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Thème

The Effects of Defects on Semiconductors Properties: Case of TiO$_2$ Nanoparticles

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Abstract

The aim purpose of this research is to study the behavior of the trapped electron in the oxygen vacancy, called color centers (F^+) present in the ionic material of titanium dioxide (TiO_2). The theory of perturbation, the notion of effective mass and linear combination of atomic orbitals (LCAO) were used to determine the energy and wave function of F^+ without and with a constant electric field. The study is expanded for the electron presents in one of four titanium cations, using LCAO and the effective mass. The findings clearly show that the F^+ center behaves like a metallic bond in an ionic crystal.

Key words

Color centers defects, titanium dioxide (TiO_2), LCAO, perturbation theory, oxygen vacancy.

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ملخص

الغرض من هذا البحث هو دراسة سلوك الإلكترون المحاصر في شاغر الأكسجين المسمى مراكز الألوان (F^+) الموجودة في المادة الأيونية لثاني أكسيد التيتانيوم (TiO_2). تم استخدام نظرية الاضطراب و فكرة الكتلة الفعالة والمزيج الخطي من المدارات الذرية (LCAO) لتحديد الطاقة و الدالة الموجية لـ F^+ في وجود و غياب مجال كهربائي ثابت. امتدت الدراسة إلى الإلكترون الموجود في واحدة من الكتيونات الاربعة من تيتانيوم، باستخدام LCAO والكتلة الفعالة، تظهر النتائج بوضوح أن مركز F^+ يتصرف مثل رابطة معدنية في بلورة أيونية.

كلمات مفتاحية: عيوب مراكز الألوان، ثاني اوكسيد التيتانيوم(TiO_2)، نظرية المزيج الخطي من المدارات الذرية، نظرية الاضطراب، شاغر الأكسجين.

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Résumé

Le but de cette recherche est d'étudier le comportement de l'électron piégé dans la lacune d'oxygène appelé le centre coloré (F^+), présent dans le matériau ionique du dioxyde de titane (TiO_2). La théorie de la perturbation, la notion de masse effective et la combinaison linéaire d'orbitales atomiques (CLOA) ont été utilisées pour déterminer l'énergie et la fonction d'onde de F^+ sans et avec un champ électrique constant. L'étude est étendue pour l'électron présent dans l'un des quatre cations de titane, en utilisant CLOA et la masse effective. Les résultats montrent clairement que le centre F^+ se comporte comme une liaison métallique dans un cristal ionique.

Mots clés :

Défauts des centres colorés, dioxyde de titane (TiO_2), CLOA, La théorie de la perturbation, lacune d'oxygène.

ACKNOWLEDGEMENT

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General introduction

Metal oxide materials, such as TiO_2, ZnO, CeO_2, and SnO_2, have attracted considerable research interest in the last years because of their great potential of applications in a lot of fields especially the photocatalytic oxidation of organic pollutants [1,2]. Compared to other metal oxide semi-conductors with wide bands gap (E_g), TiO_2 has attracted attention due to its high stability, photocatalytic activity, non-toxicity, and biocompatibility. On the other hand, TiO_2 is generally active under ultraviolet irradiation because of its $E_g = 3.2$ eV [1,3,4,5].

It is well known in material sciences that no perfect crystal exists, however scientists deal with real ones that contain some alterations in the structure due to the human being, experiments and the environment [6]. These distortions are called defects, very important factors, that strongly affect the properties of any material and determine its applications [7]. The defects can be classified to different types according to some criteria and the most important of them are localized and non-localized [7]. The color centers (F^+) belong to non-localized defects and they are responsible for the change in the coloration of the crystal. Since the very beginning of the theory of defects, the F^+ center has been extensively studied [7,8].

Many researchers focused on the wave function of the trapped electron [8]. This theoretical research is divided into two chapters. In the first one of this work, we classified and defined the defects that we might find in all crystals including color centers. The second chapter contains two parts where the F^+ center was studied using two different ways. In its first part we recall the particle in a box model [7] that has been proposed to understand the wave function of the trapped electron and we tried to know how the wave function and the energy of the electron act under an electric field using the perturbation theory [9]. On the other hand, the second part studied the electron existing in one of the four titanium cations (Ti^{+4}) surrounding the oxygen vacancy [10]. A model has been proposed, to understand the movement of the electron existing in the cations, based on the linear combination of atomic orbital (LCAO) and the effective mass theory with some approximations [11,12].

Finally, we will conclude with the new understanding of the electron moving in Ti^{+4} ions surrounding the F^+ center, which we got from the proposed model and some additional future perspectives.

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Chapter one

Defects in Materials

1. Introduction

When every atom is in its position in the crystal lattice, then we have a perfect crystal which means conserving the periodicity in the three directions of the space. But unfortunately, there are always some atoms occupying other sites after leaving their normal places giving a real crystal that we are dealing with every day. When atoms are in different places this creates defects. In linguistics, defects are negative things, however in science they can turn out to be so good and useful. Nowadays defects are a pretty good factor very well used to change the properties of the real crystal [1]. Thus defects can be important for so many things that give a new version to materials and control them. In this chapter we are going to discuss the defects that we may find in the crystals and see how they can act on them as well.

2. Definition of defects

Defects in crystals are all what make the crystal imperfect. In other words, the defects are a couple of phenomena that disturb or cut the periodicity of the crystal. Despite the linguistic meaning of defects, it is totally different in terms of physics; because they give some interesting properties to the materials [1]. According to some parameters; defects are classified into categories or types.

3. Defects types

All the things in the world have types or a different sub-thing. And speaking about defects, it also has sub-defects that we are going to mention in this section. The major types are physical and chemical defects.

3.1 Physical defects

We can also call them intrinsic defects. These ones have to do only with crystal itself. That means it does not change the chemical composition of the crystal. And we can divide them into two parts.

3.1.1 Localized defects

This part of physical defects is localizable in the crystal. In other words, we can say that this kind of defects is sitting on small region that can be known and it is divided into two parts.

3.1.1.1 Point defects

Point defects are atomistic ones called a zero dimension (0 D) defects. It could be a vacant site or self-interstitial atom or ion. They occur while the growth of the crystal or it could be thermally produced. In other words, heating the system or irradiating it by light can lead to the creation of point defects due thermal or optical energies respectively [2].

3.1.1.1.1 Vacancy (Schottky defects)

This kind of defect is an unoccupied site in the real crystal, but it is supposed to be occupied in the perfect crystal. When the atom moves from its position travelling in the crystal, it probably goes to the surface, but it leaves behind an empty place called a vacancy, represented by a letter (V). This kind of defect (Schottky defect) is illustrated by fig. 1.1.

If we have a stoichiometric crystal MX; the event of formation of an anion vacancy will happen simultaneously with the event of formation of a cation vacancy. After these two events; both (anion and cation) go to the surface. And we can describe this process by the following way.

$$(M_M + X_X)_{\text{in the crystal}} \rightarrow (V_M + V_X)_{\text{in the crystal}} + (M_M + X_X)_{\text{in the surface of the crystal}} \qquad (1.01)$$
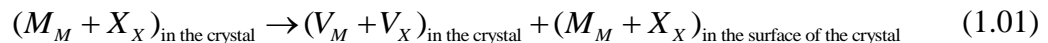
When an anion X and a cation M move from the bulk to the surface, that means those two atoms are still in the crystal. This means we can remove from the both sides of the equation (1.01) to become an equation for a quasi-chemical reaction of defects formation.

$$0(\text{zero} = \text{perfect crystal}) \rightarrow V_M + V_X \qquad (1.02)$$
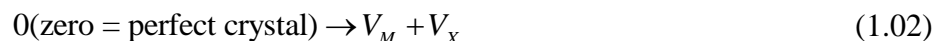
This kind of defects can be found in the following crystals: NaCl, TiO, BeO, CaO, SrO, CsCl [1].
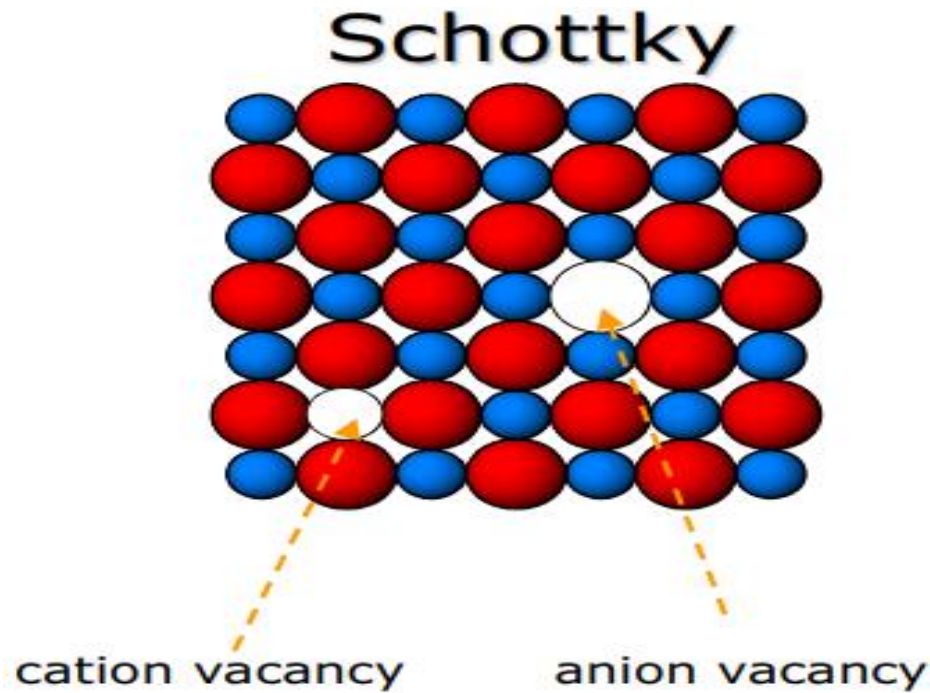
Fig. 1.1 Schottky defect [19].

3.1.1.1.2 Self-interstitial (Frankel defects)

This type of defect is known as a Frankel defect. It is about the self-occupied interstitial sites in the real crystal (self-occupied means that the interstitial sites should be occupied by the same atoms of the crystal); while it is normally empty in the perfect crystal. Moreover, it could be thought of as a superposition of Schottky defect and Frankel one. Because the atom existing in the interstitial site has already left a vacancy behind. These sites are too numerous. And let's take NaCl as an example, on one hand, all the (Na) cations are on the octahedral sites (O) of the anionic network. On the other hand, there are tetrahedral sites (T), with populations equal to twice the number of the octahedral sites. The process of passing a cation from a normal site to an interstitial site is represented by the symbol (V_i). As a result, this process gives a cation vacancy.

$$V_i + M_M \longrightarrow M_i + V_M \tag{1.03}$$

$$\text{(T)} \quad \text{(O)} \qquad \text{(T)} \qquad \text{(O)}$$
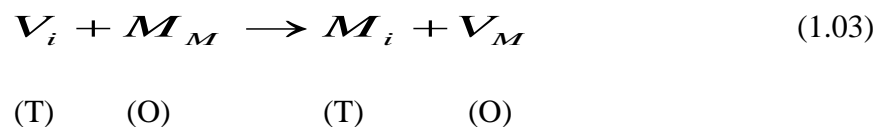
They observed anionic interstitial in materials like: CaF_2, SrF_2, BaF_2, UO_2, CeO_2, ThO_2. Where the cationic interstitial in materials like: AgCl, AgBr, $NaNO_3$, KNO_3 [1].
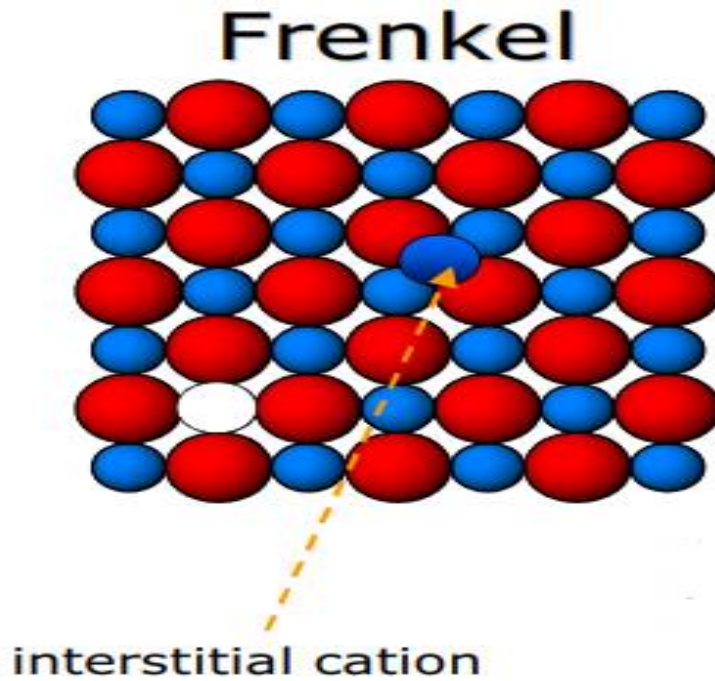
Fig. 1. 2 Frankel defect [19].

3.1.1.1.3 Anti-site

This defect is just the interchange between two neighbor atoms. A cation M will take the site of the anion neighbor X, and the X will go to the site of M as illustrated in the fig. 1.3. This type of defect was observed in the intermetallic compounds, and the compounds where the electronegativity of the atoms are quite the same. And most of them are with covalent bond. The equation of this process is given by.

$$M_M + X_X \rightarrow M_X + X_M \tag{1.04}$$

This defect showed up in the following materials. AuZn, GaP, GaS [1].
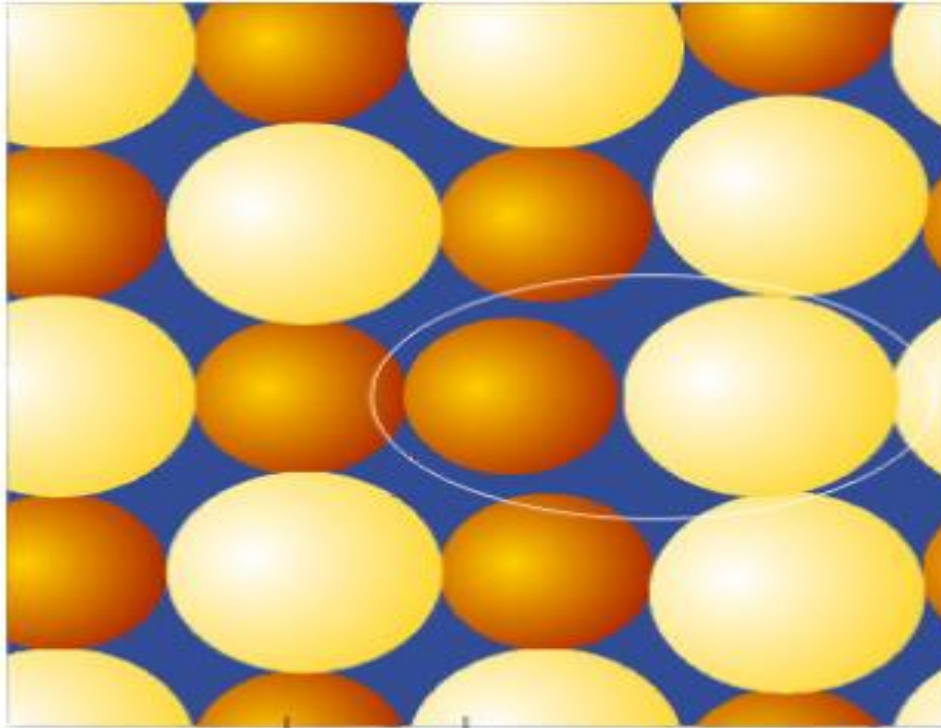
Fig. 1.3 Anti-site defect [3].

3.1.1.2 Extended Defects

Physicists do classified defects according to their dimensions. Where point defects are usually called zero dimension defects (0 D). Where extended defects are concerned about 1, 2 and 3 dimensions, they can be named also linear, planar and volume defects. We are going to explore them in this section [5].

3.1.1.2.1 Dislocations

Dislocations are considered as a linear defect. Researchers observed them experimentally after they had expected them theoretically. This type of defect is the weakness of the metals. Most of the material's deformation is caused by the movement of dislocations. However, if the movement of the dislocations is impossible; the materials become hard and tough. Since dislocation is a linear defect so it is characterized by a line of disruption. This line has three possibilities to end up. The first one is to end on the surface, the second one is to end in another dislocation, or to form a closed loop. People have seen closed loops in the crystal.

The enthalpy is the energy to create Schottky and Frankel defects, and it always gets balanced by the entropy in the case of these point defects. Dislocation also needs a creation enthalpy. But the enthalpy to create a dislocation is much higher than the enthalpy to create a point defect. So the entropy could not cancel the creation enthalpy of a dislocation. This means

that the dislocations are never in the equilibrium with their surroundings. The dislocation is characterized also by a Burger vector [4].
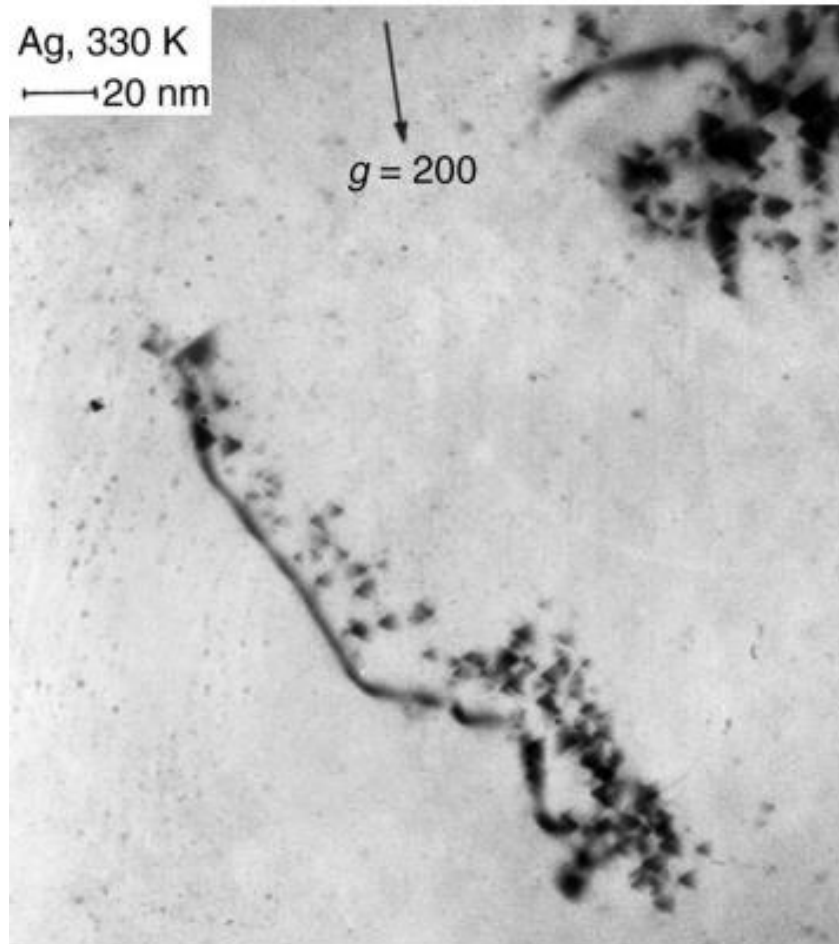
Fig. 1.4 Electron micrograph showing a dislocation in silver, imaged as a dark line [4].

➤ **Burgers vector**

The Dutch physicist Jan Burgers realized that dislocations characterized by a vector labeled (b) that represents the magnitude and the direction of the lattice distortion of a dislocation in a crystal lattice [6].

And by playing with the burgers vector directions, we can distinguish two types of dislocations: the edge dislocation and the screw dislocation.

3.1.1.2.2 Edge dislocations

They considered as a simple linear defects. They have an extra half plane of atoms inserted into the crystal as illustrated in fig 1.6.
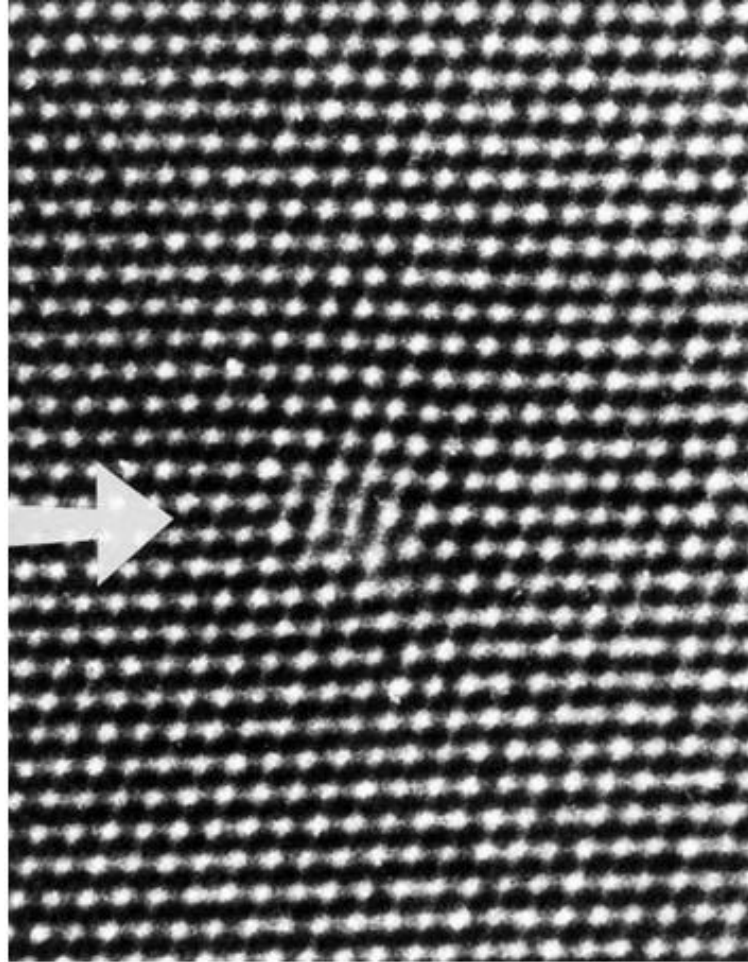
Fig. 1.5 An edge dislocation in cadmium telluride, CdTe [4].
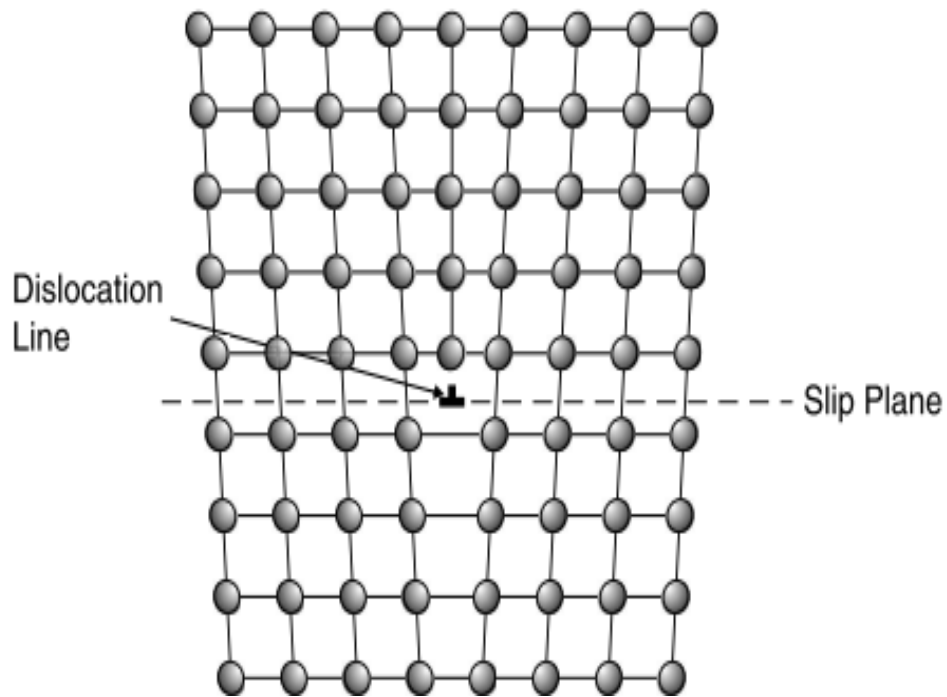
Fig. 1.6 An edge dislocation in a monatomic crystal [4].

Moreover, the edge dislocation's burgers vector is perpendicular to the dislocation line, as shown by fig 1.7.

The plan which separates the two parts of the crystal, with and without the extra half-plane is called the slip plane. The slip plane represents the deformation of the crystal because of the stress applied [4].
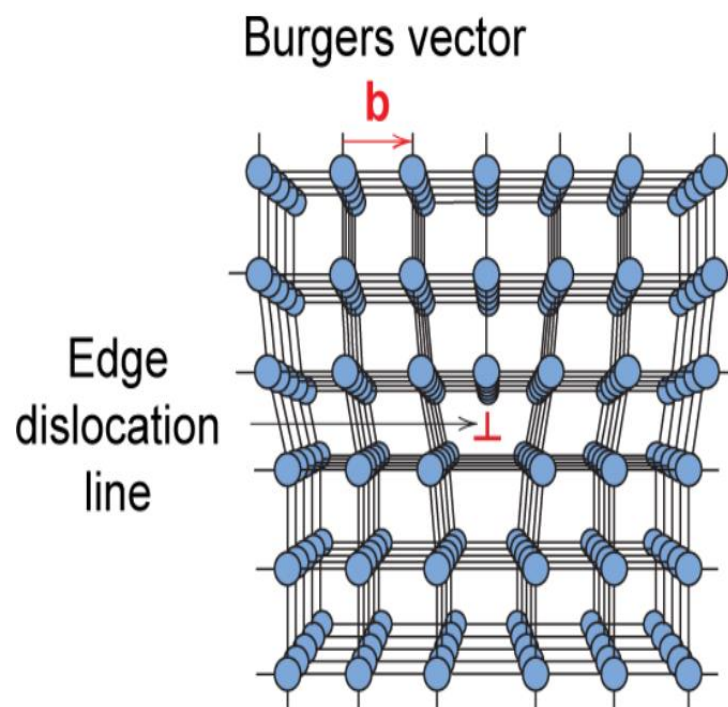
Fig. 1.7 Edge dislocation [20].

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3.1.1.2.3 Screw Dislocations

Due to a stress on the surface of the crystal screw dislocation formed. And it looks like a scroll stair. In other words, it is a couple of distorted parallel atom planes. And we can create a screw dislocation by cutting the crystal into two parts and keep sliding the two parts in the opposite way to each other. Like what happened in fig 1.8 [4].
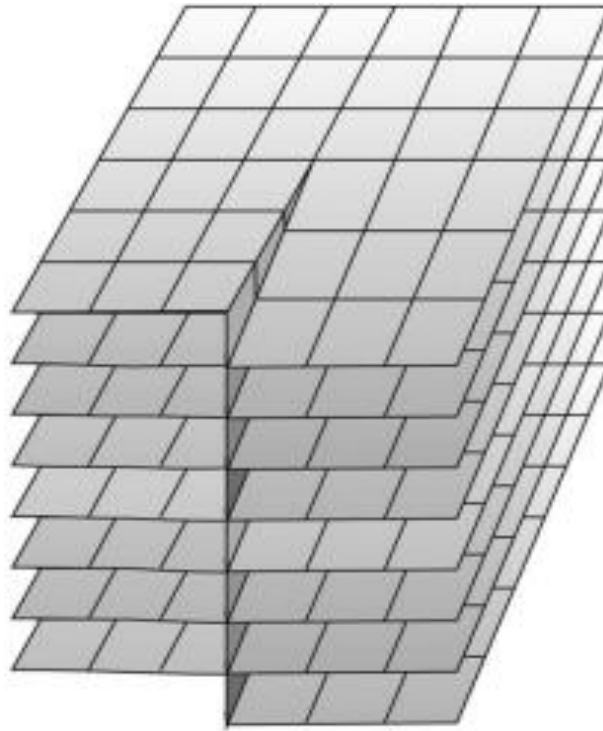
Fig. 1.8 The atom planes spiral around the dislocation line [4].

As we mentioned before the burgers vector plays a role determining the type of dislocation. And in the case of the screw dislocations, the burgers vector (b) is parallel or antiparallel to dislocation line (I) [5].
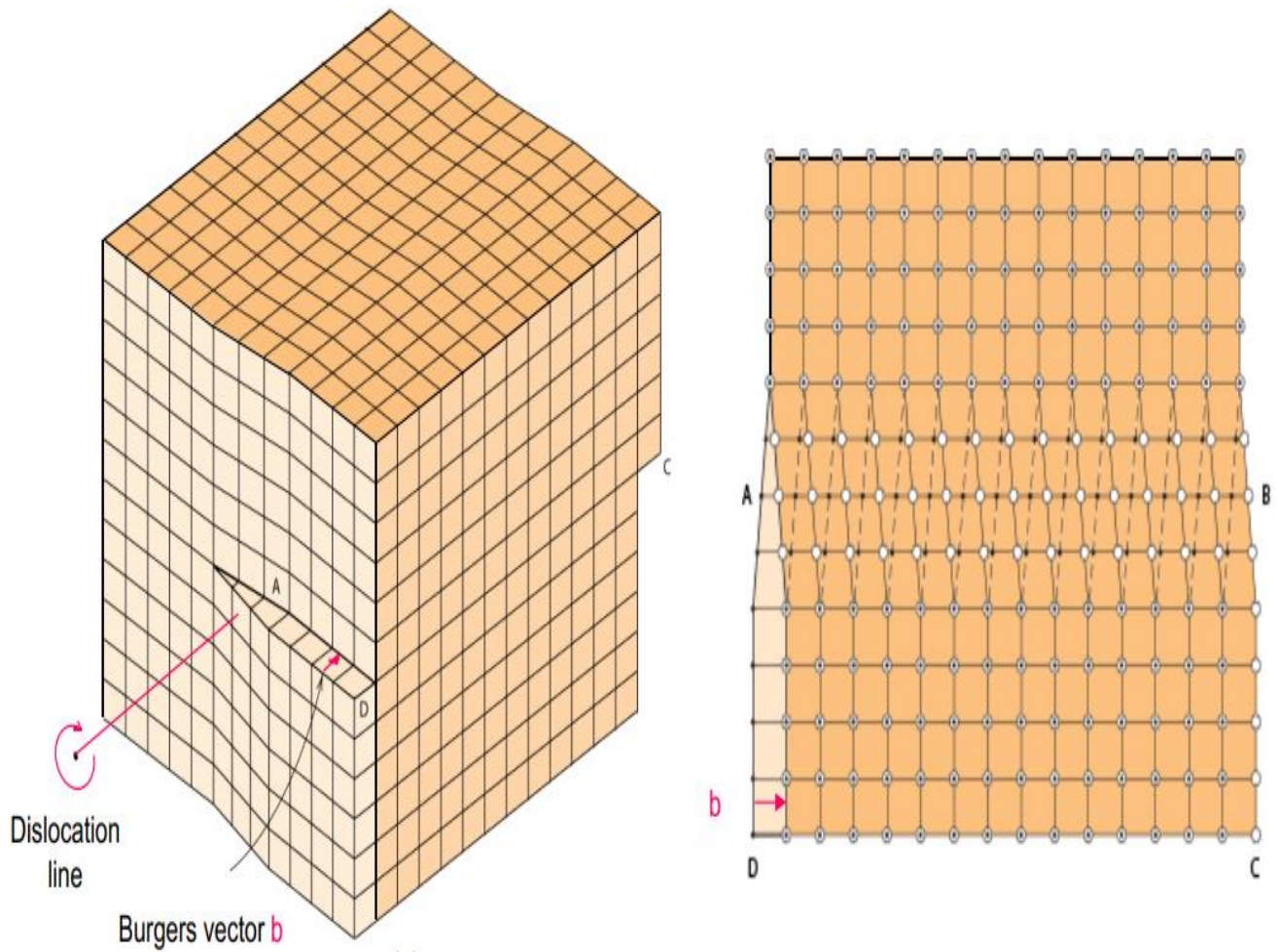
Fig. 1.9 Screw dislocation [20].

3.1.1.2.4 Mixed Dislocations

We discussed two cases of dislocations where the burgers vector was either perpendicular or parallel to the dislocation line. But this case has both characters. The place of this dislocation has a superposition of edge and screw dislocation. This complicated phenomenon is illustrated in fig 1.10 [4].
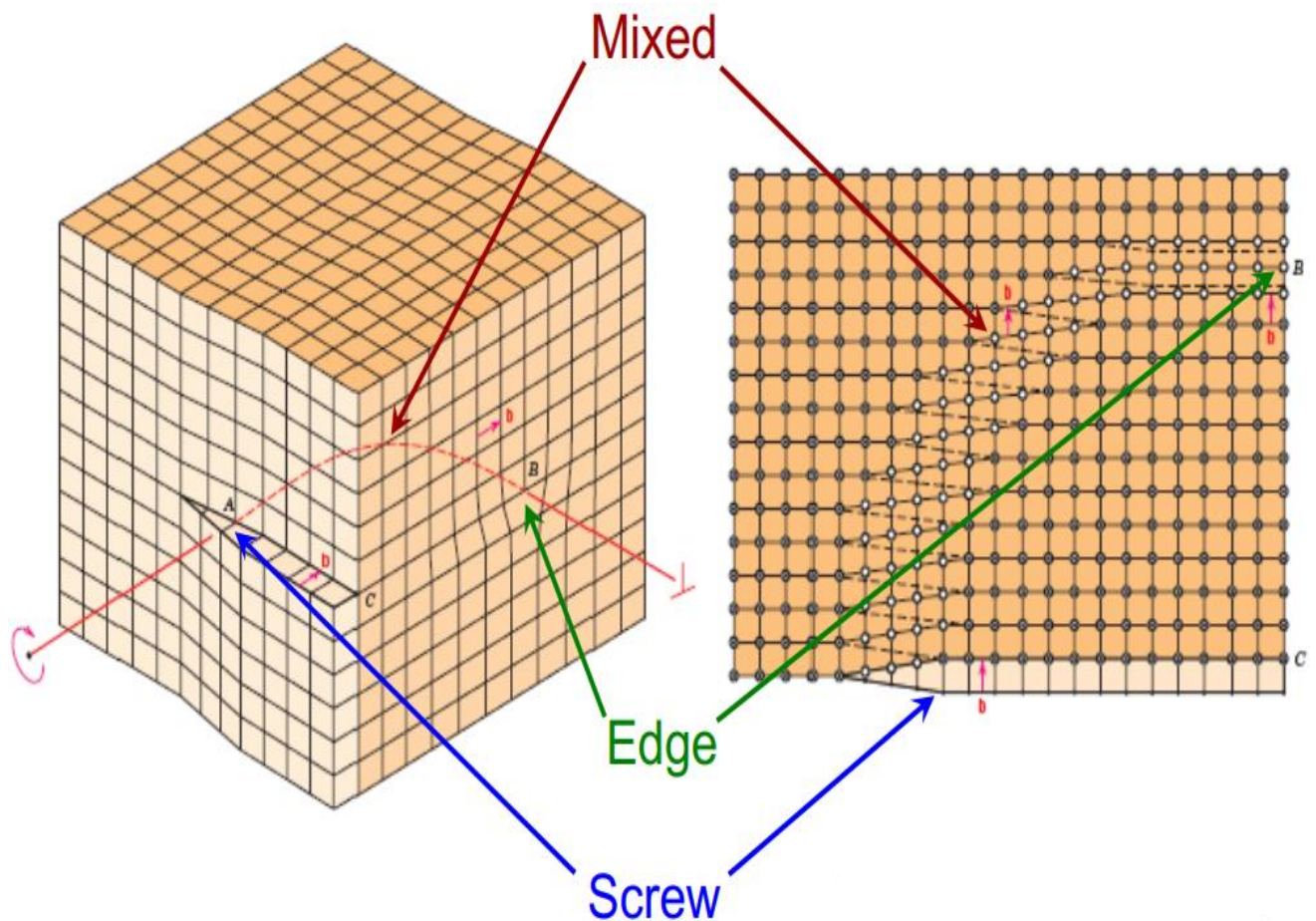
Fig. 1.10 Mixed dislocation [20].

3.1.1.2.5 Internal Boundaries

Most of the crystals look like a single crystal. But when doing the X-ray diffraction, it is realized that most of the crystals have internal boundaries. This is a 2-dimensions defect. It is a surface between two domains in the same crystal.

As all the defects, this type changes the properties of the crystal as well. Furthermore, most of the internal boundaries are a planar, but curved boundaries may occur sometimes [4].
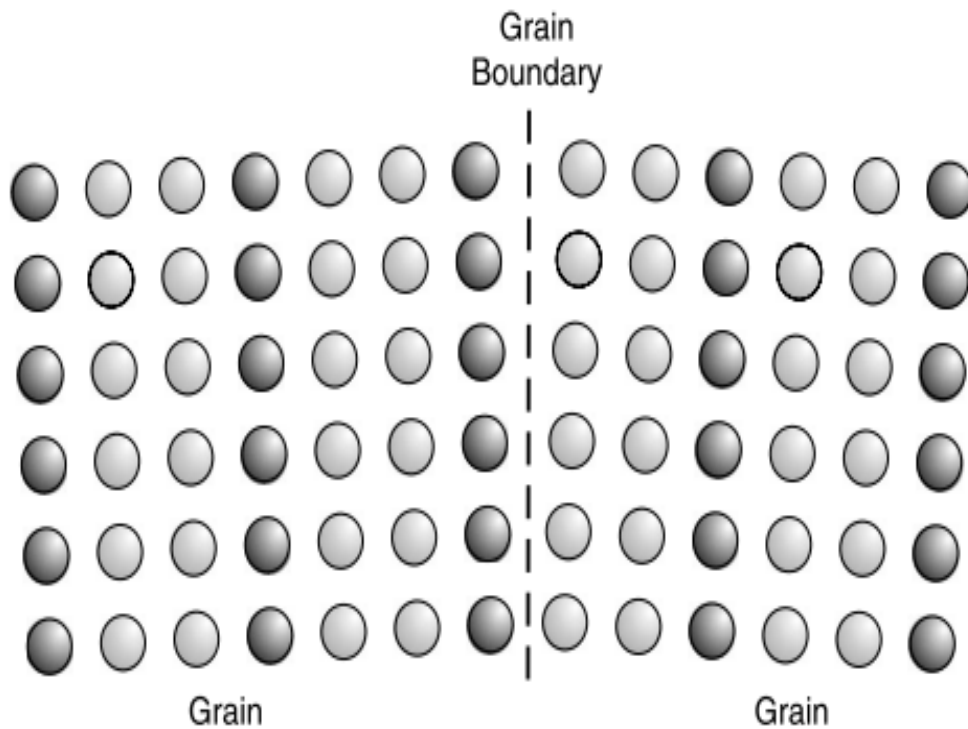
Fig. 1.11 Planar defects in solids: boundaries between slightly misaligned regions or domains [4].

3.1.1.2.6 Low-Angle Grain Boundaries

Burgers said that low-angle boundaries between neighboring crystallites or crystal grains made up by dislocations matrices. That is what makes this kind of defect a two-dimension defect. The fig.1.12 represents the simplest example of Burgers model of a grain boundary [6].
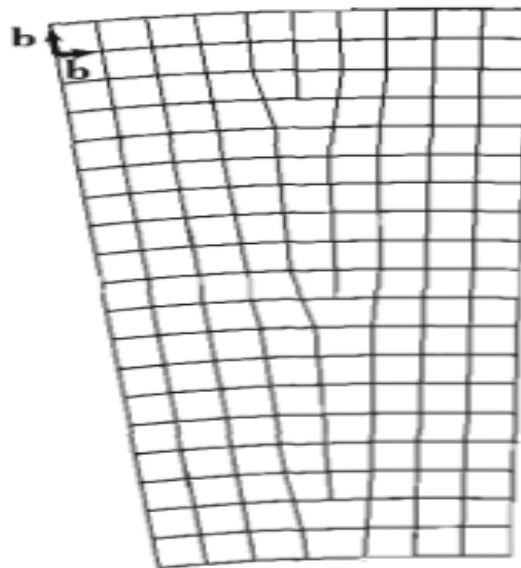
Fig. 1.12 Low-angle grain boundary [6].

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3.1.1.2.7 Twin Boundaries

This planar defect is corresponding to two intergrown crystals related with each other by reflection, rotation, or inversion. When the contact between the two twins is a well-defined plane (which is not always true), the boundary is called a composition plane. Fig. 1.12 indicates reflection twin boundaries, where one of the twins is the mirror image of the other. The mirror plane separating the two twins is usually called the twin plane. When these twins are repeated more than two so polysynthetic twins are formed [4]. Fig. 1.14 illustrates a polysynthetic twin.
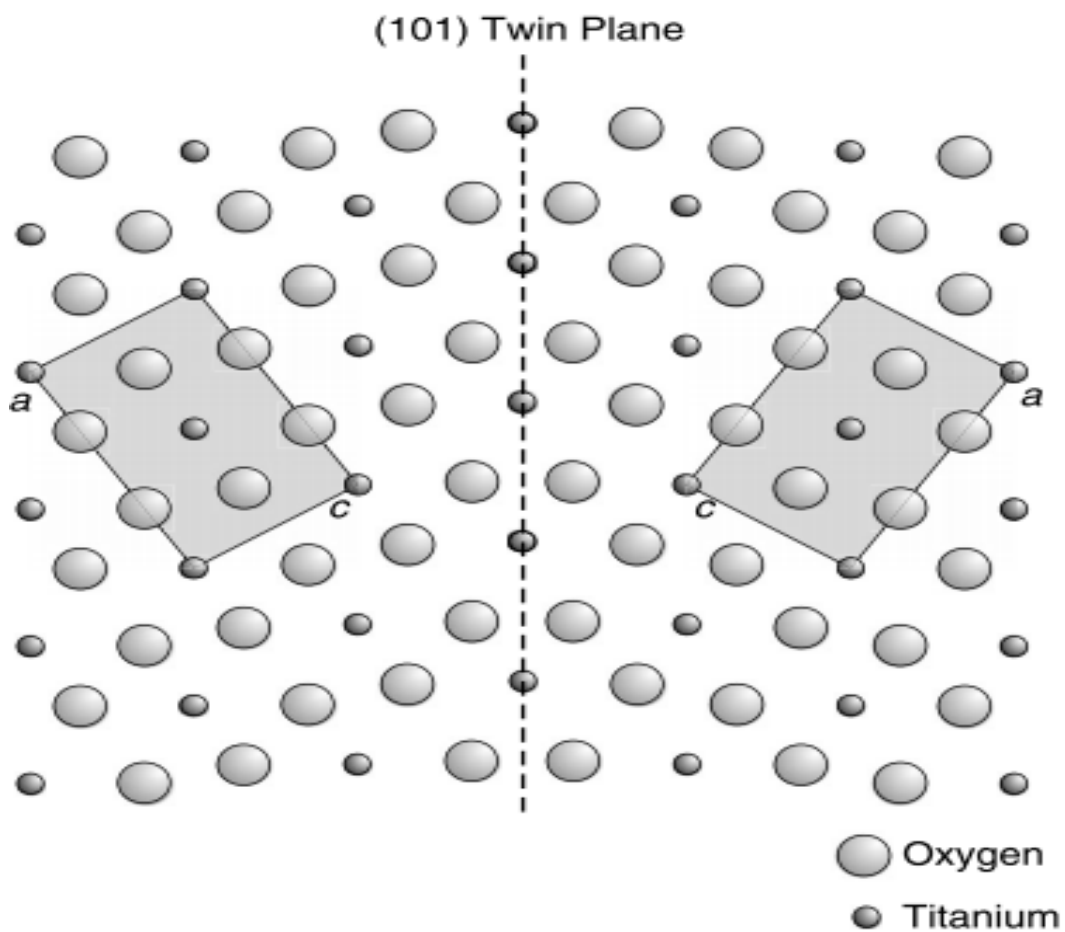
Fig. 1.13 Twin plane in rutile, TiO_2 [4].

Twin Plane
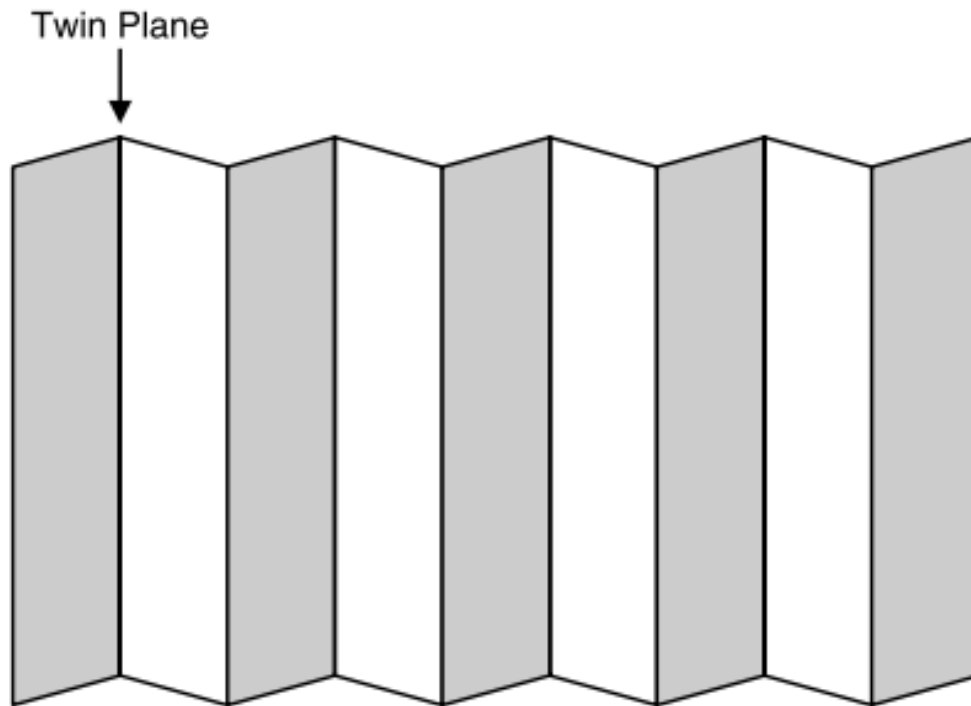
Fig. 1.14 Polysynthetic twinning [4].

3.1.1.2.8 Antiphase Boundaries

Antiphase boundaries (APBs) should be thought of as displacement boundaries within a crystal. This planar defect is characterized by a vector (R) parallel to the boundary, which can distinguish a displacement of one part from the other. Another way to think about APBs in cubic close-packed metal crystals is to consider them as faults that came from the movement of a partial dislocation.

The stacking sequence of the cubic close-packed metal atom is . . . ABCABCABC. . . and it is going to be in the following sequence after the disruption . . . ABC**AC**ABC. . . where the antiphase boundary is sitting between the layers in bold type. And they called deformation stacking faults, because they can occur during a plastic deformation of a crystal [4].
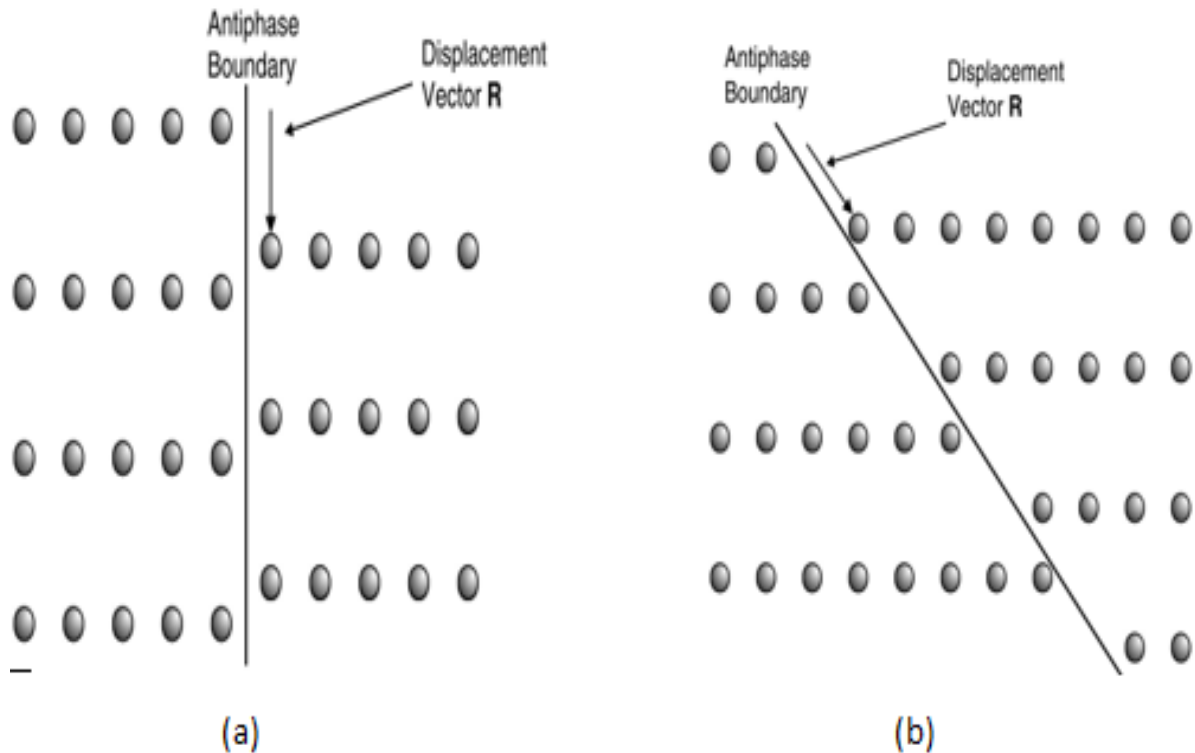
Fig. 1.15 Antiphase boundaries [4].

3.1.1.2.9 Volume Defects

Each volume that has different structures; orientation or state variables (e.g. magnetic or polarization alignment) compared to the native crystal is called a volume defect [5]. They can be like micro-cavities, voids….

3.1.2 Non localized defects

The second part of the physical defects is not localizable in the crystal. We can distinguish three of them phonons, electronic defects and color centers.

3.1.2.1 Phonons

Many books define the phonon as a quantum of vibrational energy, but the vibration carries more than just energy. It has crystal momentum also. So we can say that phonon is a discrete quantum of vibration [7].

The truth of the matter, phonons are due to the vibration of a crystal lattice with a frequency ω. And if we think about that process quantum mechanically, we will figure out that it is just a harmonic oscillator and it has discrete energy eigenstates given by the following equation [8].

$$\varepsilon_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{1.05}$$

Each excitation in the quantum number (n) is a photon. This looks similar when giving a definition of the photons, so one may think about phonons as a quantized wave, or as a particle. While thinking about it as a particle we figure out that it is possible to put more than one particle in the same state. And to sum up this paragraph, we say phonons are bosons just like photons [7].

3.1.2.2 Electronic defects

In semiconductors, all electrons are in the valence band when the temperature is 0 K. but once we raise the temperature above the absolute zero some of the electrons go to the conduction band and leave behind holes with positive charges. If we put this semiconductor in an electric field the electrons move in one way and the holes in the opposite way. This is what is called electronic defects [9].

3.1.2.3 Excitons

When heating a semiconductor with photons their energy is just below the energy gap of the semiconductor, electrons get kicked out from the atoms but they are still related with their previous places which are holes. Electron-hole bound by an electrostatic coulomb force because of their opposite charges. The pair of electron-hole is called an exciton. Another way to think about it, excitons are similar to the hydrogen atom, by considering the hole as a proton. The binding energy of the electron-hole pair is the difference between the energy of the photon absorbed and the energy gap. This energy is ranging between 1 meV to 1 eV. The fig 1.16 shows the energy levels introduced, in the band gap, by the excitons. This is called exciton levels.
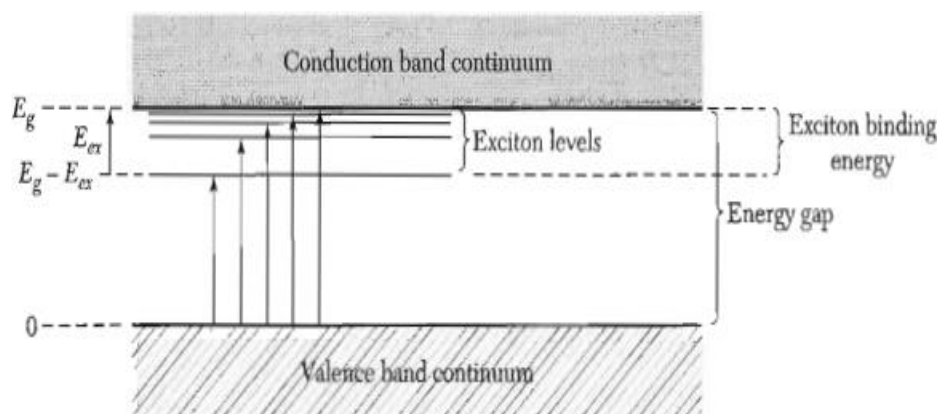
Fig. 1.16 Energy levels of exciton [6].

Excitons can transport energy by moving around in the crystal but they cannot transport charge because it is electrically neutral.

We can find Excitons in every insulating crystal. However, all of them are unstable due to the recombination process. We can also find two excitons together to make something they call bi-excitons.

Furthermore, we can think about the excitons in two different ways [6].

-    Frenkel exciton which is small and has a tight bond as shown in fig 1.17(a).

-    Mott an Wannier exciton which is large than the lattice constant and has a weak bond illustrated in fig 1.17(b).

(a)   (b)
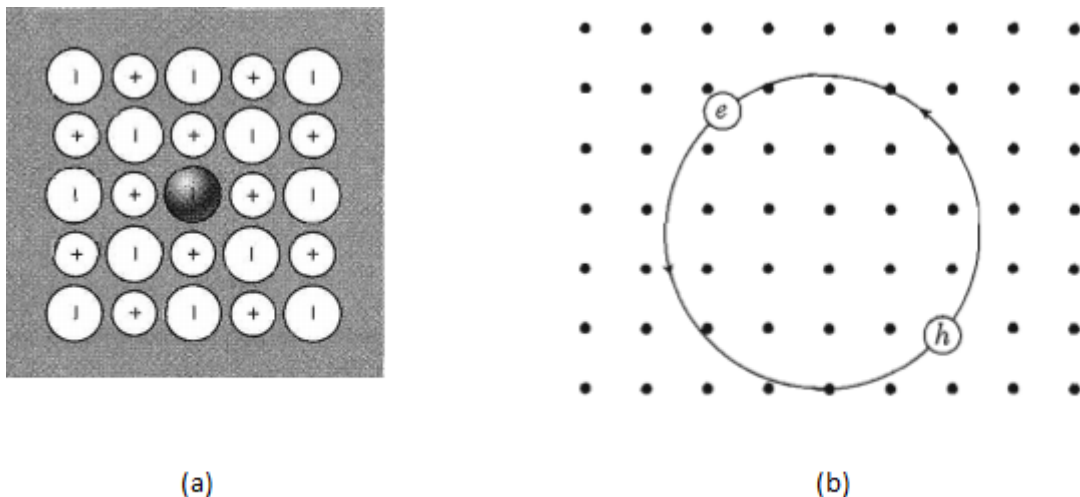
Fig. 1.17 (a) Frankel exciton, (b) Mott and Wannier exciton [6].

3.1.2.4 Color center

This defect is known also as (F) center. It is due to the absence of negatively charged ions. so inside the vacancy there is a positive charge which may attract electrons. Depending on the number of electrons attracted to the vacancy we can distinguish 3 F's centers [10].

-    F^{++} center; if the vacancy didn't attract any electron which means the vacant site is empty.

-    F^{+} center; if the vacancy is full only by one electron (the vacant site attracts one electron only)

-       F center; in the vacancy has two electrons in it (the vacant site is compensated by a pair of electrons)
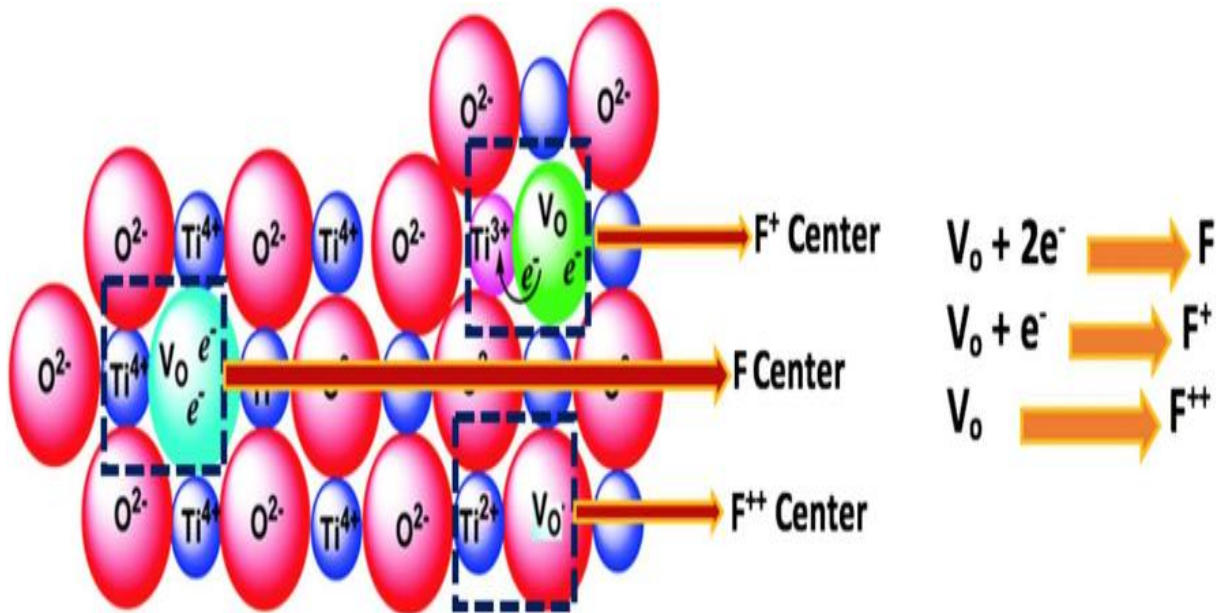
Fig. 1.18 The types of the F center [10].

3.2 Chemical defects

Chemical defects, or extrinsic defects. The reason for this name is the change of the components of the substance. The change may be by impurities (accidentally foreign atoms) or by doping (introducing foreign atoms in the crystal by different techniques).and it could be in 0, 1, 2 or 3 dimensions. These defects will lead to the change in the properties of the material [11] like changing the conductivity of a semiconductor, its color, ….

4. Defects in titanium dioxide

As every crystal, titanium dioxide has defects also. We can split them into two parts. In one hand the intrinsic defects and on the other hand the extrinsic defects. We are going to talk about this in the following section.

4.1 Intrinsic defects

As we mentioned before the intrinsic defects are generated from the crystal itself due to some external factors like heat. And in the case of our crystal (TiO_2) we are going to discuss four intrinsic defects and they are oxygen vacancies, titanium vacancies, oxygen interstitial and titanium interstitial [10]. These are zero dimension defects.

4.1.1 Oxygen vacancies

When the oxygen atom leaves its place for some reasons, it leaves behind a vacant site. That vacancy is a defect and called an oxygen vacancy. In another word it is just a missing oxygen ion from the lattice site. And we can label it using the Kroger-Vink notation by V_o , (($'$) means negative and ($\cdot$) means positive, according to Kroger-Vink notation.). Now the defect equilibrium of oxygen vacancy (V_o) formation is given by [10].

$$O_o \Leftrightarrow V_o^{\cdot\cdot} + 2e' + \frac{1}{2}O_2 \qquad (1.06)$$

4.1.2 Titanium vacancies

The vacant site where the titanium atom supposed to be, is a titanium vacancy. And according to Kroger-Vink its notation is Ti''''. And the equilibria equation is [10].

$$O_2 \Leftrightarrow 2O_2 + V_{Ti}^{\cdot\cdot\cdot\cdot} + 4h^{\bullet} \qquad (1.07)$$
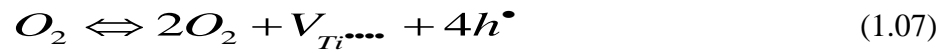
4.1.3 Oxygen interstitial

The notation on the oxygen interstitial is O_i''. When an O^{2-} ion is in an interstitial site we get this defect. And its equilibrium equation is the following [10].

$$V_i^x + \frac{1}{2}O_2 \Leftrightarrow O_i'' + 2h^{\bullet} \qquad (1.08)$$
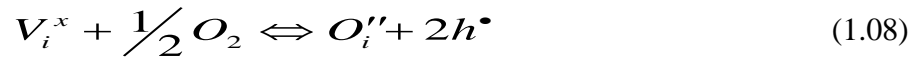
4.1.4 Titanium interstitial

We have this defect if a cation Ti^{4+} occupies an interstitial site and one can label this process by Ti_i^i and its equation is as below.

$$2O_o + Ti_{Ti} \Leftrightarrow Ti_i^{\bullet\bullet\bullet} + 3e' + O_2 \qquad (1.09)$$
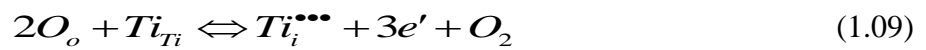
4.2 Extrinsic defects

Beside the impurities in the titanium dioxide, researchers have doped it by different atoms. In 2018 M. R. Elahifard et al [12], saw Effects of Ni-doping on the photo-catalytic activity of TiO_2 anatase and rutile by simulation and experiment. Where S. Sood et al looked for the highly effective Fe-doped TiO_2 nanoparticles photocatalysts for visible light driven photocatalytic degradation of toxic organic compounds in 2015 [13]. Before that P. Nyamukamba et al highlighted the influence of carbon doping on TiO_2 nanoparticle size, surface area, anatase to

rutile phase transformation and photocatalytic activity in 2012 [14]. This is the most recent experiment that has been done on titanium dioxide. And because the TiO_2 has a lot of applications, there are many more doping experiments on it like noble metals doing (Pt, Ag, Au, Pd, Ni, Rh and Cu), metalloids like (boron) and anions [15].

5. Influence of point defects on the properties of titanium dioxide

As reported in the definition, in general defects give new properties to the crystal. If one begins with intrinsic point defects in the titanium dioxide, the oxygen vacancies and titanium interstitials make it an n-type semiconductor where titanium vacancies make it sort of p-type semiconductor [16]. When the concentration of oxygen vacancies defect increases, the vacancies start to be ordered therefore, new phases of titanium oxides occur. Moreover, the increase of the oxygen vacancies reduces the large band gap of our crystal which is equal to 3.3 eV [10]. Another type of point defect is presented by the transformation of Ti^{4+} to Ti^{3+}. Where the cation Ti^{3+} gives to the crystal the blue coloration or coloration center, moreover, Ti^{3+} can absorb visible light spectrum, [17] and reduce the band gap just like the oxygen vacancies do.

These defects can change the electrical behavior of the titanium dioxide. Generally, titanium dioxide is a semiconductor or an insulator for higher content of oxide but for lower content of oxide it turns to metallic [10].

Titanium dioxide has a lot of applications like dye–sensitized solar cells, hydrogen production, hydrogen storage, sensors, batteries, cancer prevention and treatment, antibacterial and self–cleaning applications, electrocatalysis and photocatalytic applications [18], therefore scientists have been trying to improve its efficiency in all the different applications. So they exploit the point defects of the crystal and they introduce another type of atoms in the lattice, that is what we call doping. They saw how they improve the efficiency of the titanium dioxide in all its applications.

Starting with the C-doped TiO_2 (carbon), where the carbon atoms help the crystal to absorb more visible light that make a TiO_2 better in photocatalytic [14]. Moving now to the Fe-doped TiO_2 nanoparticles, here the iron atoms play an important role reducing the recombination of recombination of charge carriers (electrons and holes) therefore enhancing the photocatalytic behavior of our material [13]. We mentioned just a few influences in this section, but still many others that are not going to be mentioned here. To conclude this section, we can use the point defects to make our material useful for any application mentioned above.

6. Conclusion

We have been trying to talk about all the defects that may occur in the crystal, and we discussed many of them with all their different types. Finally, we came up with a result that there is no perfect crystal. The sum of perfect crystal and defects is called a real crystal. In the next chapter we are going to study the F^+ center by some methods such as the theory of perturbation and see how they behave under the application of an electric field and will we try to give them a new definition.

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Chapter two

Theoretical Study of Color Centers in TiO$_2$ Using Perturbations Theory and LCAO Methods

1. Introduction

TiO$_2$ is used in a lot of applications [1] and it is an ionic crystal [2]; that means it contains color centers due to the oxygen vacancies. We already mentioned the importance of defects [3] and the different color centers which are F, F$^+$ and F^{++} centers [4] (section 3.1.2.3 chapter 1). In this chapter we are going to study the F$^+$ center, which is just an electron trapped in the oxygen vacancy plus one electron sits on one of the four titanium cations surrounding the first electron (three of the titanium cations are Ti^{4+} and one of them is Ti^{3+}). This study is divided into two parts. In the first one, we are going to study the electron located on the oxygen vacancy with some conditions using the particle in a box model and the perturbation theory [5]. In the second part, we are going to use the linear combination of atomic orbital (LCAO) [6] and the effective mass [7] theory to study the electron which is on the Ti^{4+} to make it Ti^{3+}. Finally, we mention in the conclusion the new result that we came up with.

2. Vacancy's electron

2.1 Introduction

In this part we are going to study the electron existing inside the oxygen vacancy in an electric field using the perturbation theory.

2.2 Particle in a box model

After discovering the F center in 1937 by subjecting alkali halides to the action of the X rays [8]. Researchers started thinking about the wave function of the electron moving around in the vacancy [9]. One of the models they gave to it is the particle in a box model (quantum dot), by considering the length of the box is the lattice parameter (a). They begin with the potential V = 0 if $0 \prec x \prec a$, $0 \prec y \prec a$ and $0 \prec z \prec a$, otherwise the potential is infinity as represented in fig 2.1[10].
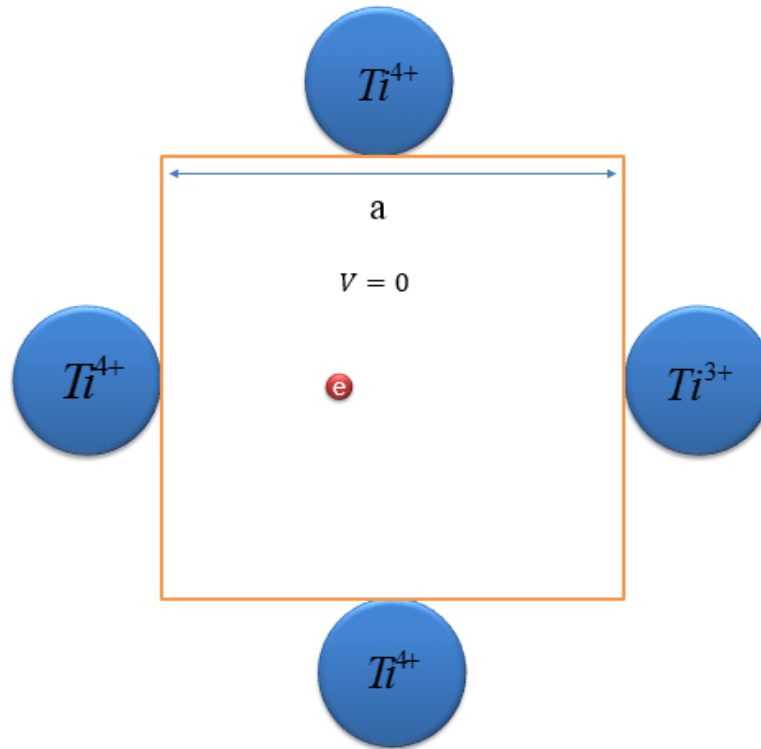
Fig. 2.1 Quantum dot of an F^+ center.

We can find the wave function of this particle in this box by solving the time independent Schrodinger equation with this potential [11].

$$\frac{-\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\psi(x,y,z)=E\psi(x,y,z) \tag{2.01}$$

Where (m) is the mass of the electron, $\psi(x,y,z)$ is the wave function, E the energy and h is the Planck's constant. The easiest way to solve (2.01) is using the separation of the variables x, y and z so the wave function can be written as indicated below [12]:

$$\psi(x,y,z)=\varphi(x)\chi(y)\kappa(z) \tag{2.02}$$

and

$$E=E_x+E_y+E_z \tag{2.03}$$

After replacing (2.02) and (2.03) in (2.01) and comparing both sides of the equation we obtain the following three equations.

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\varphi(x)\right)=E_x\varphi(x) \tag{2.04}$$

39

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\chi(y)\right) = E_y\chi(y) \tag{2.05}$$

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\kappa(z)\right) = E_z\kappa(z) \tag{2.06}$$

The solutions of the three equations are well known. We replace them in (2.02) and the wave function of the particle is going to be the following.

$$\psi(x, y, z) = \sqrt{\frac{8}{a^3}}\sin(\frac{n_1\pi}{a}x)\sin(\frac{n_2\pi}{a}y)\sin(\frac{n_3\pi}{a}z) \tag{2.07}$$

This wave function is associated with quantized energy levels written as follows.

$$E_{n_1,n_2,n_3} = \frac{\hbar^2\pi^2}{2ma^2}(n_1^2 + n_2^2 + n_3^2) \tag{2.08}$$

We can plot the energy levels and get what represented in fig. 2.2.
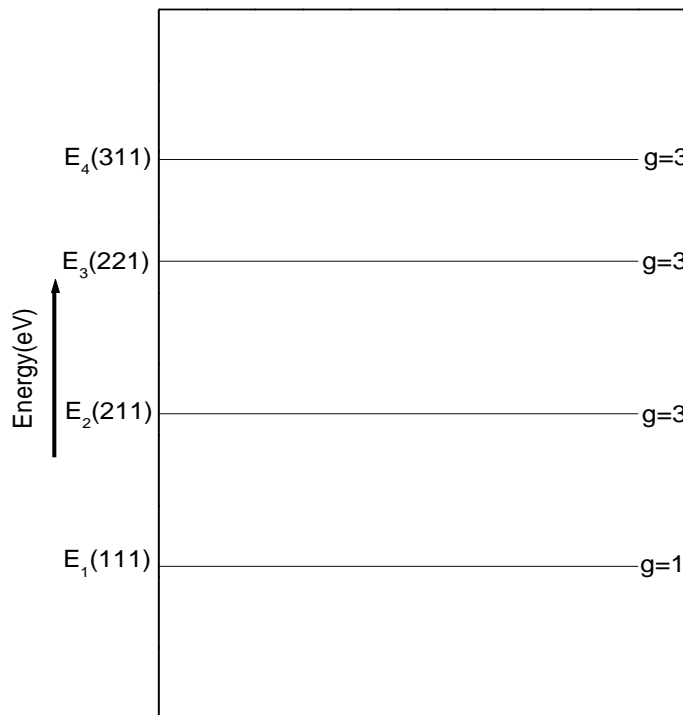
Fig. 2.2 The energy levels of a quantum dot.

From (2.08), we clearly see that the energy can have the same value for different n_1, n_2 and n_3 which means the existence of more than one wave function for the same energy. This energy level is degenerated and the number of degeneracy is g. But when $n_1 = n_2 = n_3$, the energy level is not degenerated because we have only one wave function that corresponds to this level. The table 2.1 represents the differences of the energy levels.

Table 2.1 The energy separating the levels.

Levels corresponding	The differences of the energy levels (ΔE 's) (eV)	Wavelength (nm)
$\Delta E_{2,1} = E_2 - E_1$	5.38775	230.59477
$\Delta E_{3,1} = E_3 - E_1$	10.77551	115.29738
$\Delta E_{3,2} = E_3 - E_2$	5.38775	230.59477
$\Delta E_{4,1} = E_4 - E_1$	14.36734	82.47303
$\Delta E_{4,2} = E_4 - E_2$	8.97959	138.35685
$\Delta E_{4,3} = E_4 - E_3$	3.59183	345.89222

This is how they simulate the F^+ center as a quantum dot, and they got its wave function and its energies also. The electron gets excited by absorbing photons and goes to higher levels and on its way back it will release some photons (may or may not be with same wavelength of the incident photons) and gives a nice coloration to the crystal [10]. So we see that the F center plays an important role in giving color and this is the reason why it is called color center. In this case the trapped electron was free in the box. It is really important if we can get knowledge about the behavior of this electron when applying an exterior force using an electric field for example.

In the next section we are going to perturb this box by an electric field and calculate the new energy and wave function of the ground state.

2.3 Perturbing a box

We assumed in the previous section that the F^+ center is a quantum dot. And now we are going to perturb it by a constant electric field pointing on the x direction. The fig. 2.3 is representing perturbation method.
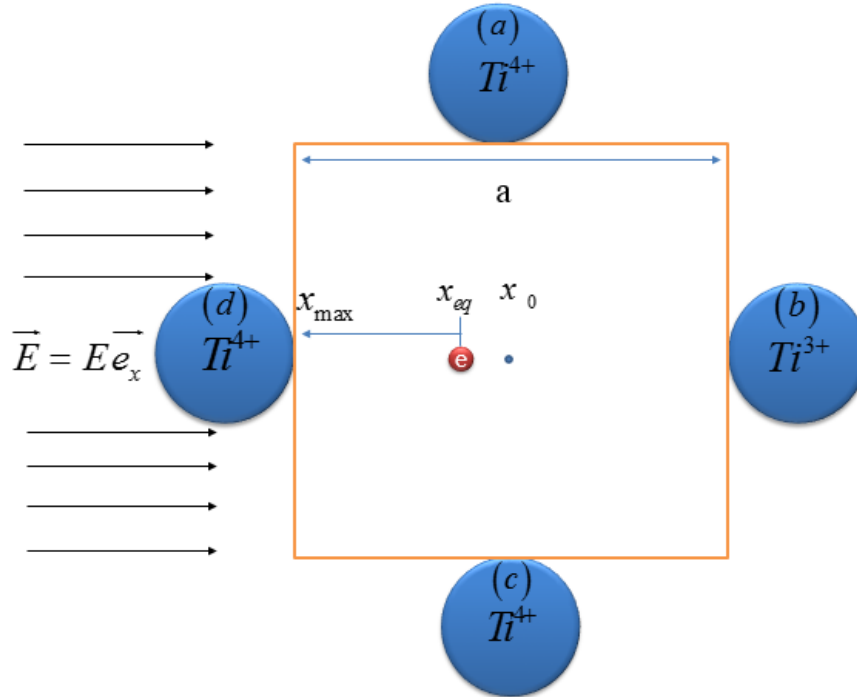
Fig. 2.3 Perturbation of the F^+ by a constant electric field.

x_0 : The position of the electron when all the neighbors are identical (without electric field).

$$x_0 = \frac{1}{2}a \tag{2.09}$$

x_{eq} : The position of the equilibrium in this case (without electric field) we are going to call it G.

x_{max} : The position of the electron when the electric field reaches its maximum.

$a = \left\|\vec{db}\right\|$: The lattice parameter.

First we are going to calculate the distance between x_0 and x_{eq} (the equilibrium position) without electric field we can call it Δx .

Using a simple mathematical tool, we have then.

$$\vec{dG} = \frac{f_b}{f_b + f_d}\,\vec{db}$$ (2.10)

$\vec{dG}$: The victor of distance between the atom (d) and the position (G).

$\vec{db}$: The victor of distance between the atom (d) and the atom (b) and it equal to the lattice parameter (a).

f_d : The force of the atom d on the electron sitting on x_0 and it is:

$$f_d = k\,\frac{4|q|^2}{(a/2)^2}$$ (2.11)

f_b : The force of the atom b on the electron sitting on x_0 and it is equal.

$$f_b = k\,\frac{3|q|^2}{(a/2)^2}$$ (2.12)

If we use the rutile TiO_2 lattice parameter a = 0.4584 nm.

So

$$f_d = 1754.337*10^{-11} \text{ N}$$

And

$$f_b = 1315.753*10^{-11} \text{ N}$$

Then

$$\vec{dG} = 0.4285\,\vec{db}$$ (2.13)

So the distance $\vec{dG}$ is equal to 0.1964 nm.

We have

$$\Delta x = x_0 - \left\| \vec{dG} \right\|$$ (2.14)

So

$$\Delta x = 0.03272 \text{ nm}$$

Now if we turn on the electric field, the force of the atom (d) will be supported by the force of the electric field applying on the electron so $F_d = f_b + eE_f$. The new equilibrium position of the electron will depend on the electric field. But if we make the electric field big enough the electron will leave the oxygen vacancy and our proposition or experiment will be boring. So there is a maximum value of the electric field E_{max} equal to.

$$\frac{f_b}{f_d + f_b + eE_{max}} = 0.1964 \tag{2.15}$$

So

$$E_{max} = 2.2682896 * 10^{11} \text{ V/m}$$

Now the electric field goes from 0 to E_{max}. Beyond E_{max} the electron will leave the vacancy and it will be no F^+ center.

$$0 \prec E \prec E_{max} \tag{2.16}$$

This electric field will make a potential inside the box equal to.

$$V = eEa \tag{2.17}$$

e : The charge of the electron.

a : The lattice parameter.

This potential may change the energy of the states. For example; the ground state and the first excited state. It may then also change the wave functions of the states. And in order to figure out the new energies and the new wave functions, we are going to use a quantum mechanical tool which is the non-degenerate perturbation theory indicated in the following section.

2.4 Tool of perturbation theory

There is no exact solution for any physical problem because a lot of factors are neglected to simplify the mathematics. In order to find the new energy and wave function of the ground state. We have to use one of the approximation methods.

Physicists use the perturbation theory once we have an extra term in the Hamiltonian δH where the extra term is too small compared to the original Hamiltonian $H^{(0)}$ [13].

$$\delta H \prec\prec\prec H^{(0)} \tag{2.18}$$

This theory has two types; the time dependent perturbation theory [14] and the time independent perturbation theory. The last one is divided into two parts; the non-degenerate and the degenerate theory [13]. In this work we are going to use the non-degenerate theory for the non-degenerate ground state of our system.

2.5 Correction of the energy

After perturbing the system by a constant electric field directed on the x direction, so:

$$\vec{E}_f = E\,\vec{i} \tag{2.19}$$

The new Hamiltonian of the system is going to be written in the following way.

$$H(\lambda) = H^{(0)} + \lambda\delta H \tag{2.20}$$

$H^{(0)}$: The well-known free electron Hamiltonian

$$H^{(0)} = \frac{p^2}{2m} \tag{2.21}$$

δH : The perturbation Hamiltonian. In the case of an electric field E_f is going to be.

$$\delta H = -qE_f a \tag{2.22}$$

λ : A mathematical parameter to make the perturbation small enough and it defined as follows. $\lambda \in [0,1]$

2.5.1 First order correction of the energy

Since the Hamiltonian was in term of the mathematical parameter λ , as a result the energy is going to be in term of λ also and it will be like shown in the equation below [13].

$$E_1(\lambda) = E_1^{(0)} + \lambda E_1^{(1)} \tag{2.23}$$

$E_1^{(0)}$: The ground state energy without perturbation.

$$E_1^{(0)} = \frac{3\pi^2\hbar^2}{2ma} \tag{2.24}$$

$E_1^{(1)}$: The first correction of the energy.

$$E_1^{(1)} = \left\langle \psi_1^{(0)} \left| \delta H \right| \psi_1^{(0)} \right\rangle \tag{2.25}$$

$\psi_1^{(0)}$: The unperturbed ground state wave function.

Since it is the ground state wave function so $n_1 = n_2 = n_3 = 1$.

$$\psi_1^{(0)} = \sqrt{\frac{8}{a^3}} \sin(\frac{\pi}{a} x) \sin(\frac{\pi}{a} y) \sin(\frac{\pi}{a} z) \tag{2.26}$$

Our aim now is to calculate the energy correction $E_1^{(1)}$ and to do so we are going to solve the equation (2.25).

$$E_1^{(1)} = \left\langle \psi_1^{(0)} \left| \delta H \right| \psi_1^{(0)} \right\rangle = \int_0^a \psi_1^{(0)*} \delta H \psi_1^{(0)} d\tau \tag{2.27}$$

Where

$$d\tau = dxdydz \tag{2.28}$$

Now let's plug ψ in the equation (2.27).

$$E_1^{(1)} = \int_0^a \sqrt{\frac{8}{a^3}} \sin(\frac{\pi}{a} x) \sin(\frac{\pi}{a} y) \sin(\frac{\pi}{a} z)(-qE_f a)\sqrt{\frac{8}{a^3}} \sin(\frac{\pi}{a} x) \sin(\frac{\pi}{a} y) \sin(\frac{\pi}{a} z) d\tau \tag{2.29}$$

We can simplify this equation to get the next equation.

$$E_1^{(1)} = \frac{-8qE_f}{a^2} \int_0^a \sin^2(\frac{\pi}{a} x) \sin^2(\frac{\pi}{a} y) \sin^2(\frac{\pi}{a} z) d\tau \tag{2.30}$$

After doing the integral we are going find the following equation.

$$E_1^{(1)} = \frac{-8qE_f}{a^2} \left[\frac{a^3}{8} \right] \tag{2.31}$$

Finally, we have the energy correction given by.

$$E_1^{(1)} = -qE_f a \tag{2.32}$$

Now we can write the total energy with the first correction only in this way.

$$E(\lambda) = \frac{3\pi^2 \hbar^2}{2ma} - \lambda qE_f a \tag{2.33}$$

Because the charge of the electron is negative so the first correction shifted up the energy of the ground state.

By fixing some factors we can draw $E(\lambda)$ and $E(E_f)$ plots in fig. 2.4 and fig. 2.5 respectively.
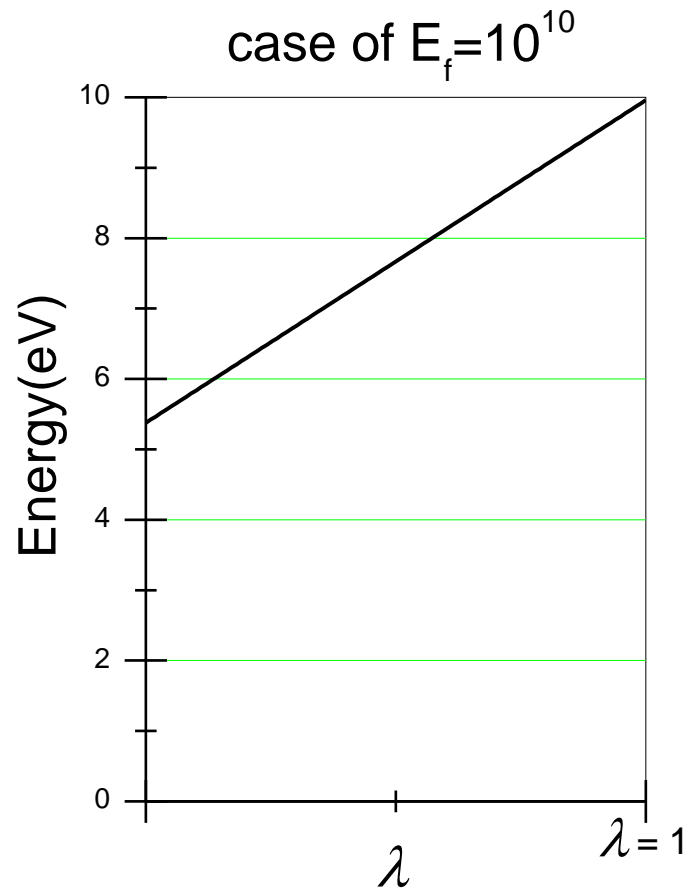
Fig. 2.4 Energy versus λ plot (first order correction).
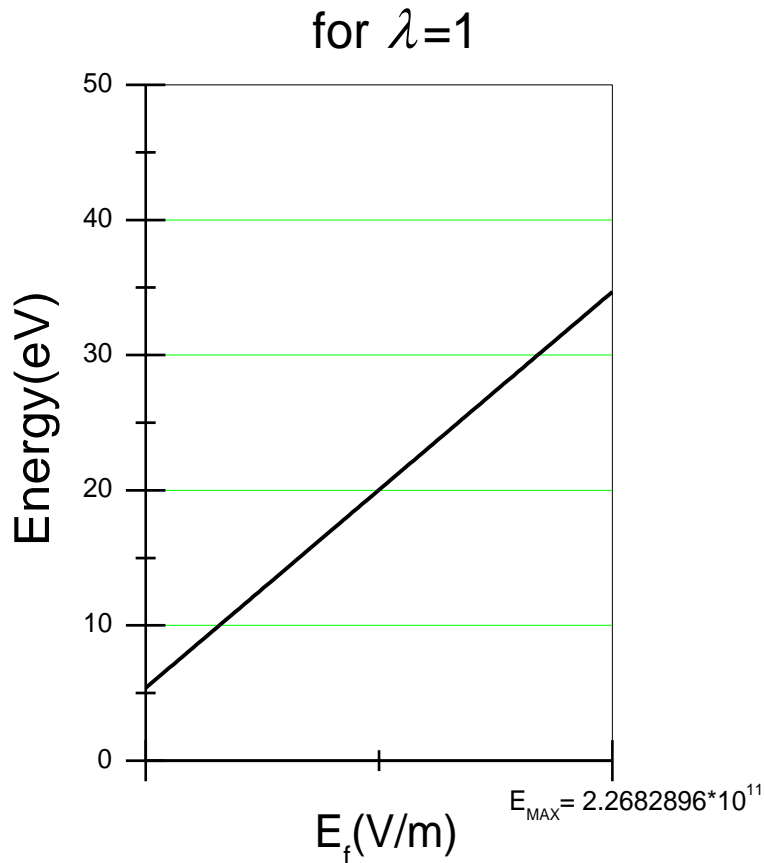
Fig. 2.5 Energy versus electric field plot (first order).

The first order correction of the energy gives the exact true energy of the non-degenerate ground state. Moreover according to these two plots, theoretically every possible value of the electric field associated with a small value of the factor λ to be as a perturbation. But if the electric field exceeds the $E_{f\,max}$ then the trapped electron leaves the box and we cannot apply the perturbation theory.

2.5.2 Second order correction of the energy

We have seen the first correction and now we are going to see the second correction of the energy. Starting the energy equation.

$$E_1(\lambda) = E_1^{(0)} + \lambda E_1^{(1)} + \lambda^2 E_1^{(2)} \tag{2.34}$$

Where $E_1^{(2)}$ is the second correction of the energy.

$$E_1^{(2)} = \sum_k \frac{\left|\left\langle \psi_k^{(0)} \left| \delta H \right| \psi_1^{(0)} \right\rangle\right|^2}{E_1^{(0)} - E_k^{(0)}} \tag{2.35}$$

To know what the second energy correction is we have to solve the equation (2.35) as well.

In order to that we have to do it step by step as follows.

$$\left\langle \psi_k^{(0)} \left| \delta H \right| \psi_1^{(0)} \right\rangle = \frac{-8qE_f}{a^2} \int_0^a \sin(\frac{k_1\pi}{a}x)\sin(\frac{\pi}{a}x)\sin(\frac{k_2\pi}{a}y)\sin(\frac{\pi}{a}y)\sin(\frac{k_3\pi}{a}z)\sin(\frac{\pi}{a}z)d\tau \tag{2.36}$$

Now we have to put the second power to our equation and separating the variables x, y and z we get the following equation.

$$\left|\left\langle \psi_k^{(0)} \left| \delta H \right| \psi_1^{(0)} \right\rangle\right|^2 = \frac{64q^2E_f^2}{a^4}\left[\int_0^{a^2} \sin^2(\frac{k_1\pi}{a}x)\sin^2(\frac{\pi}{a}x)dx\int_0^{a^2} \sin^2(\frac{k_2\pi}{a}y)\sin^2(\frac{\pi}{a}y)dy\int_0^{a^2} \sin^2(\frac{k_3\pi}{a}z)\sin^2(\frac{\pi}{a}z)dz\right]$$

$$\tag{2.37}$$

After integrating the equation (2.37) we got.

$$\left|\left\langle \psi_k^{(0)} \left| \delta H \right| \psi_1^{(0)} \right\rangle\right|^2 = \frac{64q^2E_f^2}{a^4}\left[\frac{a^6}{64}\right] \tag{2.38}$$

From the equation (2.38) we have.

$$\left|\left\langle \psi_k^{(0)} \left| \delta H \right| \psi_1^{(0)} \right\rangle\right|^2 = q^2 E_f^2 a^2 \tag{2.39}$$

We did calculate the numerator. Now we have to simplify the denominator.

So we have

$$E_1^{(0)} - E_k^{(o)} = \frac{\hbar^2\pi^2}{2ma^2}(3-k) \tag{2.40}$$

Where k represents the levels of all the possible transitions that may happened.

$$k = k_1^2 + k_2^2 + k_3^2 \tag{2.41}$$

After doing all the calculation we have now the second energy correction given by.

$$E_1^{(2)} = \sum_k \frac{2ma^4 q^2 E_f^2}{\hbar^2\pi^2(3-k)} \tag{2.42}$$

Finally, the total energy is represented by the equation below.

$$E(\lambda) = \frac{3\pi^2 \hbar^2}{2ma} - \lambda q E_f a + \lambda^2 \sum_k \frac{2ma^4 q^2 E_f^2}{\hbar^2 \pi^2 (3-k)} \tag{2.43}$$

By reducing the sum of the equation (2.43) to just one higher level so, $k_1 = 2$, $k_2 = 1$ and $k_3 = 1$. That means k will equal to 6 (equation (2.41)). The following figure representing the plot of previous equation after reducing the sum.
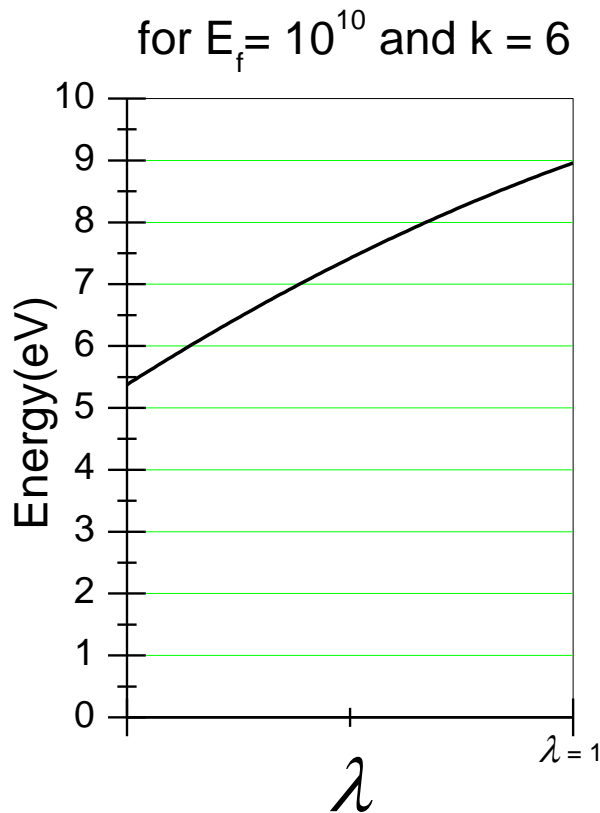
Fig. 2.6 Energy versus λ plot (second correction).

Now this result tells us that the second order correction of the energy is shifting down the energy of the ground state unlike the first order. Fig. 2.7 shows the difference between the first and the second order correction.

for $E_f = 10^{10}$ and k = 6
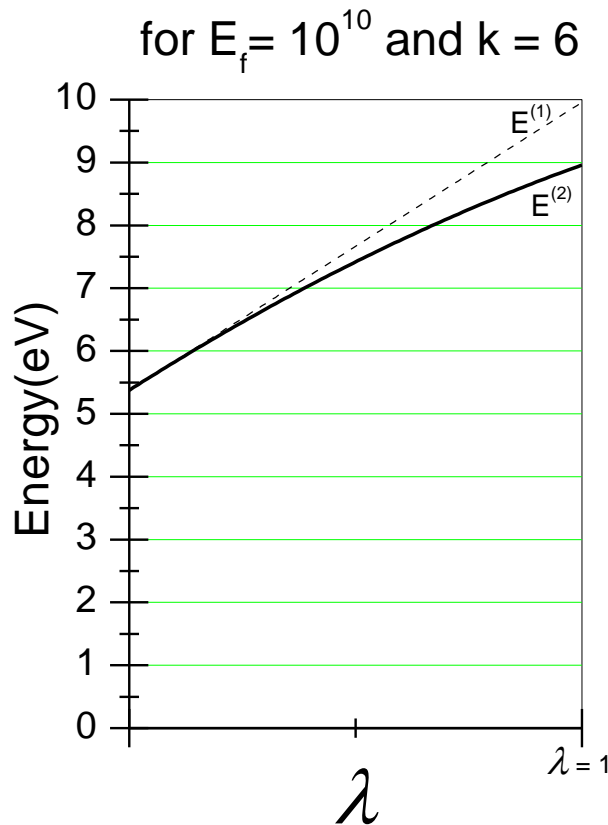
Fig. 2.7 Energy versus λ plot (The dash line represents the first order and the solid line is the second order)

If we think about another non degenerate level like (222) in terms of the second order correction; we will see that the levels below pushing the level up (giving it more energy) and the levels above pushing the level down (reducing its energy). Each level doesn't want the (222) level to get more close to it, and that is what they call the levels repulsion [13].

2.6 Correction of the wave function

As we mentioned before the wave function may or may not change due to the perturbation. In this section we will find out what will happen to the ground state wave function. And to do that we will write its equation in terms of λ [13].

$$\left|\psi_1(\lambda)\right\rangle = \left|\psi_1^{(0)}\right\rangle + \lambda\left|\psi_1^{(1)}\right\rangle \tag{2.44}$$

$\left| \psi_1^{(1)} \right\rangle$: The first correction of the wave function and it is given by the equation below.

$$\left| \psi_1^{(1)} \right\rangle = -\sum_{k \neq 1} \frac{\left\langle \psi_k^{(0)} \left| \delta H \right| \psi_1^{(0)} \right\rangle}{E_k^{(0)} - E_1^{(1)}} \left| \psi_k^{(0)} \right\rangle \tag{2.45}$$

Where

$\left| \psi_k^{(0)} \right\rangle$: The unperturbed excited wave function.

Our objective is to calculate $\left| \psi_1^{(1)} \right\rangle$ and we will do that starting be calculating the numerator.

$$\left\langle \psi_k^{(0)} \left| \delta H \right| \psi_1^{(0)} \right\rangle = \frac{-8qE_f}{a^2} \int_0^a \sin(\frac{k_1\pi}{a}x)\sin(\frac{\pi}{a}x)\sin(\frac{k_2\pi}{a}y)\sin(\frac{\pi}{a}y)\sin(\frac{k_3\pi}{a}z)\sin(\frac{\pi}{a}z)d\tau \tag{2.46}$$

This integral is zero

$$\left\langle \psi_k^{(0)} \left| \delta H \right| \psi_1^{(0)} \right\rangle = 0 \tag{2.47}$$

Thus;

$$\left| \psi_1^{(1)} \right\rangle = 0 \tag{2.48}$$

The equation (2.47) introduces the orthogonality of the levels. And the whole result means that the ground state wave function doesn't change due to the perturbation, but it remains the same unlike the energy.

2.7 Conclusion

Beside the exact energy of the ground state given by the first order correction of the perturbation theory, the physicist R. Feynman says, "It doesn't matter how beautiful your theory is. It doesn't matter how smart you are. If it doesn't agree with the experiment, it is wrong." [15] These words fit our result. Furthermore, the second correction threw the light on one of the important results which is the levels repulsion. When we started looking for the correction of the wave function we found out that the energy levels are orthogonal to each other. This is all the results that we came up with in the first part of chapter two.

3 Cation's electron

3.1 Introduction

This part will be talking about the electron existing in one of the fourth cations surrounding the oxygen vacancy and its motion. Starting by the defects equilibrium to see why we need defects in the crystal to make it stable.

3.2 Defects equilibrium

Gibbs free energy of any system is given by [16].

$$G = H - TS \tag{2.49}$$

Where ;

- G : The Gibbs free energy.
- H : The enthalpy.
- S : The entropy.
- T : The temperature.

The variation in Gibbs free energy due to the introduction of (n) vacancies in crystal with (N) sites is given by

$$\Delta G = \Delta H - T\Delta S \tag{2.50}$$

Where ;

- ΔG : The change in the Gibbs free energy.
- ΔH : The change in the enthalpy.
- ΔS : The change in entropy.

The change in the entropy should be represented by the change in vibrational entropy and the change in the configurational entropy [10].

$$\Delta S = n\Delta S_V + \Delta S_C \tag{2.51}$$

Where;

- ΔS_V : The change in the vibrational entropy.
- ΔS_C : The change in the configurational entropy.
- n : The number of defects.

Every point defect has a formation enthalpy considered the same for the defects of the same type, so the change in the Gibbs free energy is given now by the equation below.

$$\Delta G = n\Delta H - T(n\Delta S_V + \Delta S_C) \tag{2.52}$$

The configurational entropy is given by the Boltzmann equation [16].

$$\Delta S_C = k \ln(\omega) \tag{2.53}$$

K is the Boltzmann constant, and ω is the thermodynamic probability given by the following equation in the case of Schottky defects [17].

$$\omega = \frac{(N+n)!}{N!n!} \tag{2.54}$$

- N: The number of atoms.
- n: The number of point defects.

If we use Stirling approximation, we get.

$$\Delta S_c = -k\left[N\ln(\frac{N}{N+n}) + n\ln(\frac{n}{N+n}) \right] \tag{2.55}$$

At the end we get the Gibbs free energy by the equation below.

$$\Delta G = n\Delta H - T\left[n\Delta S_V - k\left(N\ln(\frac{N}{N+n}) + n\ln(\frac{n}{N+n}) \right) \right] \tag{2.56}$$

If we draw these three plots;

$$Y = n\Delta H \ , \ Y = T\left[n\Delta S_V - k\left(N\ln(\frac{N}{N+n}) + n\ln(\frac{n}{N+n}) \right) \right] \text{, and } Y = \Delta G(n) .$$
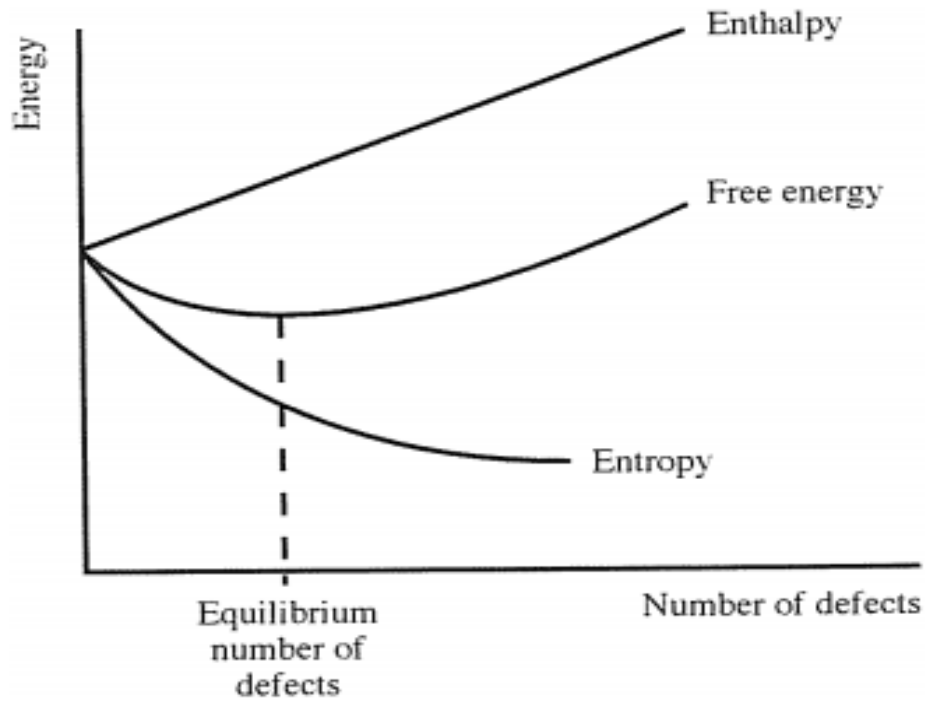
Fig. 2.8 The effect of defects in the variation of the Gibbs free energy [18].

From this plot we see that above 0 K the crystal needs a particular number of defects (the equilibrium number of defects) in order to get its stability. By differentiating the equation (2.56) with respect to the number of defects ($\dfrac{\partial \Delta G}{\partial n} = 0$) we get.

$$n_{eq} = Ne^{\frac{\Delta S_V}{k}} . e^{\frac{-\Delta H}{kT}} \tag{2.57}$$

We can get rid of the term of ΔS_V because it is pretty small so equation (2.57) is now as follow [10].

$$n_{eq} = Ne^{\frac{-\Delta H}{kT}} \tag{2.58}$$

Defects are a pretty important factor for the stability of the crystal, because its role of reducing the Gibbs free, which is the main factor that characterizes the stability of the crystal; (The smallest Gibbs free energy is the more stable crystal is.)

But the important question now is the following "why do we need defects in the crystal to make it stable?!". We are going to answer this question in the next section.

3.3 Bond model

It was shown before that we are going to give a new definition to the F^+ center. And to do that we propose this model of bond. This latter is based on two theories: the linear combination of atomic orbital and the effective mass. The model allows us to deeply understand the F^+ center which is more than we were thinking. In this section we will go through the calculation of this model and see what this method gives a good result.

The F^+ center is just one (1) electron sitting in the oxygen vacancy surrounded by 4 neighbors of Ti^{+4} or 3 neighbors of Ti^{4+} and one is Ti^{3+}. The last cation should be thought of as Ti^{4+} plus one electron. Moreover, the cation Ti^{4+} is more stable than the cation Ti^{3+}, so the last one wants to get rid of the extra electron to get more stable again. So we assume that those 4 cations neighbors of Ti are going to exchange the extra electron between them in order way and the energy needed for this phenomenon is very weak. This process is analogous to what is happening in the metallic bond. Where the electrons hop from one atom to another to lower their energy and form a strong bond, which is the metallic bond. And we can define the way of the electron hopping between the 4 cations in the fig.2.8.
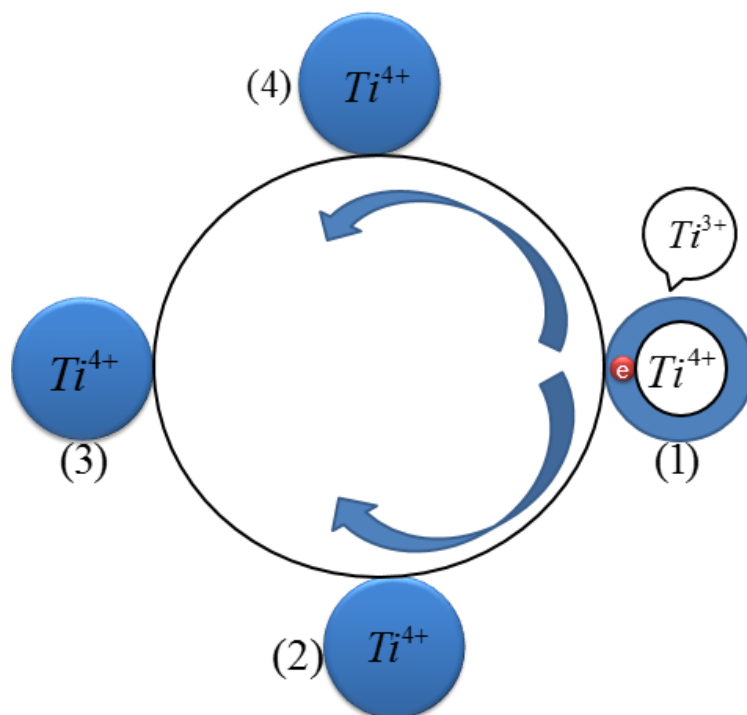
Fig. 2.9 Possible way of the electron motion between the four cations (The electron can move clockwise or anticlockwise)

The electron wants to move to nearest neighbor without considering the direction it may move with it (The electron can move from $Ti^{4+}(1)$ to $Ti^{4+}(2)$ to $Ti^{4+}(3)$ to $Ti^{4+}(4)$ and gets back $Ti^{4+}(1)$ and keep moving in the circle, and it can also move in the opposite way.)

$|1\rangle$, $|2\rangle$, $|3\rangle$ and $|4\rangle$ are the kets representing the wave functions of the atomic orbitals if the electron sits in the cations $Ti^{4+}(1)$, $Ti^{4+}(2)$, $Ti^{4+}(3)$, and $Ti^{4+}(4)$ respectively.

Now we will ignore the interaction of the other atoms in the crystal lattice with the considered electron, and ignore also the nucleus-nucleus interaction between the 4 neighbors. We will just take in consideration the interaction of those 4 Ti^{+4} cations with the electron. We will also use the Born-Oppenheimer approximation to fix the nucleus of the 4 cations, and let the electron hops from one atom to another and we will start by the Hamiltonian.

$$H = \frac{p^2}{2m} + \sum_{j=1}^{4} V(\vec{r} - \overrightarrow{R_j}) \tag{2.59}$$

$\overrightarrow{R_J}$: The position of the atoms (nucleus).

$\vec{r}$: The position of the electron.

We can abbreviate the Hamiltonian pieces to letters.

$$\frac{p^2}{2m} = k \tag{2.60}$$

And

$$\sum_{j=1}^{4} V(\vec{r} - \overrightarrow{R_j}) = \sum_{j=1}^{4} V_j \tag{2.61}$$

Where

$$V_j = \frac{e^2}{4\pi\varepsilon_\circ |r - R_j|} \tag{2.62}$$

One way to solve this Hamiltonian is to imagine that we have only one atom exist and it has an atomic orbital $|m\rangle$ with an energy e_{atomic}, so the Schrödinger equation will be as follows.

$$(k + V_m)|m\rangle = e_{atomic}|m\rangle \tag{2.63}$$

Where e_{atomic} is the energy of the 4 orbital of the Ti. I.e., $|1\rangle$ is the 4s state of the Ti^{4+} (1). We assume that the orbitals are orthogonal to each other and to describe this orthogonality we use the equation below.

$$\langle n | m \rangle = \delta_{nm} \tag{2.64}$$

We are going to use LCAO to find the wave function of the electron moving between the four atoms. To do so, we have to write the trail wave function as a sum on the wave function of the four atomic orbitals with coefficients.

$$|\Psi\rangle = \phi_1 |1\rangle + \phi_2 |2\rangle + \phi_3 |3\rangle + \phi_4 |4\rangle \tag{2.65}$$

In order to find this wave function, we have to use the effective Schrödinger equation given by the follow way [19].

$$\sum_m H_{nm} \Phi_m = E \Phi_n \tag{2.66}$$

H_{nm} is the Hamiltonian represented by four by four matrix.

Now if we use the way of only one atom exists again we can remove the interaction with m^{th} atom from the sum of the Hamiltonian to become.

$$H = k + V_m + \sum_{j \neq m} V_j \tag{2.67}$$

This time we will hit both side of the equation (2.64) by the ket $|m\rangle$ to be as follows.

$$H|m\rangle = (k + V_m)|m\rangle + \sum_{j \neq m} V_j |m\rangle \tag{2.68}$$

Using equation (2.60) we can write.

$$H|m\rangle = e_{atomic} |m\rangle + \sum_{j \neq m} V_j |m\rangle \tag{2.69}$$

Now we will hit the equation (2.66) by a bra of $\langle n|$ to get.

$$\langle n|H|m\rangle = e_{atomic} \delta_{nm} + \langle n| \sum_{j \neq m} V_j |m\rangle \tag{2.70}$$

This is very interested equation, and we have to define the second piece on right hand side.

If $n = m$ then $\langle n | \sum_{j \neq m} V_j | m \rangle =$ the interaction of the 3 atoms on the electron sitting on the fourth

one is called V_0.

If $n \neq m$ then $\langle n | \sum_{j \neq m} V_j | m \rangle = -t$, this value of $-t$ is the hopping because if we look to the

time dependent Schrödinger equation one can take an electron on the site $|m\rangle$ and have an end

up on the site $|n\rangle$ so this off diagonal term of the Hamiltonian allows the electron to hop from

one site to another. Thus we call it hopping [19].

The energy of the hopping ranges between 0.1 to 0.5 eV [18].

But if $|m - n| \succ 1$ so $t = 0$

Because very hard for the electron to hop so far.

We will sum up all what we said about that piece in the equation below.

$$\langle n | \sum_{j \neq m} V_j | m \rangle = \begin{cases} V_0 & n = m \\ -t & n = m \pm 1 \\ 0 & otherwise \end{cases} \tag{2.71}$$

By assuming that the value of $(-t)$ is the same with every hop, we will get the following matrix

element of the Hamiltonian.

$$\langle 1 | H | 1 \rangle = \langle 1 | k + V_1 | 1 \rangle + \langle 1 | V_2 | 1 \rangle + \langle 1 | V_3 | 1 \rangle + \langle 1 | V_4 | 1 \rangle = e_{atomic} + V_0 \tag{2.72}$$

$$\langle 1 | H | 2 \rangle = \langle 1 | k + V_2 | 2 \rangle + \langle 1 | V_1 | 2 \rangle + \langle 1 | V_3 | 2 \rangle + \langle 1 | V_4 | 2 \rangle = -3t \tag{2.73}$$

$$\langle 1 | H | 3 \rangle = \langle 1 | k + V_3 | 3 \rangle + \langle 1 | V_1 | 3 \rangle + \langle 1 | V_2 | 3 \rangle + \langle 1 | V_4 | 3 \rangle = 0 \tag{2.74}$$

$$\langle 1 | H | 4 \rangle = \langle 1 | k + V_4 | 4 \rangle + \langle 1 | V_1 | 4 \rangle + \langle 1 | V_2 | 4 \rangle + \langle 1 | V_3 | 4 \rangle = -3t \tag{2.75}$$

$$\langle 2 | H | 1 \rangle = \langle 2 | k + V_1 | 1 \rangle + \langle 2 | V_2 | 1 \rangle + \langle 2 | V_3 | 1 \rangle + \langle 2 | V_4 | 1 \rangle = -3t^* \tag{2.76}$$

$$\langle 2 | H | 2 \rangle = \langle 2 | k + V_1 | 2 \rangle + \langle 2 | V_2 | 2 \rangle + \langle 2 | V_3 | 2 \rangle + \langle 2 | V_4 | 2 \rangle = e_{atomic} + V_0 \tag{2.77}$$

$$\langle 2 | H | 3 \rangle = \langle 2 | k + V_3 | 3 \rangle + \langle 2 | V_1 | 3 \rangle + \langle 2 | V_2 | 3 \rangle + \langle 2 | V_4 | 3 \rangle = -3t \tag{2.78}$$

$$\langle 2 | H | 4 \rangle = \langle 2 | k + V_4 | 4 \rangle + \langle 2 | V_1 | 4 \rangle + \langle 2 | V_2 | 4 \rangle + \langle 2 | V_3 | 4 \rangle = 0 \tag{2.79}$$

$$\langle 3|H|1\rangle = \langle 3|k+V_1|1\rangle + \langle 3|V_2|1\rangle + \langle 3|V_3|1\rangle + \langle 3|V_4|1\rangle = 0 \qquad (2.80)$$

$$\langle 3|H|2\rangle = \langle 3|k+V_2|2\rangle + \langle 3|V_1|2\rangle + \langle 3|V_3|2\rangle + \langle 3|V_4|2\rangle = -3t^* \qquad (2.81)$$

$$\langle 3|H|3\rangle = \langle 3|k+V_3|3\rangle + \langle 3|V_1|3\rangle + \langle 3|V_2|3\rangle + \langle 3|V_4|3\rangle = e_{atomic} + V_0 \qquad (2.82)$$

$$\langle 3|H|4\rangle = \langle 3|k+V_4|4\rangle + \langle 3|V_1|4\rangle + \langle 3|V_2|4\rangle + \langle 3|V_3|4\rangle = -3t \qquad (2.83)$$

$$\langle 4|H|1\rangle = \langle 4|k+V_1|1\rangle + \langle 4|V_2|1\rangle + \langle 4|V_3|1\rangle + \langle 4|V_4|1\rangle = -3t^* \qquad (2.84)$$

$$\langle 4|H|2\rangle = \langle 4|k+V_2|2\rangle + \langle 4|V_1|2\rangle + \langle 4|V_3|2\rangle + \langle 4|V_4|2\rangle = 0 \qquad (2.85)$$

$$\langle 4|H|3\rangle = \langle 4|k+V_3|3\rangle + \langle 4|V_1|3\rangle + \langle 4|V_2|3\rangle + \langle 4|V_4|3\rangle = -t^* \qquad (2.86)$$

$$\langle 4|H|4\rangle = \langle 4|k+V_4|4\rangle + \langle 4|V_1|4\rangle + \langle 4|V_2|4\rangle + \langle 4|V_3|4\rangle = e_{atomic} + V_0 \qquad (2.87)$$

We will sum up all these equations in the following matrix.

$$H = \begin{pmatrix} e_0 & -3t & 0 & -3t \\ -3t^* & e_0 & -3t & 0 \\ 0 & -3t^* & e_0 & -3t \\ -3t^* & 0 & -3t^* & e_0 \end{pmatrix} \qquad (2.88)$$

Where

$$e_0 = e_{atomic} + V_0 \qquad (2.89)$$

To solve the Hamiltonian matrix, we have to diagonalize it using the equation (2.90).

$$\det(H - \lambda I) = 0 \qquad (2.90)$$

After calculating the equation (2.90) we get the following one:

$$(e_0 - \lambda)^2 \left[(e_0 - \lambda)^2 - 36t^2 \right] = 0 \qquad (2.91)$$

To find the eigenenergies we have to solve the equation above. One way to solve it is to divide it into two part as follow.

$$(e_0 - \lambda)^2 = 0 \qquad (2.92)$$

$$(e_0 - \lambda)^2 - 36t^2 = 0 \qquad (2.93)$$

After we solved these two equations, we get the eigenenergies as follows.

$$\lambda_1 = e_0 - 3t \tag{2.94}$$

$$\lambda_2 = e_0 \tag{2.95}$$

$$\lambda_3 = e_0 + 3t \tag{2.96}$$

Now we are going to quote some names from the covalent bond, and we will call the λ_1 by the energy of the bonding state, λ_3 the energy of the anti-bonding state, while λ_2 is the energy of the intermediate state.

We found three energies of three states now it is important to find the wave function of the states. And to do that we have to use the new matrix written below.

$$\begin{pmatrix} e_0 & -3t & 0 & -3t \\ -3t^* & e_0 & -3t & 0 \\ 0 & -3t^* & e_0 & -3t \\ -3t^* & 0 & -3t^* & e_0 \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \end{pmatrix} = E \begin{pmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \phi_4 \end{pmatrix} \tag{2.97}$$

In order to find the eigenfunctions [20] we have to find the ϕ's of each state. And we will start be the first state using it energy below.

$$E_1 = \lambda_1 = e_0 - 3t \tag{2.98}$$

After substituting the first energy in the matrix we found the following set of ϕ's .

$$\phi_1 = \phi_2 = \phi_3 = \phi_4 \tag{2.99}$$

By this result the wave function of the bonding state is going to be as follows.

$$|\psi_1\rangle = \phi_1(|1\rangle + |2\rangle + |3\rangle + |4\rangle) \tag{2.100}$$

And in order to normalize the wave function we have to use the following equation.

$$|\phi_1|^2 + |\phi_2|^2 + |\phi_3|^2 + |\phi_4|^2 = 1 \tag{2.101}$$

Since all of them are equal to each other then.

$$\phi = \frac{1}{2} \tag{2.102}$$

Our wave function will become as indicated in the equation (2.103).

$$|\psi_1\rangle = \frac{1}{2}(|1\rangle + |2\rangle + |3\rangle + |4\rangle) \tag{2.103}$$

This is the wave function of the bonding state which has the lowest energy. Now we have to find the wave function of the intermediate state by doing the same steps.

$$E_2 = \lambda_2 = e_0 \tag{2.104}$$

And for this energy we found.

$$\phi_1 = -\phi_3 \tag{2.105}$$

$$\phi_2 = -\phi_4 \tag{2.106}$$

So the wave function will come as follows.

$$|\psi_2\rangle = (\phi_1|1\rangle + \phi_2|2\rangle - \phi_1|3\rangle - \phi_2|4\rangle) \tag{2.107}$$

Because the atomic orbitals are of the same atom we assume.

$$\phi_1 = \phi_2 \tag{2.108}$$

By this assumption the wave function is going to be as follows.

$$|\psi_2\rangle = \phi_1(|1\rangle + |2\rangle - |3\rangle - |4\rangle) \tag{2.109}$$

After using the equation (2.101) we have now a normalized wave function below.

$$|\psi_2\rangle = \frac{1}{2}(|1\rangle + |2\rangle - |3\rangle - |4\rangle) \tag{2.110}$$

The equation (2.110) represents the wave function of the intermediate state and we still have to find the wave function of the antibonding state by the same way.

$$E_3 = \lambda_3 = e_0 + 3t \tag{2.111}$$

Using also the matrix (2.97) we found the following ϕ's for this energy.

$$\phi_1 = -\phi_2 = \phi_3 = -\phi_4 \tag{2.112}$$

And after we normalized the wave function we have now the antibonding state wave function.

$$|\psi_3\rangle = \frac{1}{2}(|1\rangle - |2\rangle + |3\rangle - |4\rangle) \tag{2.113}$$

If we want to translate all these equations into words we have to say the following.

The electron moves from one atom to another in order to lower its energy, and by doing that it is making a delocalized covalent bond between the four cations of the titanium.

The electron can take three energies which are the bonding state energy (the lower energy and the favorite), the anti-bonding state energy (the higher energy), and the intermediate energy. Each of which has a specific wave function.

3.4 Effective mass

Now the motion of the electron between the 4 neighbors should be thought of as a plan wave. So a wave function as a plan wave is given by.

$$\phi_n = \frac{e^{-ikna'}}{2} \tag{2.114}$$

If we think about the equation (2.70) for a while we will figure out that one can write it as below.

$$H_{nm} = e_0 \delta_{nm} - ct(\delta_{n,m+1} + \delta_{n,m-1}) \tag{2.115}$$

The first term of the right hand side of this equation says that no matter which cation the electron is sitting, the electron has the energy e_0, and the second piece allows the electron to hop one step to the left or one step to right while the c is a constant has to do with the hopping and the lattice constant.

If we use this Hamiltonian and the wave function in the Schrödinger equation, we will get.

$$Ee^{-ikna'} = e_0 e^{-ikna'} - ct(e^{-ik(n+1)a'} + e^{-ik(n-1)a'}) \tag{2.116}$$

By getting rid of some of exponential factors we can write the equation (2.116) in a simple way.

$$E = e_0 - ct(e^{-ika'} + e^{ika'}) \tag{2.117}$$

Finally, we can write the equation of the energy in the following way.

$$E = e_0 - 2ct\cos(ka') \tag{2.118}$$

Now the time to find the constant; if

$$\cos(ka') = 1 \qquad (2.119)$$

So the energy is going to be the following.

$$E = e_0 - 2ct \qquad (2.120)$$

Comparing the equation (2.120) with the equation (2.96), the constant will be equal to $c = \dfrac{3}{2}$

So the equation (2.118) will be.

$$E = e_0 - 3t\cos(ka') \qquad (2.121)$$

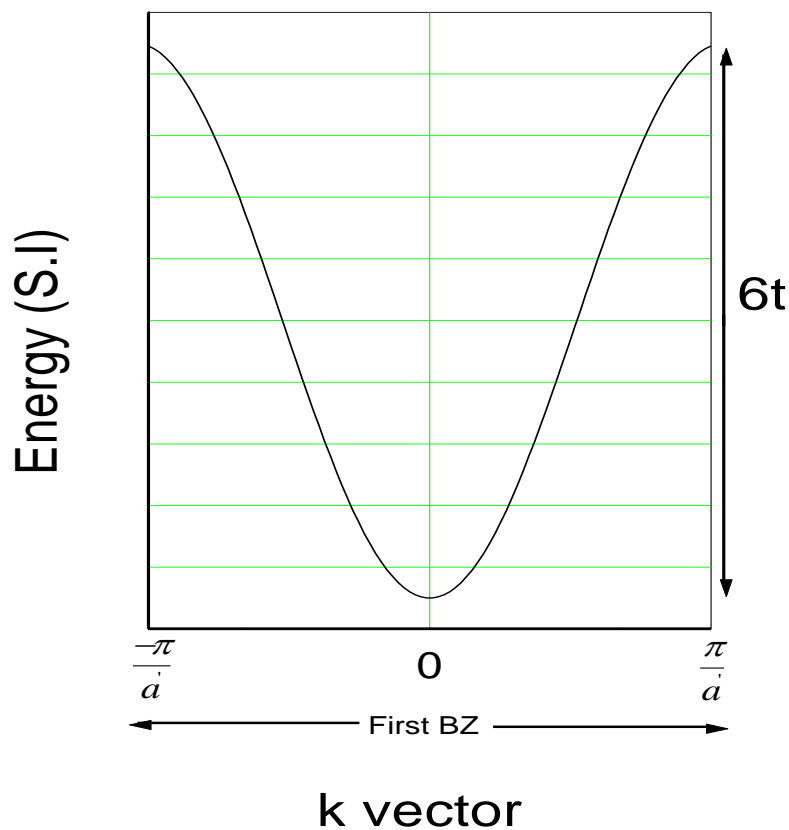The fig. 2.9 is representing the plot of $E = f(k)$.

Fig. 2.10 The energy vs wave vector plot of the electron.

By expending the energy (equation (2.121)) near the zero we will get the equation (2.122).

$$E \approx e_0 - 3t(1 - \frac{(ka')^2}{2})$$
(2.122)

We can simplify it to be as below.

$$E \approx e_0 - 3t - \frac{3}{2}ta'^2k^2$$
(2.123)

On one hand we have the energy of this electron and it looks quadratic in k with some constant and in the other hand we have the energy of the free electron which also quadratic in k as indicated in the equation below.

$$E = c + \frac{\hbar^2 k^2}{2m}$$
(2.124)

Comparing the two energies allows us to introduce the effective mass of our electron. And to realize the effective mass mathematically we have to compare the factors on each k.

$$\frac{\hbar^2}{2m^*} = a'^2 t$$
(2.125)

So the effective mass will as follow.

$$m^* = \frac{\hbar^2}{2a'^2 t}$$
(2.126)

The last equation indicates that the effective mass has nothing to do with the real physical mass of the electron, but it has to do with the hopping with greater hopping the mass gets smaller and for small hopping the mass gets bigger.

Now we can write the energy of the studied electron in terms of the effective mass.

$$E \approx e_0 - 2t - \frac{\hbar^2 k^2}{2m^*}$$
(2.127)

The plan wave motion of the electron is associated with the effective mass of the electron. Now in order to know the value of the effective mass, we have to know the value of the hopping first.

3.5 Conclusion

   The electron existing in the titanium cations would change the whole concept of the F^+ center if we plugged our bond model in it, which indicates that the electron we are talking about makes a delocalized covalent bond in the boundary of the F^+ center between four neighbors of titanium cations and moves between them like a plan wave with an effective mass. By thinking about the numbers of the F^+ centers in the crystal and each one gives a bond so that is what makes the Gibbs free energy smaller and makes the crystal more coherent so this interpretation may answer our previous questions whish say "why we need defects in the crystal to make it stable?!".

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General conclusion and perspectives

In this work, we saw that the perfect crystal does not exist in nature due to the environment and the mankind experiments. Scientists are always dealing with a real crystal, which is simply a perfect one plus defects.

The purpose of this research was to study theoretically the role and importance of defects on some semiconductors properties. This manuscript contains two main parts:

In the first part of this project, we distinguished the defects types that can be found in all materials, by their localization and their dimensions. Due to the large applications of transparent conductive oxides (TCO) such as titanium dioxide (TiO_2) which are singular materials that alloy two incompatible properties: an excellent optical transparency and a good electrical conductivity. Among a lot of TCO, TiO_2 is useful, nontoxic, and abundant in nature. Oxygen vacancies are very important dimensionless defects (zero-point defect) in TiO_2. They play a crucial role in the material by changing somehow its properties. On the other hand, oxygen vacancies are responsible for forming other defects which are the color centers (F^+).

After the calculations done in the first part of the second chapter, the energy of the trapped electron in the oxygen vacancy (F^+ center) has been changed due to the external electric field, while the second order correction of the energy in the perturbation theory allowed us to see the energy levels repulsion considered as a good result.

In its last part (second chapter), we focused on the electron existing and moving between the neighbors of Ti^{+4} cations surrounding the oxygen vacancy. After doing the math calculations, we clearly understood that the electron is moving from one cation to another, in a form of plan wave with an effective mass in order to lower its energy making a metallic bond which helps the material to get more stable.

The bond model is based on a lot of approximations. Allowing the electron to move randomly between the four cations may give us a better understanding of its wave function, its energy, and let us describe the F^+ more precisely.

We also mention that the trapped electron at the oxygen vacancy site similar to the box of potential can be also disturbed by applying a variable exterior electric field or by light that contains magnetic and electric ones. In this case the stimulation depends on time and to solve the Schrödinger equation; it is really important and mandatory to use the time dependent

perturbation theory. This work has already started but it needs more time to be achieved because of the complexity of the system.

One of the most important future perspectives, to develop this work, is to study the defects using DFT calculations where their roles on electric properties and structure can be investigated, to get knowledge, that helps understanding them more.

At the end, we clearly clarify that this project gave us an opportunity to understand well the meaning of particle in box exists in a real crystal. This research strongly indicates the importance of the theory of perturbation plus bond model. We hope this work will be improved because the defects are assumed to be one of the most important topics in the field of material sciences.