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Optical properties of the massive Vanadium dioxide

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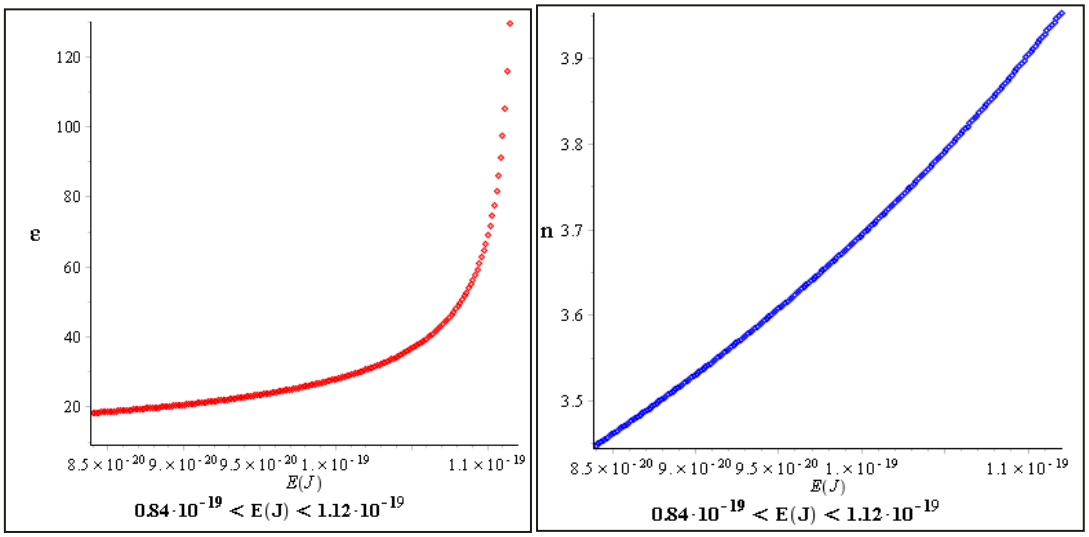
ABSTRACT

We can easily extract the optical properties from a material starting from its permittivity complexes ε; $\varepsilon = \varepsilon_1 - i\varepsilon_2$. The real part ε_1 of this dielectric function clearly takes its place in the Colombian interaction of an exciton. We are interested in exciton 1S in the case of the massive vanadium dioxide. We will solve Schrödinger's equation for this exciton by variational method and we obtain ε_1 according to energy E of the same exciton. We make a simulation by means of the Maple software of ε_1 and of the index of refraction n according to energy E of the exciton 1S, around and far from the band gap of this material while being based on the approximation of the effective mass. We will extract the reflectivity R and transmittivity T of the massive vanadium dioxide for the normal incidence of the incidental photons by considering a slightly absorbent semiconductor state.



Simulated curves of the real permittivity ε and the index of refraction n of the massive vanadium dioxide VO_2 according to the energy of the exciton 1S.

Indexing terms/Keywords

Massive vanadium dioxide, the dielectric function, the index of refraction, Semiconductor, exciton 1S, Energy of exciton, variational Method, the approximation of the effective mass, Energy of gap, the equation of Schrödinger, the Colombian interaction, Maple Simulation.

Academic Discipline And Sub-Disciplines

Science; Quatum Physics

SUBJECT CLASSIFICATION

Materials Physics; Thin Film Physics; massive.

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TYPE (METHOD/APPROACH)

Calculation by variational method, based simulation and modeling

INTRODUCTION

The vanadium dioxide VO_2 became a relevant material because of its transition from reversible phase **[1,2,13,15]** of the semiconductor state to the metal state at approximately 68 °C temperature in a few nanoseconds. Its optical and electronic properties change abruptly. Several studies were made on this material in a massive state and thin layer. At low temperature θ < 68 °C, this material behaves like a semiconductor with a gap of 0.7 ev in a monoclinical structure (M) **[5,14]**. At high temperature θ > 68 °C, this material becomes metal and is in a tetragonal rutile (R) structure. Mossaneck et al. **[11,16]** made optical studies of properties of massive VO_2. For incidental photons of energy $\omega > 0.7\ ev$, there is an electronic transition from the energy band $3d_{/\!/}$ towards the band $3d_{\pi}$; whereas, for incidental photons of energy $\omega > 2.5\ ev$ we have electronic transitions from the band $2d_{\pi}$ towards $3d_{\pi}$. For incidental photons of energy $\omega < 0.7\ ev$ we have the excitons formation.

We will simulate by Maple the considered variation of R and T according to energy E (ev) of the exciton 1S. This variation occurs on the order of a few nanoseconds.

Methods

We will calculate the energy **[6,7,8,10]** of an exciton 1S of Hamiltonian:

$$H = \frac{p_e^2}{2m_e^*} + \frac{p_h^2}{2m_h^*} - \frac{e^2}{\varepsilon r}$$

ε : the relative permittivity of material.

m_e^* : the effective mass of the electron.

m_h^* : the effective mass of the hole.

a : the ray of effective Bohr with 3D of the exciton 1S.

p_e : the impulse of the electron.

p_h : the impulse of the hole.

m : the total mass of the exciton.

μ : the reduced mass of the exciton.

$\vec{K}$: the wave vector of the exciton.

$$r = |\vec{r_e} - \vec{r_h}|\ ;\ \vec{P} = \vec{p_e} + \vec{p_h}\ ;\ \vec{K} = \vec{k_e} + \vec{k_h}\ ;\ m = {m_e}^* + {m_h}^*\ ;\ \mu = \frac{{m_e}^*.{m_h}^*}{{m_e}^* + {m_h}^*}\ ;\ P = -i\hbar\frac{\partial}{\partial R} = -i\hbar\frac{\partial}{\partial r};$$

we will work in the center of the system of the exciton mass :

$$({m_e}^* + {m_h}^*).\vec{R} = {m_e}^*.\vec{r_e} + {m_h}^*.\vec{r_h}$$

We will solve the equation of Schrödinger :

$$H\psi(\vec{r_e},\vec{r_h}) = (E - E_g)\psi(\vec{r_e},\vec{r_h})\ ;\ \psi(\vec{r},\vec{R}) = \frac{1}{\sqrt{\Omega}}\, e^{i\vec{K}.\vec{R}}\,\varphi(\vec{r});\ \Omega : \text{volume of crystal}$$

By a substitution in Schrödinger's equation **[9]**, we have :

$$E - E_g = \frac{\hbar^2 K^2}{2m} + \eta\ ;\ \varphi(\vec{r}) : \text{the test's function}$$

$$\left(\frac{p^2}{2\mu} - \frac{e^2}{\varepsilon r}\right)\varphi(\vec{r}) = \eta\varphi(\vec{r})\ ;\ \varphi(\vec{r}) = \frac{1}{\sqrt{\pi a}}e^{-\frac{\vec{r}}{a}}$$

We will do a calculation by variational method **[3,4],** where a is the variational parameter.
E: the energy of the exciton which we will minimize.

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}\ ;\ \frac{dE}{da} = 0\ \rightarrow\ E_{min} = R_0^{ex}\ ;\ \langle\psi|\psi\rangle = 1, \text{condition of noramalisation}$$

$$\langle\psi|\psi\rangle = \int \psi_{1s}\psi_{1s}^*\, d\tau = \frac{1}{\pi a^3}\int e^{-\frac{2r}{a}}4\pi r^2\, dr$$

we pose :

$$I = \langle\psi|H|\psi\rangle;\ B = \frac{1}{\sqrt{\pi a^3}};\ p \rightarrow -i\hbar\frac{\partial}{\partial r};$$

$$J = \langle\varphi|H|\varphi\rangle = L - G$$

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$$L = \frac{-\hbar^2}{2\mu} \cdot \left\langle \varphi \left| \frac{\partial^2}{\partial r^2} \right| \varphi \right\rangle ; G = \frac{e^2}{\varepsilon} \cdot \left\langle \varphi \left| \frac{1}{r} \right| \varphi \right\rangle$$

$$L = \frac{-\hbar^2}{2\mu} \cdot \frac{B^2}{a^2} \cdot \int_a^0 e^{\frac{-r}{a}} \cdot e^{\frac{-r}{a}} \cdot 4\pi r^2 dr \; ; \; L = \frac{-4\pi B^2 \hbar^2}{2\mu a^2} \int_a^0 r^2 \cdot e^{\frac{-2r}{a}} dr$$

$$G = \frac{e^2}{\varepsilon} \int_a^0 B^2 \cdot e^{\frac{-2r}{a}} \cdot \frac{1}{r} \cdot 4\pi r^2 dr \; ; \; G = \frac{e^2 \cdot B^2 \cdot 4\pi}{\varepsilon} \int_a^0 r \cdot e^{\frac{-2r}{a}} dr$$

Results

We integrate by part; we obtained the following results :

$$L = \frac{-\hbar^2}{\mu a^2} \cdot \left[\frac{5}{2} \cdot e^{-2} - \frac{1}{2} \right] \; ; \; G = \frac{e^2}{\varepsilon a} \cdot [3 \cdot e^{-2} - 1] \; ; J = \frac{-\hbar^2}{2\mu a^2} \cdot [5 \cdot e^{-2} - 1] - \frac{e^2}{\varepsilon a} \cdot [3 \cdot e^{-2} - 1]$$

We pose: $J = \alpha \cdot a^{-2} + \beta \cdot a^{-1}$; where $\alpha = \frac{-\hbar^2}{2\mu} \cdot [5 \cdot e^{-2} - 1] \cong 0.16 \frac{\hbar^2}{\mu}$; $\beta = -\frac{e^2}{\varepsilon} \cdot [3 \cdot e^{-2} - 1] \cong 0.59 \frac{e^2}{\varepsilon}$

Solving the equation $\frac{dJ}{da} = 0$, we obtain :

$$a = \frac{-\varepsilon \hbar^2}{\mu e^2} \cdot \frac{[5 \cdot e^{-2} - 1]}{[3 \cdot e^{-2} - 1]} \cong -0.54 \cdot \frac{\varepsilon \hbar^2}{\mu e^2}$$

$$J = \frac{\mu e^4}{2\hbar^2} \cdot \frac{[3 \cdot e^{-2} - 1]^2}{[5 \cdot e^{-2} - 1]} \cdot \frac{1}{\varepsilon^2}$$

Thus, the expression of the energy E of an exciton 1S:

$$E = E_g + \frac{\hbar^2 K^2}{2m} + \frac{\mu e^4}{2\hbar^2} \cdot \frac{[3 \cdot e^{-2} - 1]^2}{[5 \cdot e^{-2} - 1]} \cdot \frac{1}{\varepsilon^2} \qquad (1)$$

E_g : the gap energy of VO_2 in the semiconductor state $E_g = 0.7$ ev

$\hbar$: the reduced constant Planck

e : the elementary charge

$$E \cong E_g + \frac{\hbar^2 K^2}{2m} - \frac{0.54 \cdot \mu e^4}{\hbar^2} \cdot \frac{1}{\varepsilon^2} \qquad (2)$$

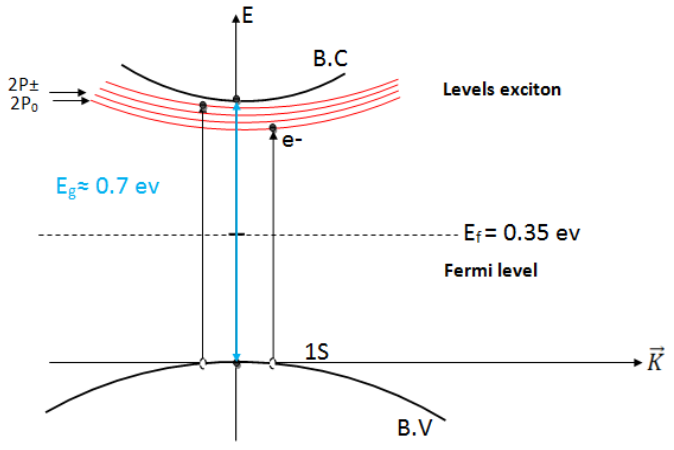
In the vicinity of the band gap (k→0) we have :

$$\varepsilon \cong (0.54 \cdot \mu)^{\frac{1}{2}} \cdot \frac{e^2}{\hbar} \cdot (E_g - E)^{-\frac{1}{2}} \qquad (3)$$

That is to say, n is the index of refraction of VO_2 which we considered slightly absorbent : $n = \sqrt{\varepsilon}$

$$n \cong (0.54 \cdot \mu)^{\frac{1}{4}} \cdot \frac{e}{\sqrt{\hbar}} \cdot (E_g - E)^{-\frac{1}{4}} \qquad (4)$$

We use the approximation of the effective mass :



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We make a simulation by means of Maple software for ε, n, R and T according to the energy E of the exciton in the vicinity of the band gap (k→0) and for (k≠0 at the edge of the first zone of Brillouin):

For k→0 we obtained the formula :

$$\varepsilon \cong 9\cdot 10^{9}\cdot (0.54\cdot \mu)^{\frac{1}{2}}\cdot \frac{e^{2}}{\hbar}\cdot \left(E_{g}-E\right)^{-\frac{1}{2}}\ ;\ R\cong \frac{(n-1)^{2}}{(n+1)^{2}}\ ;\ T\cong \frac{(1-R)^{2}}{1-R^{2}}\ ;\ n=\sqrt{\varepsilon} \qquad (5)$$

and figures **1,2,3,4,5** and **6** by using the following data in the system (S.I) :

$$\mu = 4\cdot 9.1\cdot 10^{-31}; \hbar = 1.05457\cdot 10^{-34}; E_{g} = 1.12\cdot 10^{-19};\ e = 1.6\cdot 10^{-19}$$

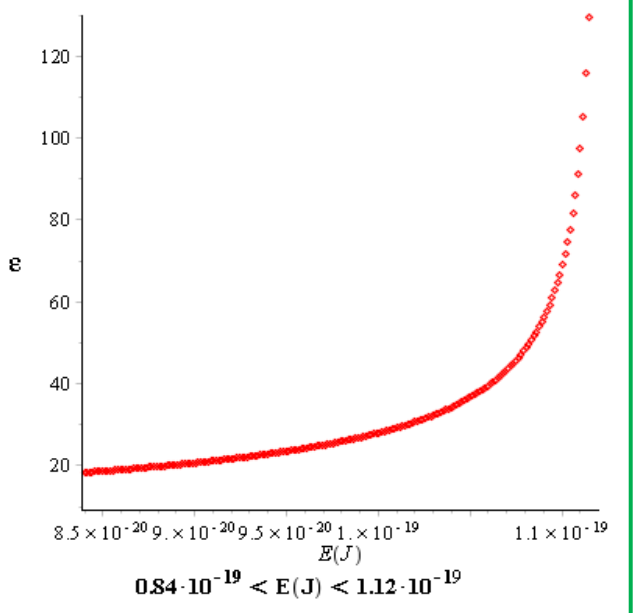

Figure.1 The permittivity ε of VO_2 variation according to the energy E of the exciton 1S for k→0

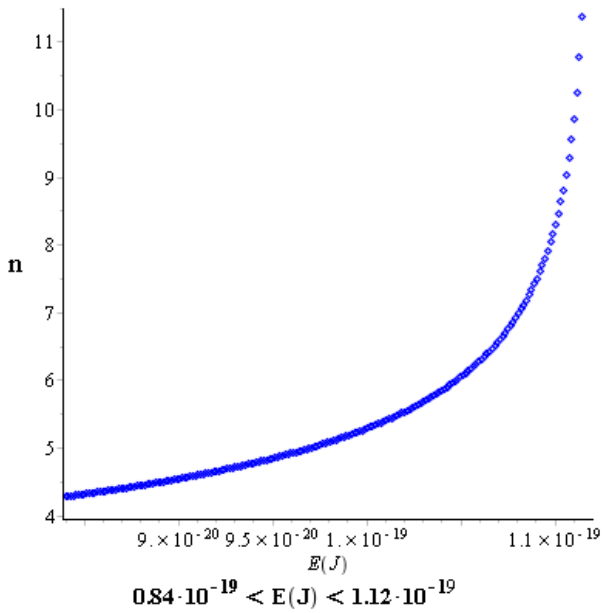

Figure.2 The index of refraction n of VO_2 variation according to the energy E of the exciton 1S for k→0

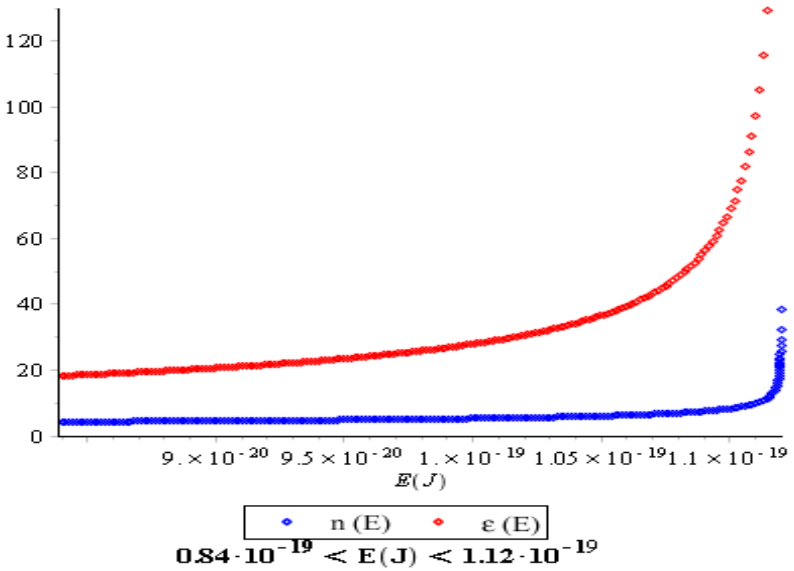

Figure.3 The permittivity ε and the index n of VO_2 refraction variations according to the energy E of the exciton 1S for k→0

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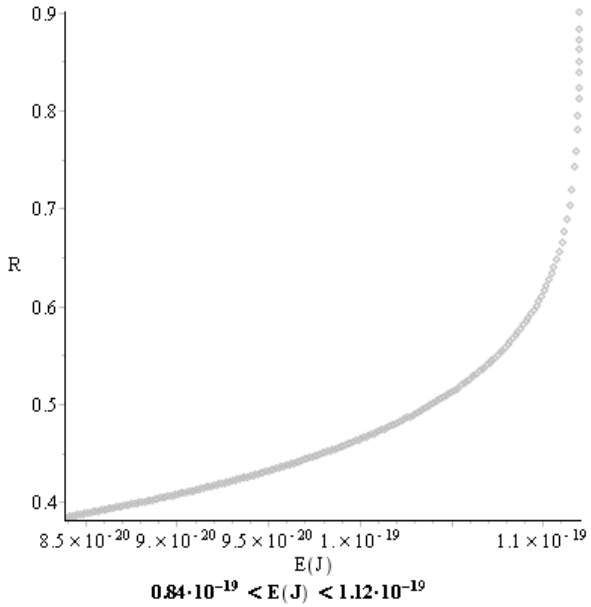

Figure.4 The reflectivity R of VO_2 variation according to the energy E of the exciton 1S for k→0

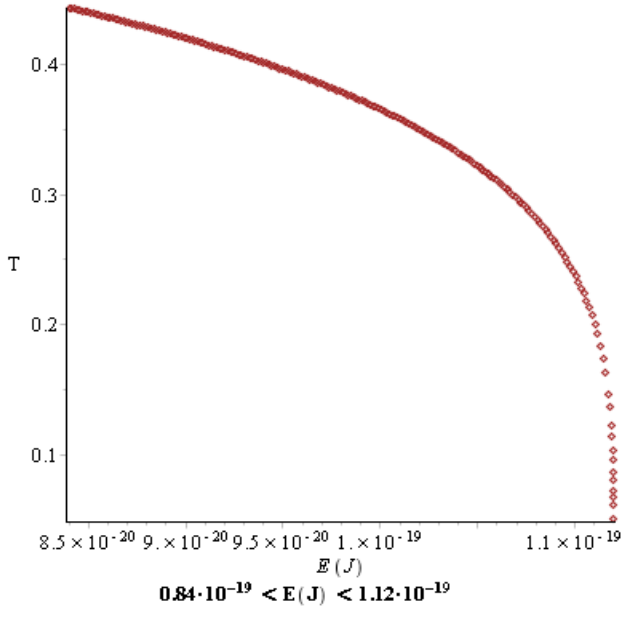

Figure.5 The transmittivity T of VO_2 variation according to the energy E of the exciton 1S for k→0

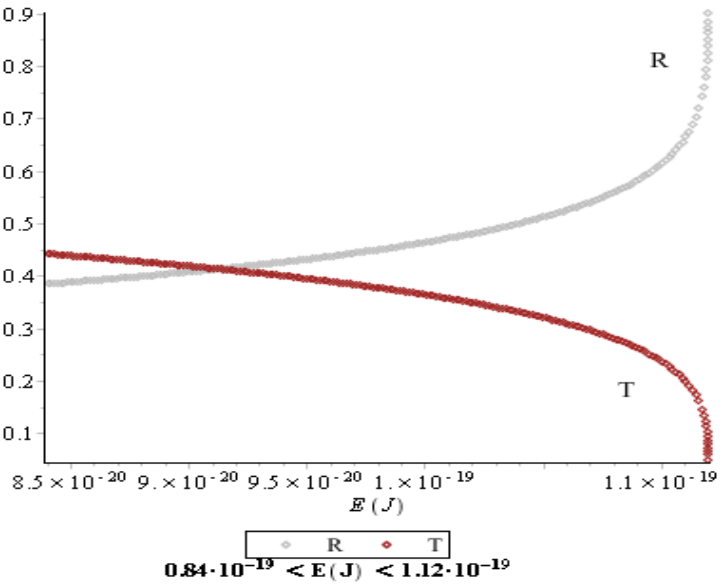

Figure.6 The reflectivity R and the transmittivity T of VO_2 variations according to the energy E of the exciton 1S for k→0

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For K ≠ 0 we obtained the formula:

$$\varepsilon \cong 9 \cdot 10^{9} \cdot (0.54 \cdot \mu)^{\frac{1}{2}} \cdot \frac{e^{2}}{\hbar} \cdot \left(E_g - E + \frac{\hbar^2 K^2}{2m} \right)^{-\frac{1}{2}} \qquad (6)$$

and figures **7,8,9,10,11** and **12** by using the following data in the system (S.I) :

$$\mu = 4 \cdot 9.1 \cdot 10^{-31}; \hbar = 1.05457 \cdot 10^{-34}; E_g = 1.12 \cdot 10^{-19}; e = 1.6 \cdot 10^{-19}; m = 173 \cdot 10^{-31}; k = \frac{2\pi}{5.75 \cdot 10^{-10}}$$

$$m = m_e^* + m_h^* = 4 \cdot m_e + 15 \cdot m_e = 19 \cdot m_e \; ; \; \mu = 4 \cdot m_e$$

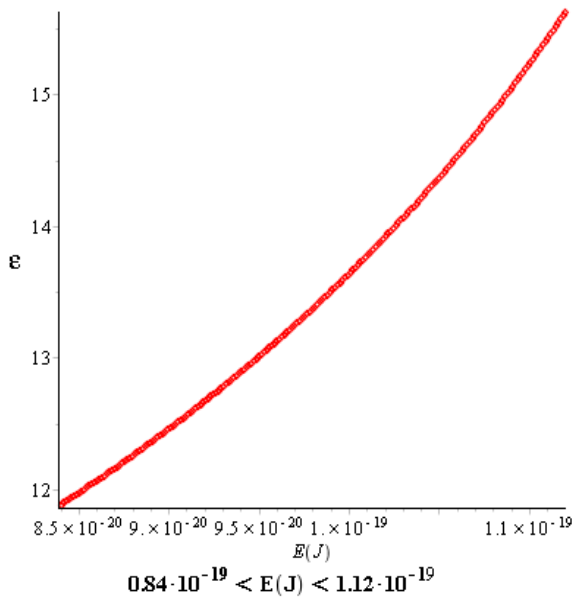

Figure.7 The permittivity ε of VO_2 variation according to the energy E of the exciton1S for k≠0

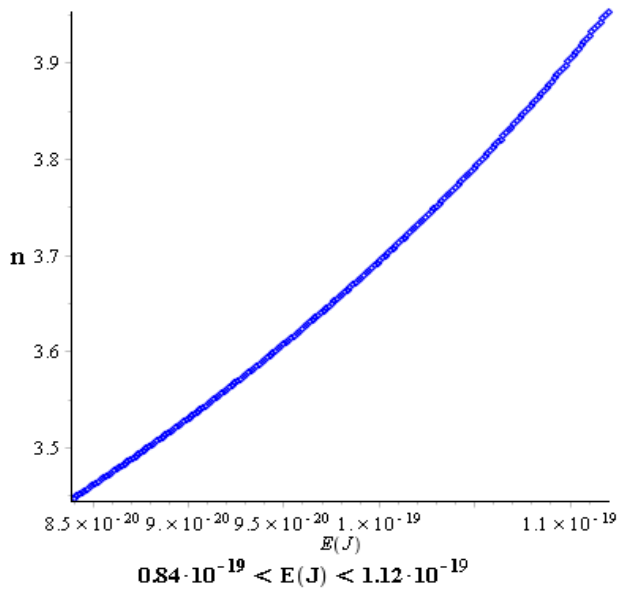

Figure.8 The index of refraction n of VO_2 variation according to the energy E of the exciton 1S for k≠0

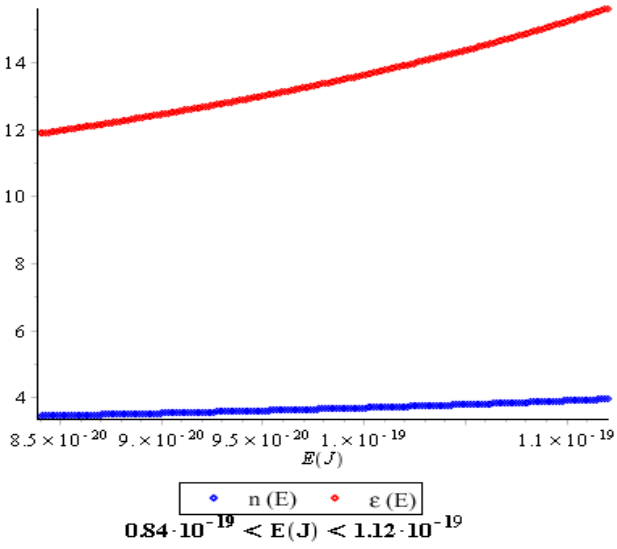

Figure.9 The permittivity ε and the index n of VO_2 refraction variations according to the energy E of the exciton 1S for k≠0

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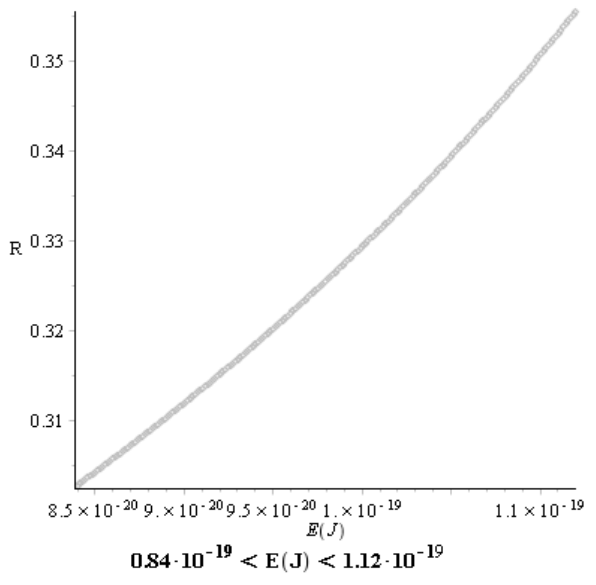

Figure.10 The reflectivity R of VO_2 variation according to the energy E of the exciton 1S for k≠0

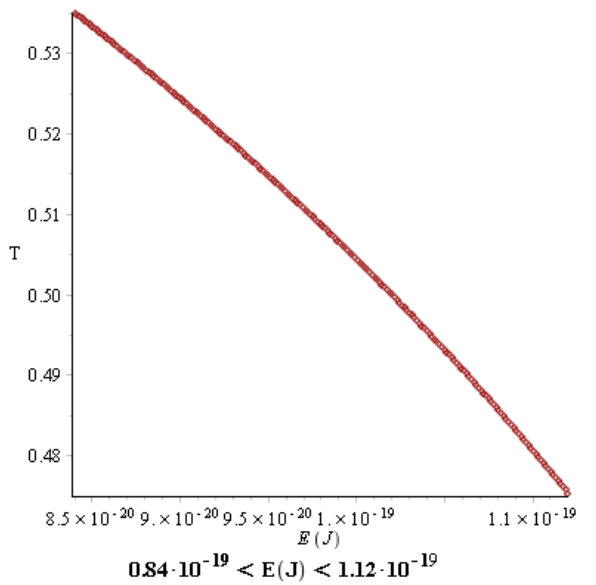

Figure.11 The transmittivity T of VO_2 variation according to the energy E of the exciton 1S for k≠0

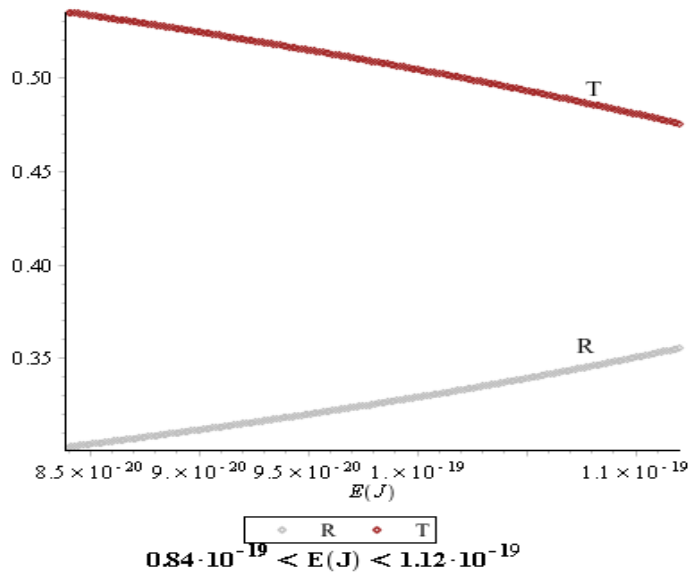

Figure.12 The reflectivity R and the transmittivity T of VO_2 variations according to the energy E of the exciton 1S for k≠0

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Discussion :

The Hamiltonian is given in the system CGS; and for the energy of the exciton we used the system (S.I) in our simulation of curves by making necessary conversion. The creation of the exciton in this material affects the variation of its optical properties, like the dielectric function ε and the index of refraction n, around the band gap and at the edge of the first zone of Brillouin of the massive vanadium dioxide, where the Colombian interaction between the electron and the hole of the exciton 1S plays an important role in our study. The variation of the permittivity ε for this interval of energy becomes important when we approach the energy gap E_g by this material; because the energy of the Colombian interaction decreases abruptly and the electron becomes almost free, it will be able to free the band gap owing to the fact that the binding energy of the exciton strongly decreases and it loses its stability. As far as the lowest energy levels of these excitons, the variation of this optical constants ε and n are slow around the band gap (k→0); whereas for (k≠0) and at the edge of the first zone of Brillouin, this variation becomes almost linear for $\frac{k}{2\pi}$, because of the kinetic energy $\frac{\hbar^2 K^2}{2m}$ of the exciton which becomes important if compared to the energy term $E_g - E$, and consequently its impulse P increases. Our results are based on the calculation of the energy E exciton 1S by the purely variational quantum method, and by using the approximation of the effective mass, and by using the values of the reduced mass, and of the total mass, which we have previously affected with the exciton **[12]**. The variations of the refraction n index of this material resemble those of the literature on the massive state. The interval energy of the exciton, that we proposed, is strongly probable in our study, by focusing on the levels of the excitons allowed by using the rules of selection of the allowed excitonic transitions, and their positioning if compared to the bottom of the conduction band (B.C), and the Fermi's level E_f of the semiconductor state of this material. The expression of the energy E of the exciton 1S, which we obtained by our working method, is an approached result of the exciton, because our obtained Schrödinger equation can be solved in an exact way while resembling the exciton S at the hydrogen atom with three dimensions.The exciton's lifespan is about a few nanoseconds; during this very weak period, we have shown that the optical response of the massive vanadium dioxide is not constant. Indeed, we have noted that, starting from this work, the dielectric function and the index of refraction vary according to the energy of the exciton created by the incidental photons.

Around the band gap (k→0):

The R≅0.442 reflectivity and the transmittivity T≅0.386, for the energy of the exciton $E = 8.4 \cdot 10^{-20}$ J. When the energy level E of the exciton approaches the band of conduction, we note that R≅0.90 and T≅0.051; the material becomes very reflective. Thus, It is noted that the reflectivity R increases slowly and the transmittivity T decreases for the vanadium dioxide in a massive semiconductor state, if energy E of the exciton grows. These variations pass in an interval of a few nanoseconds.

At the edge of the first zone of Brillouin (k≠0):

For the low energy levels E of the exciton 1S, we note that R≅0.30 if $E = 8.4 \cdot 10^{-20}$ J. The reflectivity R increases slowly until reaching the R≅0.36 value if $E = 1.12 \cdot 10^{-19}$ J. Whereas, the transmittivity T≅0.54 if $E = 8.4 \cdot 10^{-20}$ J. The transmittivity of this material decreases slowly when energy E of the exciton increases; it is about 0.475 if $E = 1.12 \cdot 10^{-19}$ J.

We see that the variations of R and T are simultaneously opposite. The transmittivity T decreases while the reflectivity R increases when energy E of the exciton approaches the conduction band. This result is logical because the Coulomb interaction of the exciton decreases and the electron becomes almost free.

These simulated results well prove that the creation of the exciton in the massive vanadium dioxide in a massive semiconductor state by incidental photons influences the reflectivity R and the transmittivity T of VO_2.

The interest of this optoquantic study concerning the excitons is to be able to control and exploit the variation of the optical constants of this material on a nanosecond scale for various nanotechnological applications at a very fast speed, like the optical detectors and the photovoltaic equipment. We think of making a similar study for the the vanadium dioxide's thin layers and of comparing the two results.

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Conclusion

The creation of the exciton 1S in the VO_2 massive material by incidental photons of energy ω lower than its gap energy $E_g = 0.7ev$, has a surely clear influence on the VO_2 optical properties, like the index of refraction n, the permittivity ε, the reflectivity R and the transmittivity T, on the one hand around the band gap of its semiconductor state (k→0), and on the other hand at the edge of the first zone of Brillouin (k≠0), this is confirmed in our study. Our results are in conformity with those of Mossaneck et al. We know in literature that the presence of an exciton causes an increase of the α coefficient absorption of the material. We have chosen to study the influence of an exciton 1S on other optical constants, like the dielectric function ε and the index of refraction n; we arrived at a confirmation, which turns this study necessary to be able to control the optical response of this material in time intervals of about a few nanoseconds.

This study based on the excitons allows us to put this intelligent material in the centre of the evolutionary nanotechnological applications, as the solar air-conditioners containing VO_2 which will be able to replace the electric air-conditioning that remains expensive in comparison.

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