density of states of each band which is derived from the energy dispersion relation of the corresponding band. By adding equation (3) with self-energy, we obtain the mean-field Green’s function as

\[
G_{\text{MF}, \lambda}(z) = \left( \frac{1}{G_{\lambda}(z)} + \Sigma_{\lambda}(z) \right)^{-1}.
\]

(4)

This is then used to compute the local interacting Green’s function defined as

\[
G_{\text{loc}, \lambda}(x, z) = \left( \frac{1}{G_{\text{MF}, \lambda}(z)} - \Sigma_{\text{loc}, \lambda}(x) \right)^{-1}
\]

(5)

where \( \Sigma_{\text{loc}, \lambda} \) is the local self-energy that carries the information of the electron-phonon interactions of our system defined as

\[
\Sigma_{\text{loc}, \lambda}(x) = gj(x).
\]

(6)

\( G_{\text{loc}, \lambda}(x, z) \) must be averaged over all values of atomic displacement. Hence, the averaged interacting Green’s function is to be obtained through

\[
G_{\text{ave}, \lambda}(z) = \int dx P(x) G_{\text{loc}, \lambda}(x, z).
\]

(7)

In equation (7), the integration is weighted by Boltzmann weighting factor, \( P(x) \), which should be obtained in Matsubara domain by

\[
P(x) = \frac{\epsilon^{-5\text{eff}}}{Z}
\]

(8)

with \( Z = \int dx e^{-\xi_{\text{eff}}} \) being the partition function acting as the normalization constant, and while \( S_{\text{eff}} \) is the effective action calculated from

\[
S_{\text{eff}} = -\sum_{\lambda, \nu} \ln \det \left( G_{\text{loc}, \lambda}(x, z) G_{\text{MF}, \lambda}^{-1}(z) \right).
\]

(9)

Having obtained the averaged interacting Green’s function, we then extract the new self-energy as

\[
\Sigma_{\lambda}(z) = \left( G_{\text{MF}, \lambda}(z) \right)^{-1} - \left( G_{\text{ave}, \lambda}(z) \right)^{-1}.
\]

(10)

We update the self-energy value in equation (3) using the new self-energy obtained in equation (10). Along the calculation, we also update the chemical potential, \( \mu \), by finding the root of the equation

\[
n_{\text{fill}} = -\int d\omega \text{DOS}(\omega) f(\omega, \mu, T) = 0.
\]

(11)

The process is then repeated until the self-energy converges. Here, \( n_{\text{fill}} = n_{\nu} + n \) is the total charge carrier density with \( n_{\nu} \) being the total carrier density in valence band, and \( n \) the carrier concentrations.
whose values are taken from the experimental measurements in Yan et al [9]. Once the self-consistency has been achieved, we do the post-process by calculating the interacting density of states defined as

\[
\text{DOS}(\omega) = -\text{Im} \left( G_{\text{ave}}(\omega + i0^+) + G_{\text{ave}}(\omega + i0^+) \right). \tag{12}
\]

Resistivity is the inverse of optical conductivity in the DC limit \((\omega \rightarrow 0)\) where the optical conductivity itself in this limit with \(T > 0\) could be defined as

\[
\sigma(\omega = 0) = \frac{\pi e^2}{\hbar v} \int_{-\infty}^{\infty} d\epsilon \frac{\Gamma(v,v,T)}{2\pi} \int_{-\infty}^{\infty} d\epsilon \rho(\epsilon) \text{Tr} \left[ \mu^\sigma(\epsilon) \right] \left[ A_0(\epsilon,\nu) \right] \left[ A^\beta(\epsilon) \right] \left[ A_0(\epsilon,\nu) \right]. \tag{13}
\]

where \([\mu^\sigma(\epsilon)]\) is the Cartesian component of the velocity matrix and \(A_0(\epsilon,\nu)\) is the spectral function matrix which could be expressed as

\[
[A_0(\epsilon,\nu)] = -\frac{1}{2m} \left( [G(\epsilon,\nu + i0^+)] - [G(\epsilon,\nu - i0^+)] \right). \tag{14}
\]

The spectral function defined above is basically similar to density of states that still carries the dependence of \(\epsilon\). In this work, we aim only to find the qualitative temperature and carrier concentration dependence of the resistivity. For this purpose, we apply an approximation by ignoring the \(\epsilon\) dependence of the spectral function in equation (13). This approximation yields

\[
\sigma \propto [A_0(\epsilon,\nu)] [A_0(\epsilon,\nu)] \propto (\text{DOS}(\mu))^2. \tag{15}
\]

Since the resistivity is the inverse of DC conductivity, \(\rho = \sigma^{-1}\), then

\[
\rho \propto (\text{DOS}(\mu))^{-2}. \tag{16}
\]

where \(\mu\) is the chemical potential of the system. Hence, to calculate the temperature-dependent resistivity, we use equation (16) as an approximate representative for the resistivity.

4. Results and discussion

As mentioned previously, in this calculation we use an energy-variable, \(\epsilon\), that has two limits which need to be specified. Hinted by the carrier concentrations used in Yan et al [9], we find that the chemical potentials of our system with those values of carrier densities are located near the edge of the conduction band. Since the phenomena we aim to explore occur near the chemical potentials, to make the calculation be efficient, we need to choose the lower and upper limits of \(\epsilon\) by zooming-in the density of states near the chemical potential while still capturing both valence and conduction bands. In this case, we use -2.0 eV and 5.2 eV as the lower and the upper limit of \(\epsilon\), respectively. Figure 1 shows the position of chemical potential for each carrier concentration in the bare density of states.
Figure 1. Bare density of states. Indices a, b, c, and d denote the locations of the chemical potential for various carrier concentrations that are used in Yan et al [9], namely, $n = 7.0 \times 10^{18}$ cm$^{-3}$, $n = 1.0 \times 10^{19}$ cm$^{-3}$, $n = 4.0 \times 10^{19}$ cm$^{-3}$, and $n = 2.0 \times 10^{20}$ cm$^{-3}$, respectively.

Since electron-phonon interactions in anatase TiO$_2$ have an intermediate coupling constant, we need to tune the electron-phonon coupling constant, $g$, to achieve a value corresponding to a large polaronic behavior. Figure 2 shows the density of states of the system for $g = 2.8$. For all carrier densities, the energy bands become wider with increasing temperature, while the chemical potential shifts to lower energy. Anatase TiO$_2$ with low carrier concentrations e.g. $n = 7.0 \times 10^{18}$ cm$^{-3}$ and $n = 1.0 \times 10^{19}$ cm$^{-3}$ show insulating properties since the chemical potentials are located in the gap. On the other hand, for $n = 2.0 \times 10^{20}$ cm$^{-3}$, in addition to the widening of the energy band with increasing temperature, the pseudogap becomes shallower as temperature increases. The pseudogap is only observed in this carrier concentration. The density of states of the other high carrier concentrations, $n = 4.0 \times 10^{19}$ cm$^{-3}$, do not show any formation of pseudogap. However, similar to the case of $n = 2.0 \times 10^{20}$, the chemical potentials are also located inside the band, indicating a metallic phase.
Figure 2. Total density of states with $g = 2.8$ at various temperatures and carrier concentrations: (a) $n = 7.0 \times 10^{18}$ cm$^{-3}$, (b) $n = 1.0 \times 10^{19}$ cm$^{-3}$, (c) $n = 4.0 \times 10^{19}$ cm$^{-3}$, and (d) $n = 2.0 \times 10^{20}$ cm$^{-3}$. The inset of each figure is the enlarged display of the density of states with the chemical potentials denoted by the vertical lines.

Figure 3 shows the inverse of the square of density of states ($\text{DOS}^{-2}(\mu)$) at the chemical potential for several values of carrier concentrations with various values of electron-phonon coupling constant, as a function of temperature, that represents the trends of the temperature dependence of resistivity of anatase TiO$_2$. For $n = 7.0 \times 10^{18}$ cm$^{-3}$, the $\text{DOS}^{-2}(\mu)$ raises with decreasing temperature which differ from the experimental results that shows the metal to insulator transition [5-8]. This discrepancy could reflect that in this regime the behavior of resistivity is not well described by the quantity $\text{DOS}^{-2}(\mu)$. On the other hand, for the higher carrier densities (figure 3(c) and 3(d)), our results are in agreement with experimental data in which the $\text{DOS}^{-2}(\mu)$ increases with increasing temperature [9]. When $n = 1.0 \times 10^{19}$ cm$^{-3}$, transition between two regimes of $\text{DOS}^{-2}(\mu)$ as function of temperatures could be seen with the transition temperature of $\sim 200$ K. This is in qualitative agreement with the experimental studies [8,9], despite that our calculated transition temperature values are much higher compared to those reported in Refs. [8,9]. In addition, as the electron-phonon coupling constant increases, the trends of the $\text{DOS}^{-2}(\mu)$ become more stable, especially for $n = 1.0 \times 10^{19}$ cm$^{-3}$. The ratios of the $\text{DOS}^{-2}(\mu)$ values for different carrier concentrations are similar to the corresponding ratios of resistivity values observed in experimental results. Despite that our calculation results show some noisy behaviors, such as in figure 3 (b), possibly due to lack of accuracy in the numerics, our calculations results have qualitatively captured that electron-phonon interactions indeed control the temperature dependence of resistivity for various carrier concentrations as revealed by the experimental data. This is an important finding as it strengthens our understanding of the mechanism.
governing the transport properties of anatase TiO$_2$, which could in turn guide experimentalists in how to prepare anatase TiO$_2$ for specific applications.

![Figure 3](image_url)

Figure 3. The inverse of the square of the density of states at the chemical potential, which is proportional to resistivity, as function of temperature at various carrier concentrations.

5. Conclusion
In conclusion, we have developed a simple model and performed calculations to investigate that the presence of electron-phonon interactions in anatase TiO$_2$ leads to the experimental results of temperature-dependent resistivity at various carrier densities. The magnitude of the electron-phonon coupling constant, $g$, suitable to describe the large polaronic behaviour is $\sim 2.8$. Using this magnitude, we could show the positive temperature dependence of resistivity, represented by the inverse of the square of density of states at the chemical potential, at high carrier concentrations and the transition from metal to insulator as temperature increases for $n = 1.0 \times 10^{19}$ cm$^{-3}$. We acknowledge that our calculations have not captured correctly the transition metal-to-insulator for the lowest carrier concentration. With regard to this, we argue that our results can be improved by performing real calculations of resistivity which fully incorporate all factors necessary to be taken into account.

Acknowledgment
We are very grateful to Universitas Indonesia for providing us a full funding for this project through PITTA B Research Grant No. NKB-0644/UN2.R3.1/HKP.05.00/2019

References
[1] Kim D, Yeo B C, Shin D, Choi H, Kim S, Park N, and Han S S 2017 Dissimilar anisotropy of electron versus hole bulk transport in anatase TiO$_2$: Implications for photocatalysis Physical
Review B 95(4) 045209

[2] He H, Zapol P, and Curtiss L A 2010 A theoretical study of CO2 anions on anatase (101) surface The Journal of Physical Chemistry C 114(49) 21474-21481

[3] Hitosugi T, Yamada N, Nakao S, Hirose Y, and Hasegawa T 2010 Properties of TiO2-based transparent conducting oxides Physica status solidi (a) 207(7) 1529-1537

[4] Yıldırım O, Cornelius S, Butterling M, Anwand W, Wagner A, Smekhova A, and Potzger K 2015 From a non-magnet to a ferromagnet: Mn+ implantation into different TiO2 structures Applied Physics Letters 107(24) 242405

[5] Forro L, Chauvet O, Emin D, Zuppiroli L, Berger H, and Levy F 1994 High mobility n-type charge carriers in large single crystals of anatase (TiO2) Journal of Applied Physics 75(1) 633-635

[6] Tang H, Prasad K, Sanjines R, Schmid P E, and Levy F 1994 Electrical and optical properties of TiO2 anatase thin films Journal of applied physics 75(4) 2042-2047

[7] Jaćimović J, Vaju C, Magrez A, Berger H, Forró L, Gaal R, Cerovski V, and Žikić R 2012 Pressure dependence of the large-polaron transport in anatase TiO2 single crystals EPL (Europhysics Letters) 99(5) 57005

[8] Gerspach D D and Wuttig M 2019 Metal-like conductivity in undoped TiO2-x: Understanding an unconventional transparent conducting oxide Thin Solid Films 669 1-7

[9] Yan B X, Wan D Y, Chi X, Li C J, Motapothula M R, Hooda S, Yang P, Huang Z, Zeng S, Ramesh A G, Pennycook S J, Rusydi A, Ariando, Martin J, and Venkatesan T 2018 Anatase TiO2 - a model system for large polaron transport ACS Appl Mater Interfaces 10(44) 38201-38208

[10] Gallart M, Cottineau T, Honerlage B, Keller V, Keller N, and Gilliot P 2018 Temperature dependent photoluminescence of anatase and rutile TiO2 single crystals: polaron and self-trapped exciton formation J Appl Phys 124(13) 133104

[11] Moser S, Moreschini L, Jacimovic J, Barisic O S, Berger H, Magrez A, Chang Y J, Kim K S, Bostwick A, Rotenberg E, Forro L, and Grioni M 2013 Tunable polaronic conduction in anatase TiO2 Phys Rev Lett 110(19) 196403

[12] Moser S, Fatale S, Kruger P, Berger H, Bugnon P, Magrez A, Niwa H, Miyawaki J, Harada Y and Grioni M 2015 Electron-phonon coupling in the bulk of anatase TiO2 measured by resonant inelastic x-ray spectroscopy Phys Rev Lett 115(9) 096404

[13] Zhukov V P and Chulkov E V 2014 Ab initio calculations of the electron-phonon interaction and characteristics of large polarons in rutile and anatase Phys Solid State 56(7) 1302-1309

[14] Verdi C, Caruso F, and Giustino F 2017 Origin of the crossover from polarons to Fermi liquids in transition metal oxides Nat Commun 8 15769

[15] Spreafico C and VandeVondele J 2014 The nature of excess electrons in anatase and rutile form hybrid DFT and RPA Phys Chem Chem Phys 16 26144-26152