T.C.
TOKAT GAZİOSMANPAŞA UNIVERSITY
INSTITUTE OF GRADUATE STUDIES
DEPARTMENT OF PHYSICS
M.SC RESEARCH

ANALYTICAL INVESTIGATION OF FREE ENERGY AND ENTROPY OF SEMICONDUCTORS BY USING EINSTEIN-DEBYE APPROACH

Prepared by:
Majdi Mahdi HUSSEIN

Department of Physics
Master thesis

Advisor
Prof. Dr. Bahtiyar MEHMETOĞLU

TOKAT - 2023

SCIENTIFIC ETHICS PAGE

According to the thesis writing guide of Tokat Gaziosmanpaşa University Institute of Social Sciences, My Master's thesis named "**Analytical Investigation Of Free Energy And Entropy Of Semiconductors By Using Einstein-Debye Approach**" that I have prepared under the consultancy of "**Prof. Dr. Bahtiyar MEHMETOĞLU**" is based on scientific ethical values and rules. I hereby declare that it is an appropriate, original work, and I will accept any legal sanctions if it is determined otherwise.

Majdi Mahdi Hussein

JÜRİ KABUL VE ONAY

Majdi Mahdi HUSSEIN tarafından hazırlanan "**Analytical Investigation Of Free Energy And Entropy Of Semiconductors By Using Einstein-Debye Approach**" adlı tez çalışmasının savunma sınavı 28.09.2023 tarihinde yapılmış olup aşağıda verilen Jüri tarafından Oy Birliği ile Tokat Gaziosmanpaşa Üniversitesi Lisansüstü Eğitim Enstitüsü fizik anabilim Dalı'nda Yüksek Lisans Tezi olarak kabul edilmiştir.

Jüri Üyeleri (Unvanı, Adı Soyadı)	**İmzası**
Doç. Dr. Mustafa Numan BAKIRCI	……
Prof. Dr. Bahtiyar MEHMETOĞLU	……
Doç.Dr. Elif SOMUNCU	……

ONAY

Doç. Dr. Yusuf TEMÜR

Lisansüstü Eğitim Enstitüsü Müdürü

ÖZET

TÜRKİYE İLE IRAK ARASINDAKİ DIŞ TİCARETİN GELİŞİMİ VE MİLLİ GELİRE ETKİSİ

Majdi Mahdi Hussein

Prof. Dr. Bahtiyar MEHMETOĞLU

28 Eylül 2023, VII, 45 sayfa

Modern elektronik teknolojinin hızlı gelişimini belirleyen yarıiletkenlerin neredeyse tüm dikkate değer özelliklerinin incelenmesi günümüzün önemli çalışma alanı olduğu bilinmektedir. Küçük boyutları ve orta düzeyde güç tüketimi nedeniyle, yarıiletken transistörleri giderek daha büyük mikro devrelere ve daha sonra mikro işlemcilere bağlamak mümkün hale geldi. Bu nedenle, yarıiletkenlerin fiziksel, kimyasal ve diğer özelliklerinin incelenmesi günümüzün aktüel konularından biridir. Bilindiği gibi yerıiletkenlerin elektronik yapısına göre elektrik, termodinamik, manyetik özellikler gibi birçok özellikleri teorik ve deneysel yöntemlere göre incelene bilinir. Bu özelliklerin en önemlilerinden biride termodinamik açıdan kristal yapıda kaçınılmaz olarak kusur oluşum süreçleri ve ilgili elektronik süreçler, malzemenin fiziksel özellikleri üzerindeki istenmeyen etkisinin incelenmesi önemli bir rol oynar. Yarıiletkenleri termodinamik özeliklerini incelenmesi önemli teorik yaklaşımlar önerilmiştir. Bu yöntemlerden birside son dönemlerde önerilen amma çok uygulaması olmayan Einstein-Debye yaklaşımıdır. Yapılan incelemeler sonucunda Einstein-Debye yaklaşımına göre yarıiletkenlerin termodinamik özelliklerinin sıcaklığa göre değişmesinden alınan sonuçların daha hassas olduğu görülmüştür. Bu tezde, Einstein-Debye yaklaşımına göre entropi ve Gibbs enerjisini için analitik ifade oluşturularak, tüm sıcaklık aralığında $InP, InAs, GeS\ ve\ ZnO$ yarı iletkenlerinin entropi ve Gibbs enerjisinin hesaplama sonuçları farklı deneysel-teorik çalışmaların sonuçları ile karşılaştırmalı olarak incelenmiştir. Alınan sonuçlar sıcaklığın farklı değerlerine göre grafik ve tablo olarak verilmiş ve incelenmiştir.

Anahtar Kelimeler: Yarı iletkenler, Einstein-Debye yaklaşımı, mikro devreler, termodinamik ve manyetik özellikler.

ABSTRACT

THE DEVELOPMENT OF FOREIGN TRADE BETWEEN TURKIYE AND IRAQ AND ITS EFFECT ON NATIONAL INCOME

Majdi Mahdi HUSSEIN

Prof. Dr. Bahtiyar MEHMETOĞLU

28 September 2023, VII, 45 pages

It is known that the study of almost all remarkable properties of semiconductors, which determine the rapid development of modern electronic technology, is today's important field of study. Due to their small size and moderate power consumption, it has become possible to connect semiconductor transistors to increasingly larger microcircuits and later microprocessors. Therefore, the study of physical, chemical and other properties of semiconductors is one of today's hot topics. As it is known, many properties of semiconductors such as electrical, thermodynamic and magnetic properties according to their electronic structure can be studied by theoretical and experimental methods. One of the most important of these properties is the inevitable defect formation processes in the crystal structure from the thermodynamic point of view and the related electronic processes play an important role in the study of the undesirable effect on the physical properties of the material. Important theoretical approaches have been proposed to study the thermodynamic properties of semiconductors. One of these methods is the Einstein-Debye approach, which has been proposed recently but has not been widely applied. As a result of the investigations, it has been observed that the results obtained from the temperature dependence of the thermodynamic properties of semiconductors are more sensitive than the Einstein-Debye approach. In this thesis, an analytical expression for the entropy and Gibbs energy according to the Einstein-Debye approach is established and the results of the calculation of the entropy and Gibbs energy of InP, InAs, GeS and ZnO semiconductors over the entire temperature range are compared with the results of different experimental-theoretical studies. The results are presented and analyzed graphically and tabularly for different values of temperature.

Key Words: Semiconductors, Einstein-Debye approach, microcircuits, thermodynamic and magnetic properties.

ACKNOWLEDGEMENTS

We praise and thank God who gave us the gift of knowledge and reason and gave us the determination and will to complete this work.

I would like to thank my supervisor Prof. Dr. Bahtiyar MEHMETOĞLU for guiding me and providing me with the tools that I needed to successfully complete my thesis.

I'm indebted to my family, especially my father and mother, who unconditionally loved, trusted, supported and believed in me and in my choices.

DEDICATED TO

Praise be to God, the Great, the Generous, He opens to whomever He wills of His servants with the truth, and He is the All-Knowing Fattah.

I dedicate this humble deed to those who are my pride and my treasure, to those who have supported me throughout life, and those to whom pleasing God is linked, to the candle of my way and the balm of my life, Father. Mother.

To my sisters, brothers.

To the people dearest to my heart, my faithful father and mother.

LIST OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

By the conclusion of the nineteenth century, the principles of electromagnetism, as originally postulated by Newton and later refined by Maxwell, had gained widespread recognition and were universally acknowledged within the scientific community as the fundamental tenets of physics (Tipler and Llewellyn, 2012; Young et al., 2013; Jammer, 1997; Melissinos and Napolitano, 2003; Hutten and Hutten, 1956). Furthermore, it became apparent through practical applications that there existed certain constraints on the applicability of these principles, which underpin classical mechanics. Consequently, to explore the intricacies of atomic structure and its underlying submicroscopic components, it became imperative to explore novel advancements and conceptualizations, ultimately giving rise to the field of quantum mechanics. During that period, numerous experimental observations found their elucidation through innovative concepts, yielding remarkable achievements. These concepts laid the foundation for the emergence of quantum mechanics as the discipline dedicated to the study of microscopic systems. Quantum mechanics is concerned with the examination of the movement and interplay of substance at the atomic level and the fundamental particles that comprise it. Experimental evidence demonstrated that under specific conditions, light exhibits characteristics akin to both particles and waves. Within the framework of quantum mechanics, it is established that light, alongside all forms of electromagnetic radiation, assumes the role of particles denoted as photons, with predictive capabilities encompassing their energy, color, and spectral properties. A solitary photon represents a discrete unit within the electromagnetic field, constituting the smallest observable entity, given that no instance of a fraction of a photon has ever been observed (Walecka, 2008; Thornton and Rex, 2012; Galindo and Pascual, 2012; Ludwig, 2012; Cohen-Tannoudji et al., 1986; Kramers, 2018).

In light of the aforementioned information, it presents a challenge to embrace the seemingly conflicting notions that radiation exhibits a dual nature—simultaneously behaving as a propagating wave through space and as a localized particle at a specific point in space. However, this dualistic nature is an indispensable aspect of our understanding because radiation exhibits wave-like and particle-like characteristics under varying circumstances, as elucidated in the subsequent discussion:

1) Various forms of radiation, encompassing visible light, infrared, ultraviolet, X-rays, and analogous entities, exhibit wave-like behaviors during experimental observations, which are discernible through their tendencies for interference and diffraction phenomena. This arises from the necessity for concurrent coexistence of two waves in an identical spatial location at a given moment. Evidently, it appears implausible for two particles to occupy precisely the same spatial position concurrently. Consequently, we deduce that radiation exhibits wave-like characteristics.
2) Planck's quantum theory achieved considerable success in elucidating phenomena such as blackbody radiation, the photoelectric effect, the Compton Effect, and the Bohr atomic model. It notably clarified that radiant energy, in its interactions with matter, conforms to particle-like behavior, with radiation engaging with matter in the form of discrete photon particles. Consequently, we infer that radiations exhibit particle-like attributes (Tipler and Llewellyn, 2012; Young et al., 2013; Jammer, 1997; Melissinos and Napolitano, 2003; Hutten and Hutten, 1956; Serway et al., 2004).

These advancements collectively gave rise to the advent of quantum mechanics, a field that provided the means to elucidate the physical characteristics of microscopic systems. Quantum mechanics offered a fresh perspective from which to comprehensively account for the physical attributes of substances in diverse states of matter, encompassing those that had hitherto eluded explication within the framework of classical physics. One of the challenges encountered pertained to the unexplained variation in the resistivity of semiconductors in response to temperature fluctuations. As commonly recognized, solids are categorized into three distinct groups based on their electrical conductivity characteristics: conductors, semiconductors, and dielectrics. The electrical conductivity of materials within the semiconductor category demonstrates variability within the specified range.

On the basis of the relative values of electrical conductivity (σ) or resistivity ($\rho = 1/\sigma$), solids are generally classified as follows:

(i) Metals (Conductors): They have very low resistance (or high conductivity).

$\rho \sim 10^{-2} - 10^{-8}\ \Omega$ m

$\sigma \sim 10^{2} - 10^{8}$ S m–1

(ii) Semiconductors: They have some resistivity or conductivity to metals and insulators.

$\rho \sim 10^{-5} – 10^{6}\ \Omega m$

$\sigma \sim 10^{5} – 10^{-6}\ S\ m–1$

(iii) Insulators: They have high resistance (or low conductivity).

$\rho \sim 10^{11} – 10^{19}\ \Omega m$

$\sigma \sim 10^{-11} – 10^{-19}\ S\ m–1$

The values of ρ and σ given above are ranges of variation and can be exceeded. The relative values of resistivity are not the only reason to distinguish between metals, insulators and semiconductors. Semiconductors are also divided into the following groups:

(i) Simple semiconductors: Si and Ge

(ii) Compound semiconductors: For example:

- Inorganic: CdS, GaAs, CdSe, InP, and others.
- Organic: doped phthalocyanines, anthracene, and others.
- Organic polymers: polypyrrole, polyaniline, polythiophene, and others.

The predominant semiconductor devices within contemporary electronic technology predominantly rely on fundamental semiconductors like Silicon (Si) or Germanium (Ge), alongside compound inorganic semiconductors. Nevertheless, post-1990, a noteworthy evolution emerged with the introduction of semiconductor devices incorporating organic semiconductors and semiconducting polymers, signifying a pivotal milestone in the advent of molecular electronics technology. The overarching principles presented herein for the investigation of elementary semiconductors are likewise applicable to a broad spectrum of compound semiconductors in a general context (Kittel et al., 1996; Burns, 2016; Kittel and McEuen,2018; Ehrenreich and Spaepen, 2001; Castro et al., 2006; Ibach and Lüth, 2009; Zak, 1967; Elliott and Franz, 2015; Haug, 2016; Peverati and Truhlar, 2012; Hoffmann, 1987).

Semiconductors were initially identified by Michael Faraday in 1833, yet it was only when scientists recognized their significance with the advent of the first metal-semiconductor junction device that their true importance became evident (Neamen, 2003; Balkanski et al., 2000; Grahn, 1999). Certain attributes of these latter devices remained unexplained until several decades later, and numerous concepts regarding

authentic transistors and field-effect devices were swiftly called into question subsequent to the actual unveiling of the first transistor at Bell Laboratories. Until recently, an in-depth exploration of semiconductor transport and the functioning of devices fashioned from them was attainable through the utilization of straightforward models of quasi-one-dimensional electronic devices, reliant on various characteristics such as diversity and diffusion coefficients within the materials. Current research endeavors are dedicated to precisely delineating the circumstances under which these elementary models prove insufficient and determining the necessary adaptations required to refine them.

Conventional elementary semiconductors include germanium and silicon, and an examination of the periodic table of elements reveals that these substances fall within the fourth group. This is in contrast to typical metals like alkalis found in the first group and typical nonmetals such as halogens and noble gases that tend to crystallize at lower temperatures and are located in the seventh and eighth groups. Additional semiconductors belonging to the fourth group comprise diamond, a carbon derivative, whereas gray tin (a-Sn), which retains stability solely at reduced temperatures, falls within the category of semimetals. All semiconductors within the fourth group adopt the diamond structure for their crystalline arrangement, wherein adjacent atoms are organized in tetrahedral symmetry. Notably, boron, the least massive element in the third group, and the heavier elements selenium and tellurium in the sixth group, also exhibit semiconducting properties. An exemplar of a semiconductor can be found in bismuth, which stands as the most massive member of the fifth group on the periodic table. Additionally, the lighter constituents of this group, namely arsenic and antimony, fall within the semiconductor category, although their exploration has been comparatively less extensive at present (Grahn, 1999; Liu et al., 2015; Blancon et al., 2020; Schmidt and Molenkamp, 2002; Peter and Cardona, 2010; Anile et al., 2003; Guillot, 1990).

Semiconductors have the following properties:

a) Within a pristine semiconductor, its conductivity exhibits exponential augmentation in response to rising temperatures, a phenomenon known as thermistor action. This behavior necessitates a lower impurity concentration to manifest at lower temperatures.

b) In an impure semiconductor, the degree of conductivity is markedly contingent on the concentration of impurities. As an illustration, consider nickel oxide (NiO), which inherently serves as an insulator in its pristine state. Introducing 1% lithium oxide (Li2O) through deliberate impurity addition elevates its conductivity by a staggering factor of 10^13. Nevertheless, in heavily doped materials, the conductivity remains relatively constant with temperature variations, akin to the behavior observed in metals.

c) Conductivity is subject to modification, typically experiencing enhancement, through processes such as exposure to light irradiation, high-energy electron irradiation, or the introduction of carriers via an appropriate metallic contact.

d) Depending on the specific doping type, the charge transfer can involve either electrons or entities known as positive holes. Positive holes exhibit an electrical behavior akin to that of positrons; however, apart from this similarity, no other parallels exist. It is feasible to manipulate a single crystal in a non-uniform manner, resulting in areas with charge-carrying negative electrons coexisting with regions containing positive holes. Semiconductor diodes and transistors exemplify instances of such single crystals designed in this manner (Li, 1995; McKinley et al., 1994; Mishra and Singh, 2008; Seeger, 1999).

The semiconducting characteristics of materials extend beyond the realm of solids. Presently, there is acknowledgment of the creation of liquid semiconductors that find diverse applications. However, the rapid atomic diffusion within these liquids results in the mingling of regions featuring distinct doping levels, rendering the establishment of stable devices with non-uniform structures unattainable. Lately, focus has been directed towards glassy and non-crystalline semiconductors, which hold the potential for practical utilization in solar cell technology. It is worth reiterating that semiconductors transition into a metallic state when subjected to heavy doping. Superconductivity, a phenomenon traditionally associated with certain metals, inorganic and organic compounds at low temperatures, has been detected in specific heavily doped semiconductors as well. These semiconductors exhibit transition temperatures that fall below 150 K. In addition to coal and diamond, select aromatic hydrocarbons and even fullerenes, which constitute a distinct carbon modification, display semiconductor properties (Seeger, 1999; Aspnes, 1988; Huang et al., 2020; Kapon,

1999; Wang et al., 2018; Shi et al., 2020; Stradling, 1991; Ravindra et al., 1998; Li et al., 2018; Marko and Sweeney, 2015; Tamargo, 2002; Demkov et al., 2001; Mil'vidskij, 1986; Hu et al., 2010; Calow et al., 1967). Karlheinz Seeger, Semiconductor Physics).

As evident from the aforementioned progressions, semiconductors serve as the cornerstone of contemporary technology. The physical characteristics of all semiconductors, and thus their practical applications, hinge upon the fluctuations in their thermodynamic parameters. Consequently, it is imperative to conduct an exhaustive investigation into the thermodynamic attributes of semiconductors. It is a recognized fact that the atomic heat capacity of solids at constant pressure, a pivotal property, was elucidated through the Dulong-Petit law. Empirical investigations have demonstrated that beyond a specific temperature threshold, there is a non-constant variation in the quantity of heat. In 1907, Einstein employed the fundamental tenets of quantum mechanics to explicate the origin of this phenomenon in the thermal characteristics of solids. However, Einstein's approach, which did not consider the intricate particle motions, proved to be incongruent with experimental outcomes, particularly at low temperatures. In 1912, Debye resolved this quandary by formulating an equation for the comprehensive energy and heat content of solids. His model was rooted in Einstein's framework but incorporated more comprehensive and generalized assumptions (Grosso and Parravicini, 2013; Kittel et al., 1996; Jones and March, 1985; Mandl, 1991; Huang, 2009; Olla, 2015). (Askerov and Cankurtaran, 1994; Askerov and Figarova, 2009; Cankurtaran and Askerov, 1996) have recently introduced an extended framework, which amalgamates the Einstein and Debye approaches, thereby providing a more comprehensive means to investigate the thermodynamic characteristics of solids. The outcomes derived from the application of the Einstein-Debye methodology demonstrate a favorable concurrence with experimental findings. Given that the Einstein-Debye approximation represents a recent advancement, there is presently a concentrated effort towards extensive investigations concerning the computation of thermodynamic attributes of solids employing this approach.

This thesis aims to explore the thermodynamic characteristics, specifically energy and entropy, of select semiconductors across various temperature ranges. This investigation will be conducted utilizing the Einstein-Debye approach's equations for total energy and entropy. The research will concentrate on assessing the fluctuations in

free energy and entropy concerning temperature for semiconductors such as InP, InAs, GeS, and ZnO. The anticipated outcomes are expected to offer valuable insights into the technological utilities of these semiconductors, particularly InP, InAs, GeS, and ZnO.

The exploration of the distinctive attributes inherent in contemporary semiconductors remains an ongoing endeavor. We believe that a comprehensive examination, encompassing both theoretical analysis and experimental investigations conducted under diverse conditions, holds the potential to shed light on numerous intricate challenges that persist today. It's worth noting that the 21st century has been forecasted as the era of information technology. The advent of the semiconductor transistor, born in the mid-20th century, precipitated profound transformations in science, technology, and societal structures, ushering in the epoch of the information revolution. Presently, it enables the expansion of capabilities in micro and nano-electronic communication, serving as the foundation for diverse computing systems. Moreover, it finds applications in mechanical engineering, space technology, medicine, education, and numerous other domains.

2. RESOURCE SUMMARIES

2.1. Thermodynamic Potentials

Every thermodynamic system naturally gravitates toward a condition of minimum energy, often referred to as phase equilibrium. Crucial prerequisites for achieving thermodynamic equilibrium include the constancy of system parameters such as density, pressure, temperature, among others, over time (commonly known as a steady state), as well as the absence of heat transfer within the system. The thermodynamic equilibrium state of the system is distinguished by the presence of distinct thermodynamic potentials. Let us examine the thermodynamic potentials for the cases when the number of particles in the system does not change ($N = const$) and when it changes ($N \neq const$) (Grosso and Parravicini, 2013; Kittel et al., 1996; Jones and March, 1985). Let us first look at the case where the number of particles does not change ($N = const$):

Internal Energy: Directly from the first and second laws of thermodynamics, we get the following basic thermodynamic equation:

$$dU = TdS - PdV \tag{2.1.1}$$

Here U is internal energy, T is temperature and V is volume. Only one equation U = U(S,V) can be given instead of the thermal and caloric equations, but then all thermodynamic parameters can be determined:

$$T = \left(\frac{\partial U}{\partial S}\right)_V, P = -\left(\frac{\partial U}{\partial V}\right)_S \quad (2.1.2)$$

Here S is entropy and P is pressure. The second derivatives of the internal energy will make it possible to obtain experimentally measured parameters of thermodynamic processes:

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_v = \left(\frac{\partial T}{\partial S}\right)_v = T\frac{1}{Cv} \Rightarrow \quad (2.1.3)$$

$$Cv = \frac{T}{\left(\frac{\partial^2 U}{\partial S^2}\right)_v} = \frac{\left(\frac{\partial T}{\partial S}\right)_v}{\left(\frac{\partial^2 U}{\partial S^2}\right)_v} \quad (2.1.4)$$

Free Energy: Note that the value of entropy S chosen as a parameter is not measurable in practice, because there is no "entropy meter" device. This problem can be solved if we switch to another thermodynamic potential by subtracting the total differential d(TS) from both parts of equation (2.1.1):

$$-\ dU = TdS - pdV \quad (2.1.5)$$

$$\frac{d(TS)=TdS+SdT}{d(U-TS)=-sdT-PdV} \quad (2.1.6)$$

Here F=U-TS is the thermodynamic function F(T,V) and is called free energy. We can write the derivative expressions of entropy and pressure with respect to free energy as follows:

$$S = -\left(\frac{\partial F}{\partial T}\right)_v\ ,\ P = -\left(\frac{\partial F}{\partial V}\right)_T \quad (2.1.7)$$

Moreover, the second derivatives allow us to determine the thermodynamic parameters of the system according to the free energy of the second derivative:

$$\left(\frac{\partial^2 F}{\partial T^2}\right)_V = -\left(\frac{\partial S}{\partial T}\right)_V = -C_V\frac{1}{T} \Rightarrow \quad (2.1.8)$$

$$C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V; \quad (2.1.9)$$

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_T = -\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{V_{ET}} \Rightarrow \quad (2.1.10)$$

$$ET = -\frac{1}{V\left(\frac{\partial^2 F}{\partial V^2}\right)_T}\ , \tag{2.1.11}$$

Gibbs potential: If temperature T and pressure P are chosen as independent variables, the differential of the new characteristic function thus introduced can be obtained by adding the total differential d(PV) to both sides of equation:

$$dF = -SdT - PdV$$

$$\frac{d(PV) = PdV + VdP}{d(F + PV) = -SdT + VdP} \tag{2.1.12}$$

Here the expression G=F+PV=U-TS+PV is the new thermodynamic function G(T,P) and is called Gibbs function. We can write the derivative expressions of the Gibbs function with respect to temperature and pressure as follows:

$$S = -\left(\frac{\partial G}{\partial T}\right)_P\ , \qquad V = \left(\frac{\partial G}{\partial P}\right)_T \tag{2.1.13}$$

Moreover, the second derivatives allow us to determine the thermodynamic parameters of the system according to the Gibbs function in the second derivative:

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial G}{\partial T}\right)_P = -C_P\frac{1}{T} \Rightarrow \tag{2.1.14}$$

$$C_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P \quad ; \tag{2.1.15}$$

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = \left(\frac{\partial V}{\partial P}\right)_T = V_{\varepsilon T} \Rightarrow \tag{2.1.16}$$

$$\varepsilon_T = \frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T\ , \tag{2.1.17}$$

Enthalpy Let us consider the case where entropy depends on the variation of S and pressure P. Such a potential can be obtained by adding the total differential d(PV) to both sides of equation (2.1.1):

$$dU = TdS - PdV \tag{2.1.18}$$

$$\frac{d(PV) = PdV + VdP}{d(U + PV) = TdS + VdP} \tag{2.1.19}$$

Here the expression H=U+PV is the new thermodynamic function H(S,P) and is called enthalpy. We can write the derivative expressions of enthalpy with respect to entropy and pressure as follows:

$$T = (\frac{\partial H}{\partial S})_P \quad , \quad V = (\frac{\partial H}{\partial P})_S \tag{2.1.20}$$

In addition, the second derivatives allow us to determine the thermodynamic parameters of the system according to the enthalpy of the second derivative:

$$\left(\frac{\partial^2 H}{\partial S^2}\right)_P = \left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P} \Rightarrow \tag{2.1.21}$$

$$C_P = \frac{T}{\left(\frac{\partial^2 H}{\partial S^2}\right)_P} = \frac{\left(\frac{\partial H}{\partial S}\right)_P}{\left(\frac{\partial^2 H}{\partial S^2}\right)_P} \tag{2.1.22}$$

$$\left(\frac{\partial^2 H}{\partial P^2}\right)_S = \left(\frac{\partial V}{\partial P}\right)_S = V_{\varepsilon S} \Rightarrow \tag{2.1.23}$$

$$\varepsilon S = \frac{\left(\frac{\partial^2 H}{\partial P^2}\right)_S}{V} = \frac{\left(\frac{\partial^2 H}{\partial P^2}\right)_S}{\left(\frac{\partial H}{\partial P}\right)_S} \quad , \tag{2.1.23}$$

2.2. States with varying particle number

In a system where the number of particles undergoes variations, alterations in the system's internal energy occur not only as a consequence of heat transfer and the work executed by the system but also due to fluctuations in the number of particles within the system (denoted as dN). Hence, by applying the previously introduced parameter representing the energy contributed to the system by an individual particle, referred to as the chemical potential (μ), we derive the ensuing equations:

$$dU = +TdS - PdV + \mu dN \; ; \tag{2.2.1}$$

$$dF = -SdT - PdV + \mu dN \; ; \tag{2.2.2}$$

$$dG = -SdT + VdP + \mu dN \; ; \tag{2.2.3}$$

$$dH = +TdS + VdP + \mu dN \; ; \tag{2.2.4}$$

In the examination of systems characterized by a fluctuating number of particles, a commonly employed thermodynamic potential comes into play. By taking the

derivative of this potential with respect to its corresponding characteristic variables, it becomes feasible to determine the quantity of particles for each type, denoted as Ni, present within the system. To derive this potential and its differential expression, the Legendre transform is applied to transform the system's variables into new differentials, namely T, V, and μi, akin to the procedures outlined in previous sections:

$$d\Omega = -\mathrm{SdT} - \mathrm{PdV} - \sum_i N_i \ d\mu_i \tag{2.2.5}$$

here

$$\Omega(T, V, \mu_i) = U - TS - \sum_i N_i \mu_i = F - G = -PV \tag{2.2.6}$$

The function is called the large thermodynamic potential. From formula (2.2.5)

$$N_i = \left(\frac{\partial \Omega}{\partial \mu_i}\right)_{T,V} \ , S = -\left(\frac{\partial \Omega}{\partial T}\right)_{\mu_i,V} \ , P = -\ \left(\frac{\partial \Omega}{\partial V}\right)_{\mu_i,T} \tag{2.2.7}$$

2.3. Classical Theory of Thermodynamic Properties of Solids

It is known that at large values of temperature T ≥θ D the vibrational motion of a crystal lattice can be described according to the laws of classical physics. In this chapter, we will consider the classical theory of thermodynamic properties of solids with a simple crystal lattice at T ≥θ D values of temperature. In this chapter we will establish all expressions for thermodynamic functions and quantities according to classical physics at high temperatures.

2.3.1. Free energy, entropy, total energy, thermal equation of state, isothermic and isohoric heat quantities

Let us first establish the free energy formula by considering the Gibbs method (Huang, 2009; Olla, 2015; Askerov and Cankurtaran, 1994):

$$F = -K_o T \ln Z_{cl} \tag{2.3.1}$$

Where Z_{cl} is the static integral and is expressed as follows:

$$Z_{cl} = \frac{1}{(2\pi\hbar)^{3N}} \int e^{-E(X_{qj}, P_{qj})/K_o T} \left(dX_{qj}, dP_{qj}\right), \tag{2.3.2}$$

If we integrate (2.3.2), we can get the following result for the static integral Z_{cl}:

$$Z_{cl} = \prod_q \left(\frac{K_o T}{\hbar W_q}\right)^3 \tag{2.3.3}$$

If we substitute (2.3.3) for (2.3.1), we obtain the free energy

$$F = -3K_oT\sum_q \ln\left(\frac{K_oT}{\hbar W_q}\right) \quad (2.3.4)$$

We get the expression. To calculate this integral, let us consider$W_q = V_o i$ and move to the spherical coordinate system. Integration over angles gives 4π and we get the following result:

$$F = \frac{3K_oTV}{2\pi^2}\int_0^{q_{max}} \ln\left(\frac{\hbar w_q}{K_oT}\right) q^2\, dq \quad (2.3.5)$$

Where q_{max} is the maximum possible value of the wave number of a crystal. Let's define a variable as follows:

$$x = \frac{\hbar\, w_q}{K_oT} = \frac{\hbar\, v_o\, q}{K_oT} \quad (2.3.6)$$

If we switch to the variable we defined in expression (2.3.5) for the free energy

$$F = \frac{3K_oTV}{2\pi^2}\left(\frac{k_oT}{\hbar v_o}\right)^3 \int_0^{x_{max}} x^2\, ln\, x\; dx \quad (2.3.7)$$

We will take his statement. Here we have

$$x_{max} = \frac{\hbar v_o}{k_oT} q_{max} = \frac{\hbar w_{max}}{k_oT}\ , \quad (2.3.8)$$

is the maximum possible frequency in the solid. If we perform the integral operation in expression (2.3.7)

$$F = \frac{k_oTV}{6\pi^2}\left(\frac{w_{max}}{v_o}\right)^3 \left[3\ln\left(\frac{\hbar w_{max}}{k_oT}\right) - 1\right] \quad (2.3.9)$$

We get the free energy result. According to the free energy expression we can also calculate the entropy.

For entropy

$$s = -(\partial F/\partial T)_v \quad (2.3.10)$$

If we substitute (2.3.9) in the formula (2.3.10) and perform the necessary operations

$$s = -3k_oN\ln(\theta/T) + 4k_oN \quad (2.3.11)$$

we get the following result. If we consider the expressions (2.3.9) and (2.3.11) in the formula

$$E = F + TS\ , \quad (2.3.12)$$

for total energy, we get the following result:

$$E = 3k_oTN\,;T \gg \theta\,, \tag{2.3.13}$$

From expression (2.3.13) it can be seen that for large values of the temperature the average total energy depends only on the temperature. Note that this result also follows from the theorem about the equal distribution of energy with respect to degrees of freedom, obtained on the basis of Boltzmann statistics.

In formula (2.3.13) the dependence of the free energy on the volume V is not clearly visible. Since it is known by the volume dependence of the Debye temperature θ(V) we write the equation of state of a solid using the formula $P = -(\partial F/\partial V)_T$ as follows:

$$P = -3k_oTN\frac{1}{\theta}\frac{d\theta}{dV} \tag{2.3.14}$$

If we substitute the formulas for total energy and entropy in the expressions $C_V = (\partial E/\partial T)$ and $C_V = T(\partial S/\partial T)$, we get the following result for isohoric heat capacity:

$$C_V = 3k_oN\,;T \gg \theta \tag{2.3.15}$$

It can be seen from (2.3.15) that at high temperatures T > θ the isochoric heat capacity is a constant quantity that does not depend on the nature of the crystal and temperature. This theoretical result corresponds to the experimental Dulong-Petit law. Thus, the results obtained from the classical theory of solids prove the correctness of the Dulong-Petit law determined by experiment. The difference between isobaric and isochoric heat capacities is as follows:

$$C_P = C_V = -T\left(\frac{\partial P}{\partial T}\right)^2_V\left(\frac{\partial P}{\partial V}\right)^{-1}_T \tag{2.3.16}$$

If we substitute the formula (2.3.14) in (2.3.16) $C_P - C_V$ for the difference

$$C_P - C_V = 3k_oN_{\gamma G}\,; \tag{2.3.17}$$

we get the formula Here $_\gamma$ is the Gruneisen parameter $_G$

$$\gamma G = -\frac{V}{\theta}\frac{d\theta}{dV}\,, \tag{2.3.18}$$

is calculated according to the formula.

2.4. Pure Semiconductors. n-type and p-type semiconductors

In a broader sense, the physical characteristics of semiconductors can be elucidated more effectively through the band structure framework. According to this perspective, when the Fermi energy level resides between two distinct bands, the higher one is designated as the conduction band, while the lower one is identified as the valence band. The band gap is the energy difference between the valence and conduction bands. In a metal (conductor) the Fermi energy level is within a band, so the valence and conduction bands overlap. In an insulator there is a large band gap. In a semiconductor, it is somewhere between an insulator and a conductor: they typically have a band gap with an energy of 1 eV. As can be seen from Table 1, metals have no band gap, semiconductors have a small band gap and insulators have a large band gap (Neamen, 2003; Balkanski et al., 2000; Grahn, 1999). (K/basic semiconductor.pdf

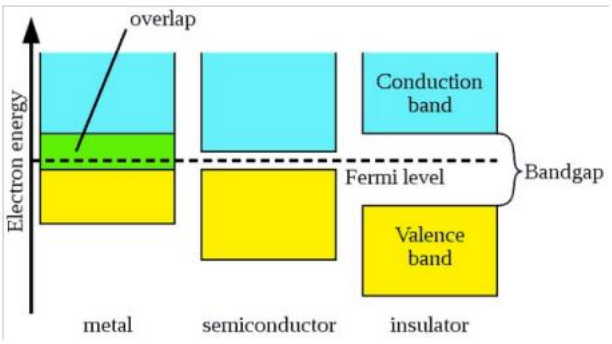

Figure 1: Band gaps of metals, semiconductors and insulators

For example, silicon is a semiconductor and copper is a conductor. The Bohr diagrams of the silicon atom and the copper atom are shown in Figure 2. Note that the nucleus of the silicon atom has a net charge of +4 (14 protons - 10 electrons), while the nucleus of the copper atom has a net charge of +1 (29 protons - 10 electrons). We know that the nucleus holds the electrons other than valence electrons under its influence.

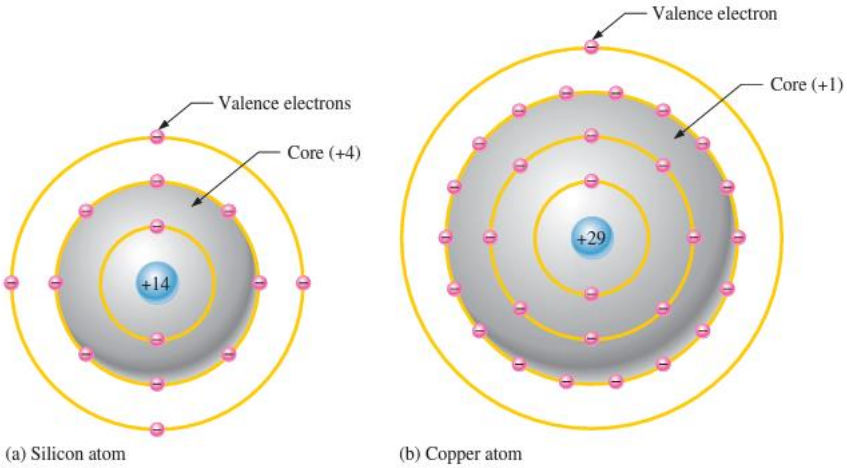

Figure 2: Atomic structures of silicon and copper atoms (Neamen, 2003).

Since the number of valence electrons in the copper atom is +4 and the silicon atom has a valence of +1, the force trying to hold the valence electron to the atom is greater in silicon than in copper. The valence electron of copper is at the fourth energy level, farther from the nucleus than the valence electron of silicon in the third shell. Recall that the electrons furthest from the nucleus have the most energy. The valence electron in copper has more energy than the valence electron in silicon. This means that the valence electrons in copper have less additional energy to break away from their atoms and become free electrons than in silicon. In fact, the large number of valence electrons in copper already have enough energy to become free electrons at normal room temperature. In a silicon semiconductor, covalent bonding occurs between atoms, which can be shown schematically in Figure 3.

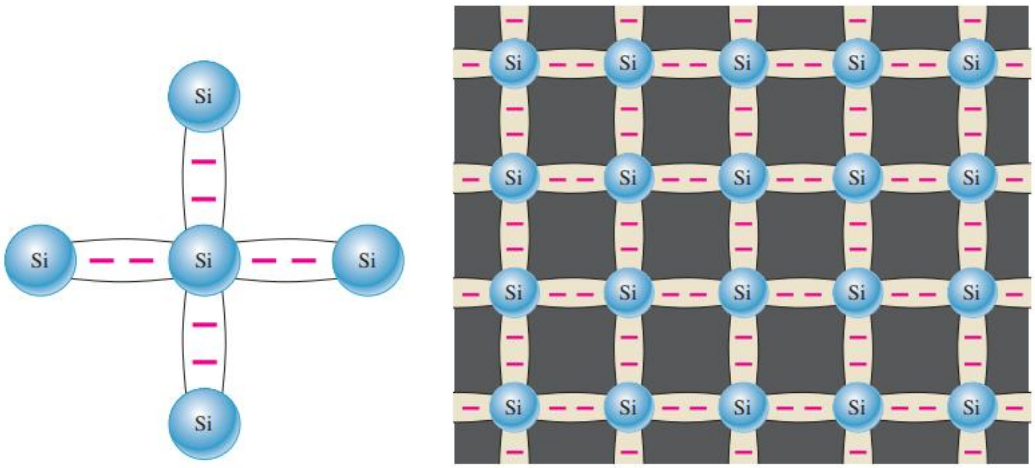

Figure 3: Structure of a silicon crystal (Balkanski et al., 2000).

A silicon (Si) atom with four valence electrons shares one electron with each of its four neighbors. In a pure silicon crystal at room temperature, this is sufficient for some valence electrons to jump from the valence band to the conduction band and become free electrons. Free electrons are also called conduction electrons. This is shown in the energy diagram in Figure 4(a) and the diagram in Figure 4(b).

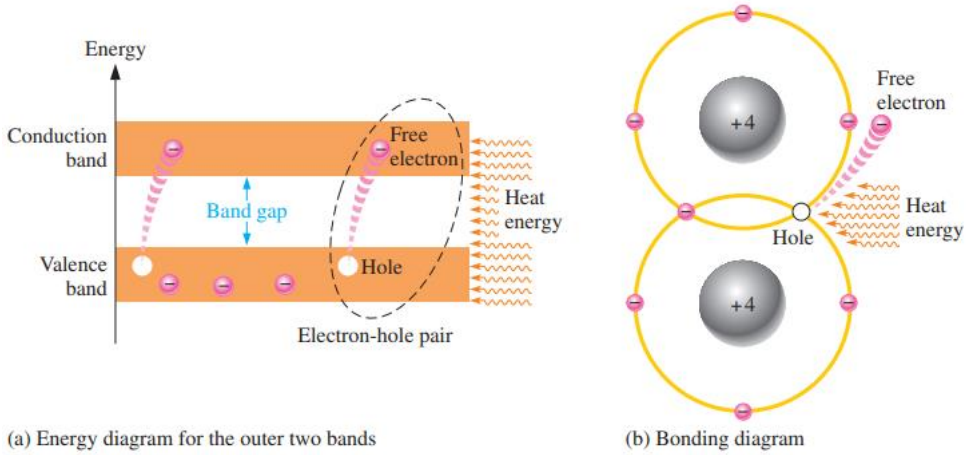

Figure 4: Formation of electron-hole pairs in a silicon crystal. Free electrons in the conduction band (Grahn, 1999).

Thus, two types of free charges, free electrons and holes, are created to provide electric current in semiconductors. We see that the hole as a whole moves in the direction of the field lines, i.e. in the direction in which positive charges should move. We emphasize once again that the directed motion of a hole along the field is due to the passage of valence electrons from atom to atom, which occurs predominantly in the direction opposite to the field. Therefore, there are two types of charge carriers in a silicon crystal: free electrons and holes.

When an external electric field is applied, an electric current arises caused by their sequential counter-movement: free electrons move in the direction opposite to the field strength vector and holes in the direction of the E vector.

Semiconductor materials do not conduct current well and have a limited value in their pure state. This is due to the limited number of free electrons in the conduction band and vacancies in the valence band. Pure silicon (or germanium) can be improved by increasing the number of free electrons or holes to increase its conductivity and make it useful in electronic devices. This is done by adding dopants to the pure material.

There are two types of doped (impure) semiconductor materials, n-type and p-type, which are the basic building blocks for most types of electronic devices.

To obtain a semiconductor with n-type electrical conductivity, a pure semiconductor is doped with a dopant that increases only the number of free electrons in the semiconductor. The added dopant increases the number of electrons and is therefore called a donor impurity. For germanium and silicon, which belong to group IV of the Periodic Table of Elements, the donor impurity is the elements of group V, which are atoms with five valence electrons (antimony, phosphorus, arsenic, etc.).

When such a dopant is added, the dopant atoms replace the atoms of the original semiconductor at individual nodes of the crystal lattice (Figure 5a,b). Four electrons of each atom of the donor dopant are involved in a covalent bond with neighboring atoms of the source material, and the fifth ("excess") electron, not involved in the covalent bond, is much more weakly bound to its atom. It takes much less energy to detach it from the atom and turn it into a free charge carrier than to release an electron from a covalent bond. As a result of obtaining such an energy (for example, the energy of a phonon at room temperature in the crystal), the "excess" electron leaves the atom and remains free, and the impure atom is transformed into a positive ion (ionization). Under conditions of a sufficiently high concentration of dopant atoms, their ionization creates a certain concentration in the semiconductor crystal of free electrons and immobile positive ions localized at the positions of impurity atoms. This type of semiconductor is called n-type semiconductor (Balkanski et al., 2000).

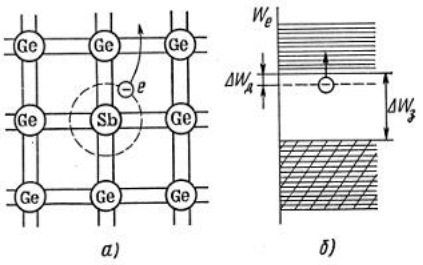

Figure 5: (a) the appearance of a hole in a p-type semiconductor crystal and (b) the energy diagram of this process (Grahn, 1999).

In p-type semiconductors, the addition of a dopant aims to increase the hole concentration. The problem is solved by using elements of Group III of the Periodic Table (indium, gallium, aluminum, boron) as impurities, elements whose atoms have three valence electrons. In the case of such a doping, each of their atoms forms only

three filled covalent bonds with neighboring atoms of the original semiconductor in the crystal lattice (Figure 6, a,b). The fourth covalent bond remains empty.

To fill this bond, the missing valence electron is taken from one of the neighboring atoms of the crystal lattice. The transfer of an electron leads to the formation of a hole in the covalent bond of the neighboring atom from the place where the electron leaves, and the impure atom is transformed into a stable negative ion. As a result, an increase in the concentration of holes in the semiconductor is achieved due to the doping. Dopant atoms that accept the valence electrons of neighboring atoms are called acceptor atoms, and the dopant itself is called acceptor atoms.

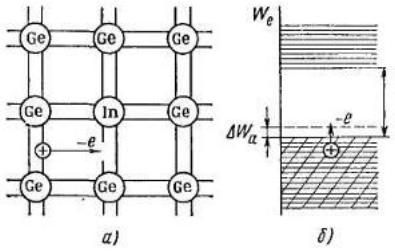

Figure 6: (a) view of a hole in a p-type semiconductor crystal and (b) energy diagram of this process (Grahn, 1999).

2.5. Concentration of electrons and dislocations in a semiconductor

Let us calculate the concentration of electrons in the conduction band of the semiconductor. The number of electrons in the dZ states of the energy band, dN, is determined by the following expression (Huang, 2009; Olla, 2015; Askerov and Cankurtaran, 1994):

$$dN = f(E)dZ \tag{2.5.1}$$

Considering that dZ = g(E) dE, we obtain the following:

$$dN = f(E)\, g(E)\, dE \tag{2.5.2}$$

The total number of electrons in the conduction band can be found by integrating the expression (2.5.2) across the band:

$$N(E) = \int_{E_c}^{E_\pi} f(E)\, g(E)\, dE \tag{2.5.3}$$

where En is the energy of the upper level of the conduction band. Since the Fermi-Dirac distribution function decreases very rapidly with increasing energy, the

upper limit of integration can be taken equal to infinity. If the degree of energy state retention of electrons in the conduction band is small (f(E)<< 1), which is almost always the case in semiconductors, then for the electron concentration in the conduction band.

$$n = \frac{N}{V} = \frac{(2m_n^*)^{\frac{3}{2}}}{2\pi^2\hbar^3}\ exp\left(\frac{E_F}{KT}\right)\int_{E_c}^{\infty}\frac{(E-E_C)^{\frac{1}{2}}\ dE}{exp\left(\frac{E}{KT}\right)} \quad (2.5.4)$$

We can transform this expression as follows:

$$n = \frac{1}{2\pi^2}\left(\frac{2m_n^*}{\hbar^2}\right)^{\frac{3}{2}}(KT)^{\frac{1}{2}}exp\left(\frac{E_F-E_C}{KT}\right)\int_{E_c}^{\infty}\frac{\left(\frac{E-E_C}{KT}\right)^{\frac{1}{2}}dE}{exp\left(\frac{E-E_C}{KT}\right)} \quad (2.5.5)$$

Let's move to the variable $x = \left(\frac{E-E_c}{KT}\right)$ in the integral:

$$n = \frac{1}{2\pi^2}\left(\frac{2m_n^*KT}{\hbar^2}\right)^{\frac{3}{2}}exp\left(\frac{E_F-E_C}{KT}\right)\int_0^{\infty}\frac{x^{\frac{1}{2}}\,dE}{exp(x)} \quad (2.5.6)$$

Since the result of the integral in this expression is $\frac{\sqrt{\pi}}{2}$, the result is

$$n = N_C exp\left(\frac{E_F-E_C}{KT}\right), \quad (2.5.7)$$

we'll take it. Here we have

$$N_C = 2\ \left(\frac{m_n^*KT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \quad (2.5.8)$$

The value of Nc in (2.5.8) is called the effective density of states in the conduction band. Similarly, the concentration of holes in the valence band can be calculated. Since an empty state in the valence band is the result of the transition of an electron from this state to the conduction band, the probability that the state with energy E in the valence band is not occupied is equal to $1 - f_{\Phi-}\ (E)$

In this case, the concentration of dechic

$$P = N_V exp\ \left(\frac{E_V-E_F}{KT}\right), \quad (2.5.9)$$

in the form Where N_v is the effective density of states in the valence band

$$N_V = 2\left(\frac{m_P^* KT}{2\pi\hbar^2}\right)^{\frac{3}{2}} \quad (2.5.10)$$

If we multiply (2.5.7) and (2.5.9) side by side, we get:

$$np = n_i^2 = N_c N_V \, exp\left(\frac{-E_g}{KT}\right) = 4\left(\frac{KT}{2\pi\hbar^2}\right)^3 \left(m_n^* m_p^*\right)^{\frac{3}{2}} exp\left(\frac{-E_g}{KT}\right), \quad (2.5.11)$$

where n_i is the concentration of intrinsic charge carriers in the semiconductor, Eg=Ec -Ev is the band gap. In constructing this formula, we used the assumption that the degree of occupancy of energy levels by charge carriers is less than one. Such a carrier gas is called non-degenerate. Gases consisting of particles in a gas with quantum mechanical and classical gas properties are generally called degenerate gases in physics. A degenerate gas obeys Fermi-Dirac or Bose-Einstein quantum mechanics statistics, a non-degenerate gas obeys Maxwell-Boltzmann statistics.

2.6. Fermi energy level in semiconductors

Since the distribution function of electrons over states in semiconductors has the same form as in metals, the Fermi energy in semiconductors has the same physical meaning: The Fermi energy is the maximum energy at the top level, below which, at zero absolute temperature, all energy levels are occupied [f(E) = 1] and above which all levels are empty [f(E) = 0]. For semiconductors, where at absolute zero the valence band is completely occupied and the conduction band is completely free, the distribution function has a discontinuity. As a result, the Fermi level in a semiconductor must necessarily be zero in the forbidden bandgap. For a pure semiconductor, the concentrations of electrons and vacancies are equal (n =pii), because each electron leaving the valence band creates a vacancy. In this case, if we equalize (2.5.7) and (2.5.9), we get,

$$\exp\left(\frac{2E_F}{KT}\right) = \left(\frac{m_P^*}{m_n^*}\right)^{\frac{3}{2}} \exp\left(\frac{2E_C - E_g}{KT}\right) \quad (2.6.1)$$

We get the following expression for Urada E_F:

$$E_F = E_C - \frac{1}{2}E_g + \frac{3}{4}\,KT \ln\frac{m_P^*}{m_n^*} \quad (2.6.2)$$

If the effective masses of electrons and holes are equal to[$m_n^* = m_p^*$, then $\ln\left(m_p^*/m_n^*\right) = 0$],the Fermi level of a pure semiconductor at any temperature is

located in the middle of the band gap. The temperature dependence of the position of the Fermi level in a pure semiconductor is determined by the third term in equation (2.6.2). If the effective mass of a gap in the valence band is greater than the effective mass of an electron in the conduction band, the Fermi level shifts towards the base of the conduction band with increasing temperature. In the opposite case, the Fermi level shifts towards the top of the valence band. For most semiconductors, the effective mass of a gap is not much larger than the effective mass of an electron and the shift of the Fermi level with temperature is negligible. However, indium antimonide (InSb) has a small band gap (e.g. Eg = 0.17 eV), so that at T > 450 K the Fermi level shifts in the conduction band. At this temperature, the semiconductor enters a degenerate state (Figure 7).

Figure 7: Position of the Fermi level in the intrinsic semiconductor

1- $m_p^* = m_n^*$; $2 - m_p^* > m_n^*$; $3 - m_p^* < m_n^*$

3. MATERIAL AND METHOD

3.1. Einstein Model for the amount of Self-Heat of Solids

According to the results obtained from classical physics, according to the Dulong-Petit law, the heat capacity of solids at the atomic level at constant pressure is equal to 3R for a large number of substances. According to the results obtained from experimental studies, it was seen that the amount of specific heat changes at values smaller than a certain value of the temperature. At small temperatures, the results of

Dulong-Petit's law are not in agreement with the experimental results. The solution to this problem using Planck's new quantum theory was given by Einstein (1907) in a fundamental paper applying it to the motion of particles constituting solid matter. Although the basic difficulties were generally solved according to Einstein's approach, one could not expect a result that was very consistent with the experiment, since the details of the motion of the particles were not taken into account. In particular, Einstein's self-heat formula did not give very satisfactory results at low temperatures. In Einstein's model, the atoms at the nodes of the crystal are viewed as harmonic oscillators and all oscillators are considered to have the same frequency. In this case we write the total energy of all oscillators as follows (Eınsteın, 1907; Debye, 1912):

$$U = \frac{1}{2}\sum_{i=1}^{3N} (m\dot{r_i}^2 + Kr_i^2) = \sum_{i=1}^{3N} h\nu n_i + 3N\frac{h\nu}{2} \tag{3.1.1}$$

But Einstein's model ignores the fact that atomic vibrations are interconnected: the potential energy of an atom in a crystal depends on the distance from its neighbors:

$$U = \frac{1}{2}\sum_{i=1}^{3N} m\dot{r_i}^2 + \frac{1}{2}\sum_{i=1}^{3N} K(r_i - r_j)^2 \tag{3.1.2}$$

In 1907, in the first application of quantum theory to a problem other than radiation, Einstein modeled a solid body containing N atoms as a collection of 3N harmonic oscillators. The work function of a single oscillator:

$$Z_1 = \sum_{n=0}^{\infty} \exp(-\beta\varepsilon_n) = \sum_{n=0}^{\infty} \exp\left[-\beta\left(n+\frac{1}{2}\right)h\nu\right] = \exp\left(-\frac{\beta h\nu}{2}\right)\sum_{n=0}^{\infty}\left[\exp(-\beta h\nu)\right]^n$$

$$= \frac{\exp\left(-\frac{\beta h\nu}{2}\right)}{1-\exp(-\beta h\nu)} = \frac{1}{2}\operatorname{cosech}\left(\frac{\beta h\nu}{2}\right)$$

$$Z_1 = \sum_{n=0}^{\infty} \exp(-\beta\varepsilon_n) = \sum_{n=0}^{\infty} \exp\left[-\beta\left(n+\frac{1}{2}\right)h\nu\right]$$

$$= \exp\left(-\frac{\beta h\nu}{2}\right)\sum_{n=0}^{\infty}[\exp(-\beta h\nu)]^n$$

$$= \frac{\exp(-\frac{\beta h\nu}{2})}{1-\exp(-\beta h\nu)} = \frac{1}{2}cosech\left(\frac{\beta h\nu}{2}\right) \tag{3.1.3}$$

can be written as. Since oscillators are independent of each other, therefore:

$$Z = Z_1^N \tag{3.1.4}$$

In this sense, total energy can be written as follows:

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z_1 = \frac{1}{2} hv \coth\left(\frac{\beta hv}{2}\right) = hv\left(\frac{1}{2} + \frac{1}{\exp(\beta hv) - 1}\right) \tag{3.1.5}$$

Internal energy is not a directly measurable quantity and instead we can calculate the heat capacity:

$$C_V(T) = \frac{dU}{dT} = -K_B \beta^2 \frac{\partial U}{\partial \beta} = [U = 3N\langle E \rangle] = 3NK_B (\beta hv)^2 \frac{\exp(\beta hv)}{[\exp(\beta hv) - 1]^2} \tag{3.1.6}$$

(3.1.6) is the formula for self-heat according to the Einstein approach. The result obtained gives the Dulong-Petit law $T(K_B T \gg hv)$ in the special case$C_V(T) = 3NK_B$ at high temperatures. At low temperatures, in the case of$T(K_B T \gg hv)$, the specific heat is.

$$C_V(T) = 3NK_B\ (\beta hv)^2 \exp(-\beta hv) \tag{3.1.7}$$

3.2. Debye Model for Solids Self-Heat

In Debye's model (1912), the atomic structure is ignored, considering the solid as a continuum medium. The continuum at the nodes has arbitrary low-frequency modes of vibration, and only these low-frequency modes are excited at a sufficiently low temperature T. These low-frequency normal modes are simply standing sound waves. These low-energy modes remain active at low temperatures while the high-frequency modes are already frozen.

The large λ values corresponding to these modes justify the use of a continuum model. These low-energy modes remain active at low temperatures while the high-frequency modes are already considered dormant. The large λ values corresponding to these modes justify the use of a continuum model. If we look at each normal mode as a harmonic oscillator, the total energy per unit volume can be written as follows (Debye, 1912; Landsberg, 1971; Ziman, 1965):

$$\langle E \rangle = hv\left[\frac{1}{2} + \frac{1}{\exp(\beta hv) - 1}\right] \tag{3.2.1}$$

$$U = \int_0^{V_D} g(V)\,\langle E(T,V)\rangle dV = U_o + \int_0^{V_D} \frac{hv\,g(v)}{\exp(\beta hv)-1}\,dV \tag{3.2.2}$$

Using the general expression$C = \frac{dU}{dT}$ for the amount of heat in terms of energy and considering (3.2.2), we obtain the following result:

$$C_V = 3k_0 N_A L(T,\theta) \tag{3.2.3}$$

$$L(T,\theta) = (n+1)D_n\left(1,\frac{\theta_D}{T}\right) - n\left(\frac{\theta_D}{T}\right)\frac{1}{e^{\theta_D/T}-1} \tag{3.2.4}$$

here θ_D It is the Debye temperature and varies between n=3-5 for solids. In Equation (3.2.3) $D\left(\frac{\theta_D}{T}\right)$ It is a Debye function and is generally defined as follows (Landsberg, 1971; Ziman, 1965):

$$D_n(\beta,\mathrm{x}) = \frac{n}{x^n}\int_0^x \frac{t^n}{(e^t-1)^\beta}\,dt. \tag{3.2.5}$$

There are multiple studies on the Debye function in the literature. In a recent study (Guseinov and Mamedov, 2007), a more accurate formula for the n-dimensional Debye function has been established:

$$D_n(\beta,x) = \frac{n}{x^n}\lim_{N\to\infty}\sum_{i=0}^{N}(-1)^i F_i(-\beta)\frac{\gamma(n+1,(i+\beta)x)}{(i+\beta)^{n+1}} \tag{3.2.6}$$

here $F_i(-\beta)$ binomial coefficients [6]

$$F_m(n) = \begin{cases} \frac{n(n-1)\ldots(n-m+1)}{m!}\ \text{forinteger}n \\ \frac{(-1)^m\Gamma(m-n)}{m!\Gamma(-n)}\ \text{fornonintegern} \end{cases} \tag{3.2.7}$$

and $\gamma(n+1,(i+\beta)x)$ is the incomplete gamma function

$$\gamma(\alpha,y) = \int_0^y t^{\alpha-1}e^{-t}dt. \tag{3.2.8}$$

As can be seen from Figure 8, the results obtained from Einstein and Debye approaches are in agreement with the experimental results at high temperatures. Thus, the reason for the temperature dependence of the core heat of solids is explained theoretically. Using this approach, the temperature dependence of the core temperature of a large number of suitable solids in the literature has been investigated and has made a great contribution to its application in technology (Gradsteyn and Ryzhik, 1980; Neumann, 2004; Grimvall, 1986; Pyda et al., 1988; Gaur et al., 1978; Lu et al., 2005;

Magomedov, 2002; Avsec and Marcic, 2002; Eymet et al., 2002; Windsor, C.G. and Sinclair, 1976; Abu-Eishah, 2001; Pathak and Pandya, 1975).

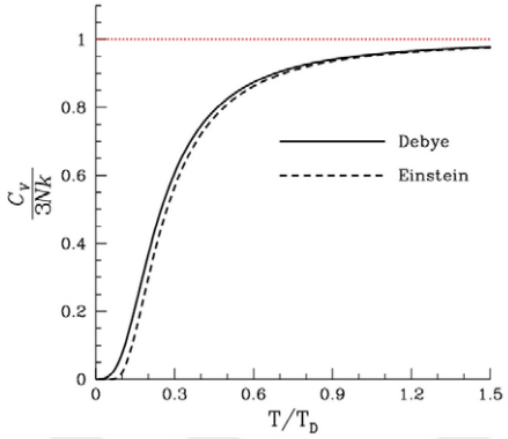

Figure 8: Variation of the results obtained from Einstein and Debye approaches with respect to temperature.

3.3. Einstein-Debye approximation for solids

Recently, Askerov and Cankurtaran (Ibach and Lüth, 2009; Elliott and Franz, 2015) proposed the Einstein-Debye approach, which is a more comprehensive approach to study the thermodynamic properties of solids by combining the Einstein and Debye methods. According to this approach, the specific heat capacity can be calculated according to the following formula (Cankurtaran and Askerov, 1994; Cankurtaran, B.M. Askerov, 1996):

$$C_V = 3N_A k_B M\left(\frac{\theta_D}{T}, \frac{\theta_E}{T}\right) \tag{3.3.1}$$

Here θ_E Einstein temperature and $M\left(\frac{\theta_D}{T}, \frac{\theta_E}{T}\right)$ function is defined as follows:

$$M\left(\frac{\theta_D}{T}, \frac{\theta_E}{T}\right) = L_V\left(\frac{\theta_D}{T}\right) + (s-1)A\left(\frac{\theta_E}{T}\right) \tag{3.3.2}$$

where s is the number of atoms at the node and $L_V\left(\frac{\theta_D}{T}\right)$ and $A\left(\frac{\theta_E}{T}\right)$ functions are defined as follows:

$$A\left(\frac{\theta_E}{T}\right) = \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}}-1\right)^2} = \left[\frac{\theta_E}{2T}\frac{1}{sinh\left(\frac{\theta_E}{2T}\right)}\right]^2. \tag{3.3.3}$$

And

$$L_V\left(\frac{\theta_D}{T}\right) = (n+1)D_n\left(1, \frac{\theta_D}{T}\right) - \frac{\theta_D}{T}\frac{n}{e^{\frac{\theta_D}{T}}-1} \quad (3.3.4)$$

It is seen from the investigations that the results of the calculations made according to the Einstein-Debye approach are more in agreement with the experimental data. There are few studies on the thermodynamic properties of solids according to the Einstein-Debye approach in the literature. In the proposed thesis, the entropy and free energy of some semiconductors will be analyzed over a wide range of temperature by considering the Einstein-Debye approach. Let us first look at the study of entropy and free energy according to the Debye approach.

Using the Debye model, the following expression was obtained for the free energy of the free electron gas (Cankurtaran and Askerov, 1994; Cankurtaran, B.M. Askerov, 1996):

$$F = E_0 + 9Nk_0T\left(\frac{T}{\theta}\right)^3 \int_0^{\frac{T}{\theta}} Ln(1-e^{-x})x^3dx \quad (3.3.5)$$

Here E_0 is the zeroth energy and is defined as follows:

$$E_0 = \frac{9}{8}Nk_0\theta \quad (3.3.6)$$

After the necessary operations on formula (13), it can be written as follows:

$$F = E_0 + 9Nk_0TLn\left(1-e^{-\frac{\theta}{T}}\right) - 9Nk_0T\left(\frac{T}{\theta}\right)^3 \int_0^{\frac{\theta}{T}} \frac{x^3}{e^x-1}dx \quad (3.3.7)$$

Here the integral expression is the Debye function and is defined in general terms as follows:

$$D_n\left(\frac{\theta_D}{T}\right) = \left(\frac{T}{\theta_D}\right)^n \int_0^{\frac{\theta_D}{T}} \frac{x^n}{e^x-1}dx \quad (3.3.8)$$

If we consider formula (3.3.8) in (3.3.7), for the free energy

$$F = E_0 + 9Nk_0TLn\left(1-e^{-\frac{\theta}{T}}\right) - 9Nk_0TD_3\left(\frac{\theta_D}{T}\right) \quad (3.3.9)$$

we get the general formula.

Furthermore, the following formula is given for free energy using the Einstein model:

$$F_{op} = 3N(s-1)k_0TLn\left(1-e^{-\frac{\theta_E}{T}}\right) \quad (3.3.10)$$

Here s is the number of atoms at a node, θ_E is the Einstein temperature. In this case, we write the expression of the free energy according to the Einstein-Debye approximation in general form as follows:

$$F = E_0 + 9Nk_0TLn\left(1 - e^{-\frac{\theta_D}{T}}\right) - 9Nk_0TD_3\left(\frac{\theta_D}{T}\right) + 3N(s-1)k_0TLn\left(1 - e^{-\frac{\theta_E}{T}}\right) \quad (3.3.11)$$

We can also calculate the Gibbs free energy based on the values of S entropy and H enthalpy according to the formula below:

$$F = H - ST \quad (3.3.12)$$

As it is known, using the Debye model, the entropin according to the free energy expression

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \quad (3.3.13)$$

we can calculate it according to the formula. The general expression for entropy according to the Debye model is as follows:

$$S = -3Nk_0Ln\left(1 - e^{-\frac{\theta}{T}}\right) + 4Nk_0D_3\left(\frac{\theta_D}{T}\right) \quad (3.3.14)$$

In this study, a general expression for entropy is established using the Einstein-Debye approximation. If we substitute (3.3.11) for free energy from the Einstein-Debye approximation in (3.3.13) and perform the necessary operations, we get the following formula for entropy:

$$S = -3Nk_0Ln\left(1 - e^{-\frac{\theta_D}{T}}\right) + 4Nk_0D_3\left(\frac{\theta_D}{T}\right)$$

$$-3N(s-1)k_0\left[Ln\left(1 - e^{-\frac{\theta_E}{T}}\right) - \frac{\theta_E}{T}\frac{e^{-\frac{\theta_E}{T}}}{1-e^{-\frac{\theta_E}{T}}}\right] \quad (3.3.15)$$

According to the Einstein-Debye approach, using the formulas (3.3.11), (3.3.12) and (3.3.15), the entropy and free energy of InP, InAs, ZnO, GeS semiconductors will be studied over a wide temperature range. As it can be seen from formulas (3.3.11), (3.3.12) and (3.3.14), the precise calculation of free energy and entropy depends on the results obtained from the analytical formulas for the Debye function. It is seen from the

studies that the formulas for the Einstein-Debye approach give results with the desired precision compared to the Einstein and Debye approaches.

3.4. Variation of free energy and entropy of *InP* semiconductor with temperature

Indium phosphide (InP) is a binary semiconductor with a zinc blend crystal structure similar to GaAs and almost all III-V semiconductors. Indium phosphide semiconductor has important application areas:

1. It has superior electron velocity for use in high frequency and high power electronics.
2. Unlike many semiconductors it has a direct bandgap, so it is used for optoelectronic devices such as laser diodes.
3. Indium phosphide is also used as a substrate for optoelectronic devices based on epitaxial indium gallium arsenide.

By fitting the experimental studies, we get the following expression for the temperature dependence of the Gibbs free energy change of the InP semiconductor:

$$\Delta G_f = a + bT\ln(T) + cT^3 + dT^{-1} + eT \qquad (3.4.1)$$

Here a b c d and e constants are given in Table 1.

Table 1: Values of a b c d and e constants in Equation (3.4.1) (Pankratz, 1994)

Temperature (K)	a	b	c	d	e
298.15-317.3	-20.732	-6.068×10^{-3}	8.049×10^{-6}	110.100	45.620×10^{-3}
317.3-429.78	-20.419	-3.575×10^{-3}	4.864×10^{-6}	110.100	31.284×10^{-3}
429.78-550	-20.059	0.772×10^{-3}	0.092×10^{-6}	77.250	6.318×10^{-3}
550- 910	-23.520	0.566×10^{-3}	0.096×10^{-6}	27.100	21.216×10^{-3}
910-1300	-19.969	6.135×10^{-3}	-3.259×10^{-6}	-41.650	25.207×10^{-3}

Table 2: Variation of entropy $S(T)$ as a function of temperature for *InP* ($\theta_D = 425K$, $\theta_E = 195K$, $J/mol.K$).

T	(Dabhi and Jha, 2016)	(Pankratz, 1994)	(Ihsan, 1995)	This study Eq. (3.3.14)
295	61.258			61.118
298.15		63.178	59.802	61.613
300	62.000	63.459	60.083	61.901
400	75.102	77.007	73.363	75.546
500	85.626	89.931	83.992	85.114
550		92.671		90.996
600	94.380	97.019	92.944	95.273
700	101.859	104.701	100.739	102.836
800	108.380	111.529	107.688	109.426
900	114.156	117.503	113.990	115.252
910		118.064	114.590	115.799
1000	119.340	123.168	120.213	120.473
1100		128.198	125.477	125.201
1200		133.026	130.282	129.522
1300		137.687	134.703	133.499

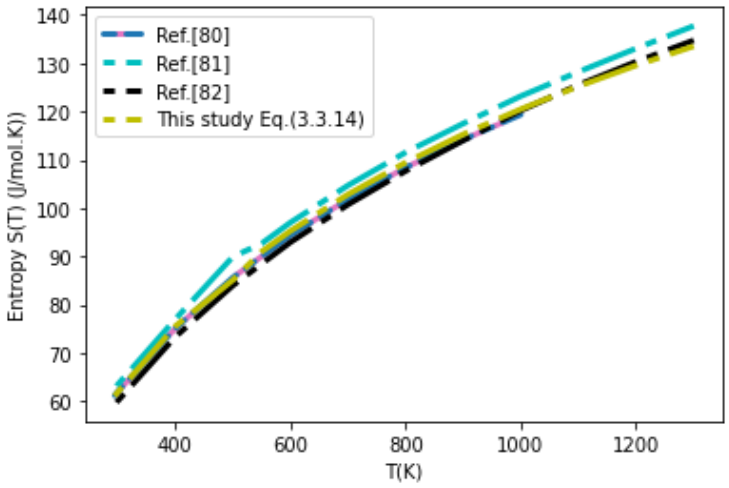

Figure 9: Variation of entropy S(T) as a function of temperature for InP ($\theta_D = 425K$, , $\theta_E = 195K$, J/ mol .K).

In Figure 9 the Ref. [80] is corresponded to (Dabhi and Jha, 2016) and Ref.[81] is corresponded to (Pankratz, 1994) and Ref.[82] is corresponded to (Ihsan, 1995).

Table 3: Variation of $F(T)$ Gibbs free energy and Gibbs free energy change ΔG_f as a function of temperature for InP ($\theta_D = 425\,K$, $\theta_E = 195\,K$, KJ/mol)

T	(Ihsan, 1995).	This study Eq. (3.3.12)	ΔG_f Eq.(3.4.1)
298.15	-106.531	-107.071	-16.354
300	-106.642	-107.187	-16.339
400	-113.342	-114.215	-15.420
500	-121.227	-121.788	-14.523
600	-130.085	-131.483	-12.898
700	-139.778	-141.245	-11.195
800	-150.205	-151.596	-9.498
900	-161.294	-162.430	-7.803
910	--162.437	-163.537	-7.635
1000	-173.025	-173.255	-6.122
1100	-185.314	-185.010	-4.444
1200	-198.105	-197.192	-2.778
1300	-211.357	-209.792	-1.128

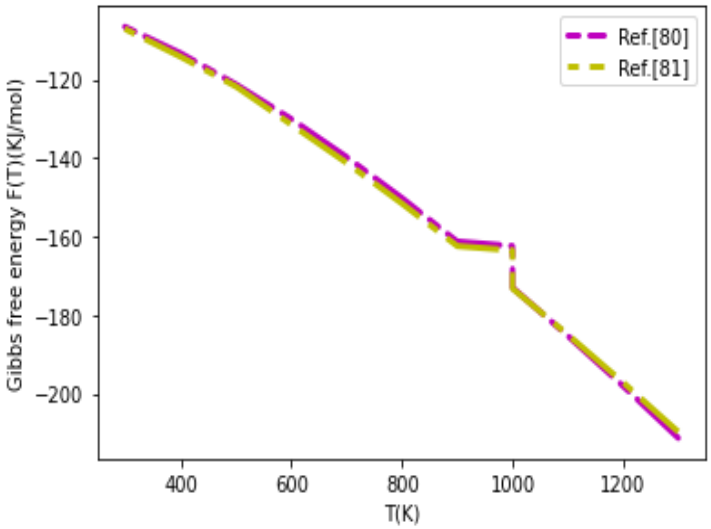

Figure 10: Variation of $F(T)$ Gibbs free energy and Gibbs free energy change ΔG_f as a function of temperature for InP ($\theta_D = 425\,K$, $\theta_E = 195\,K$, KJ/mol)

In Figure 10 the Ref. [80] is corresponded to (Dabhi and Jha, 2016) and Ref.[81] is corresponded to (Pankratz, 1994).

The temperature dependence of the entropy of the InP semiconductor using the formula (3.3.14) based on the Einstein-Debye approximation is calculated and compared with the results of (Dabhi and Jha, 2016), (Pankratz, 1994) and (Ihsan, 1995) in Table 2 and Figure 9. F(T) The temperature dependence of Gibbs free energy and ΔGf Gibbs free energy change with respect to temperature is calculated according to the formulas (3.3.12) and (3.4.1) and the comparative results of reference (Ihsan, 1995) are given in Fig. 10 and Table 3. As can be seen from Figures 9, 10 and Tables 2, 3, the results obtained from the method proposed in the thesis are in agreement with the results obtained from theoretical and experimental sources.

3.5. Variation of free energy and entropy of *InAs* semiconductor with temperature

Indium arsenide is one of the semiconductors with the fewest applications in technology. Its application is mainly as a substrate for mid-infrared LEDs and detectors and as a magnetic field sensor due to its large Hall coefficient. Indium arsenide has similar properties to gallium arsenide. Indium arsenide is sometimes used together with indium phosphide. When alloyed with gallium arsenide it forms indium gallium arsenide - a material with a band gap that depends on the In/Ga ratio. InAs is a semiconductor known for its high electron mobility and narrow energy band gap. It is widely used as a source of terahertz radiation because it is a strong photo-doping emitter. With n and p type doped states, it is of fundamental importance for application in light emitting devices. By fitting the experimental studies, we get the following expression for the temperature dependence of the Gibbs free energy change of the InAs semiconductor:

$$\Delta G_f = a + bTLn(T) + cT^3 + dT^{-1} + eT\,. \tag{3.5.1}$$

Here *a b c d* and *e* constants are given in Table 3.

Table 4. Values of *a b c d* and *e* constants in Equation (3.5.1) (Pankratz, 1994).

Temperature (K)	*a*	*b*	*c*	*d*	*e*
298.15-429.78	-15.051	-3.031×10^{-3}	3.843×10^{-6}	72.950	23.103×10^{-3}
429.78-876	-14.692	1.316×10^{-3}	0.929×10^{-6}	40.100	1.862×10^{-3}
876-1200	-24.020	0.618×10^{-3}	-1.507×10^{-6}	24.350	14.043×10^{-3}
1210- 1300	-9.842	-4.040×10^{-3}	-0.017×10^{-6}	13.450	33.613×10^{-3}

Table 5: Variation of entropy $S(T)$ as a function of temperature for InAs ($\theta_D = 280\,K,\ \theta_E = 165\,K$, $J / mol.K$)

T	(Dabhi and Jha, 2016).	(Pankratz, 1994)	This Study Eq. (3.3.14)
295	74.116		74.871
298.15		75.647	75.383
300	74.904	75.940	75.681
400	88.588	90.073	89.665
500	97.386	101.554	100.625
600	108.286	111.261	109.627
700	115.848	119.704	117.260
800	122.418	127.210	123.885
900	128.228	133.997	129.735
1000	133.430	140.205	134.973
1100		145.946	139.714
1200		151.293	144.044

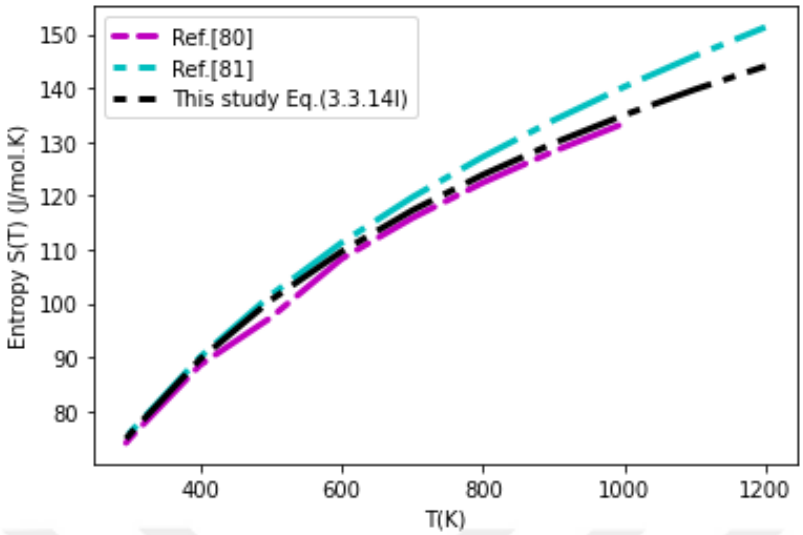

Figure 11: Variation of entropy $S(T)$ as a function of temperature for InAs ($\theta_D = 280\,K,\ \theta_E = 165\,K$, $J / mol.K$)

In Figure 10 the Ref. [80] is corresponded to (Dabhi and Jha, 2016) and Ref.[81] is corresponded to (Pankratz, 1994).

Table 6: Variation of $F(T)$ Gibbs free energy and Gibbs free energy change ΔG_f as a function of temperature for $InAs$ ($\theta_D = 280\,K,\ \theta_E = 165\,K$, KJ / mol)

T	(Ihsan, 1995).	This Study Eq. (3.3.12)	ΔG_f Eq.(3.5.1)
298.15	-81.171	-81.076	-12.726
300	-81.312	-81.217	-12.717
400	-89.635	-89.562	-12.729
500	-99.185	-99.115	-11.685
600	-109.726	-109.612	-11.027
700	-121.106	-120.875	-10.359
800	-133.213	-132.782	-9.689
900	-145.967	-145.242	-8.796
1000	-159.303	-158.155	-7.195
1100	-173.170	-171.553	-5.617
1200	-187.527	-185.301	-4.064

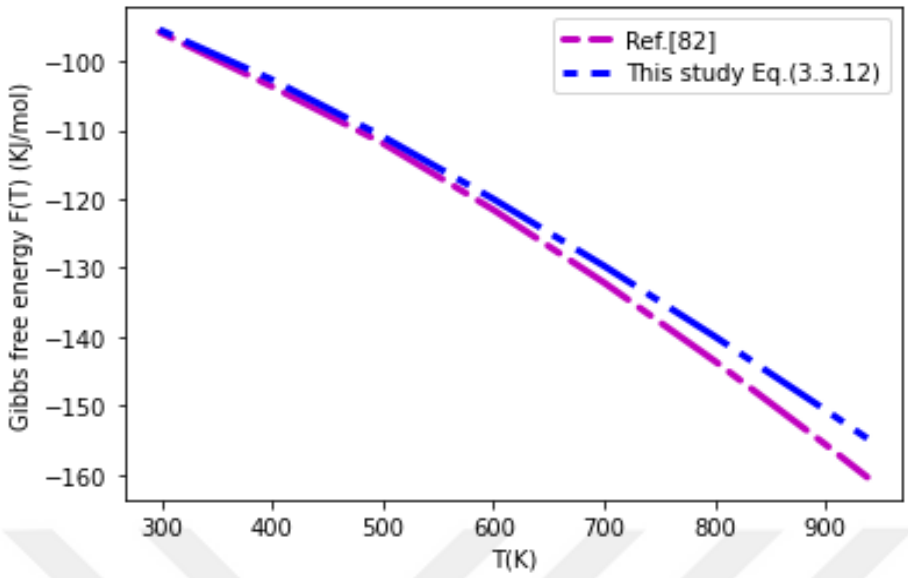

Figure 12: Variation of $F(T)$ Gibbs free energy and Gibbs free energy change ΔG_f as a function of temperature for $InAs$ ($\theta_D = 280\,K$, $\theta_E = 165\,K$, KJ / mol)

In Figure 12 the Ref [82] is corresponded to (Ihsan, 1995).

The temperature dependence of the entropy of the *InAs* semiconductor is calculated using the formula (3.3.14) based on the Einstein-Debye approximation and the results are given in Table 5 and Figure 10 in comparison with the results in (Dabhi and Jha, 2016) and (Pankratz, 1994). The temperature dependence of F(T) Gibbs free energy and ΔGf Gibbs free energy change of InAs semiconductor according to the formulas (3.3.12) and (3.5.1) are calculated and the results are given in Fig. 12 and Table 6. As can be seen from Figures 11, 12 and Tables 5, 6, the results obtained from the method proposed in this thesis are in agreement with the results obtained from theoretical and experimental sources.

3.6. Variation of free energy and entropy of *GeS* semiconductor with temperature

Germanium sulfide (GeS) is a 2D semiconductor with a band gap of 1.65 eV in pure form. They exhibit strong in-plane crystal anisotropy leading to highly anisotropic excitons, high carrier mobility channels and thermal conduction pathways. They are theoretically predicted to undergo a structural phase transition at temperatures around 400 C. Group IV-VI diatomic semiconductor nanocrystals such as SnS, SnSe, GeS and GeSe have recently attracted great interest due to their potential applications in photodetectors, solar cells, thermoelectric devices and anode materials for lithium-ion batteries.

Table 7: Variation of entropy $S(T)$ as a function of temperature for *GeS* ($\theta_D = 360\,K$, $\theta_E = 200\,K$, $J/mol.K$).

T	(Ihsan, 1995).	This Study Eq. (3.3.14)
298.15	65.982	64.806
300	66.277	65.100
400	80.315	78.875
500	91.654	89.737
600	101.287	98.684
700	109.743	106.285
800	117.337	112.889
900	124.272	118.724
938	126.766	120.775

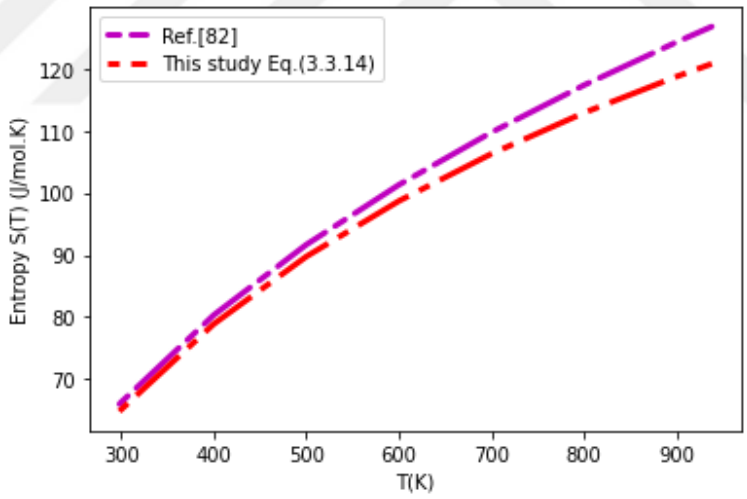

Figure 13: Variation of entropy $S(T)$ as a function of temperature for *GeS* ($\theta_D = 360\,K$, $\theta_E = 200\,K$, $J/mol.K$).

In Figure 13 the Ref [82] is corresponded to (Ihsan, 1995).

Table 8: Variation of $F(T)$ Gibbs free energy and Gibbs free energy change ΔG_f as a function of temperature in the high temperature GeS ($\theta_D = 360\,K$, $\theta_E = 200\,K$, KJ/mol)

T	(Ihsan, 1995).	This study Eq. (3.3.12)	Free change ΔG_f
298.15	-95.821	-95.471	-76.995
300	-95.944	-95.591	-77.001
400	-103.302	-102.726	-77.217
500	-111.918	-110.959	-76.821
600	-121.577	-120.014	-76.205
700	-132.136	-129.715	-75.486
800	-143.497	-139.935	-74.726
900	-155.582	-150.588	-72.786
938	-160.352	-154.732	-70.219

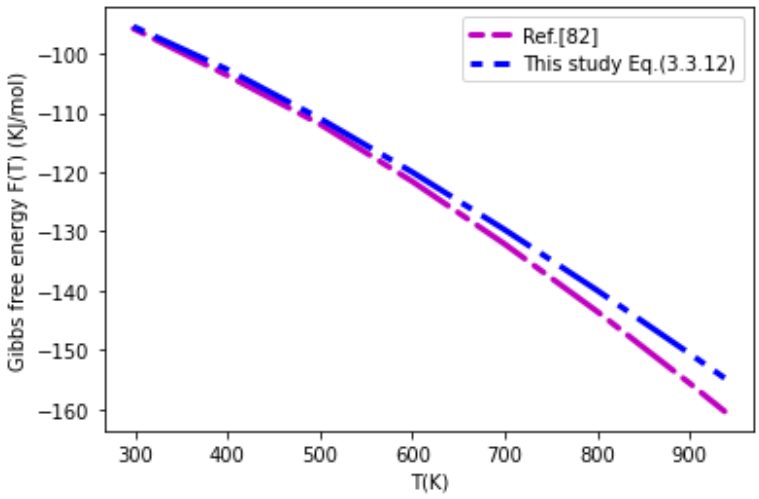

Figure 14: Variation of $F(T)$ Gibbs free energy and Gibbs free energy change ΔG_f as a function of temperature in the high temperature GeS ($\theta_D = 360\,K, \theta_E = 200\,K$, KJ/mol).

In Figure 14 the Ref. [82] is corresponded to (Ihsan, 1995).

The temperature dependence of the entropy of the GeS semiconductor using the formula (3.3.14) based on the Einstein-Debye approximation is calculated and the results are given in Table 7 and Figure 13 in comparison with the results in (Ihsan, 1995). The temperature dependence of F(T) Gibbs free energy and ΔGf Gibbs free energy change of the GeS semiconductor according to the formula (3.3.12) is calculated and the comparative results with the source (Ihsan, 1995) are given in Fig. 14 and Table 8. As can be seen from Figures 13, 14 and Tables 7, 8, the results obtained from the method proposed in the thesis are in agreement with the results obtained from theoretical and experimental sources.

3.7. Variation of free energy and entropy of *ZnO* semiconductor with temperature

Zinc oxide (ZnO) is one of the most important group II-VI semiconductor materials. It is a wide bandgap oxide semiconductor with a direct energy band gap of about 3.37 eV and has high chemical and mechanical stability; it is also non-toxic and widespread in nature. Zinc oxide is very promising material for semiconductor device applications and has a direct and broad band gap in the near UV spectral region and a large free exciton binding energy.

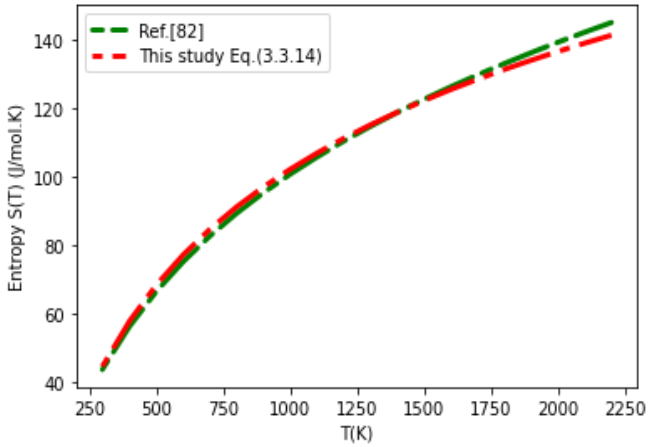

Figure 15: Variation of entropy $S(T)$ as a function of temperature for *ZnO* ($\theta_D = 440\,K$, $\theta_E = 395\,K$, $J/mol.K$).

In Figure 15 the Ref. [82] is corresponded to (Ihsan, 1995).

Table 9: Variation of entropy $S(T)$ as a function of temperature for ZnO ($\theta_D = 440\,K,\ \theta_E = 395\,K$, $J/mol.K$).

T	(Ihsan, 1995).	This Study Eq. (3.3.14)
298.15	43.639	44.533
300	43.894	44.805
400	56.277	57.866
500	66.480	68.385
600	75.128	77.143
700	82.633	84.628
800	89.280	91.156
900	95.255	96.940
1000	100.694	102.130
1100	105.694	106.836
1200	110.330	111.140
1300	114.659	115.104
1400	118.724	118.778
1500	122.562	122.201
1600	126.202	125.405
1700	129.666	128.416
1800	132.976	131.257
1900	136.147	133.945
2000	139.194	136.496
2100	142.128	138.923
2200	144.960	141.238

Table 10: Variation of $F(T)$ Gibbs free energy as a function of temperature in the high temperature ZnO ($\theta_D = 440\,K$, $\theta_E = 395\,K$, KJ/mol)

T	(Ihsan, 1995).	This Study Eq. (3.3.12)
298.15	-363.471	-363.737
300	-363.552	-363.825
400	-368.582	-369.217
500	-374.735	-375.687
600	-381.826	-383.036
700	-389.722	-391.119
800	-398.324	-399.824
900	-407.556	-409.072
1000	-417.357	-418.794
1100	-427.680	-428.936
1200	-438.484	-439.456
1300	-449.736	-450.315
1400	-461.407	-461.482
1500	-473.473	-472.901
1600	-485.913	-484.638
1700	-498.708	-496.582
1800	-511.841	-508.746
1900	-525.298	-520.714
2000	-539.066	-533.661
2100	-553.133	-546.402
2200	-567.489	-559.300

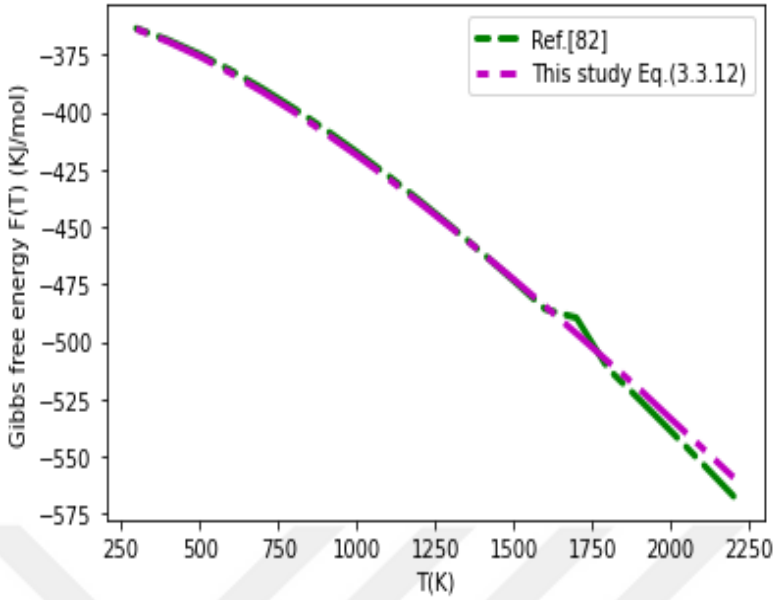

Figure 16: Variation of $F(T)$ Gibbs free energy as a function of temperature in the high temperature ZnO ($\theta_D = 440\,K$, $\theta_E = 395\,K$, KJ/mol)

In Figure 16 the Ref. [82] is corresponded to (Ihsan, 1995).

The temperature dependence of the entropy of the ZnO semiconductor is calculated using the formula (3.3.14) based on the Einstein-Debye approach and the results are given in Table 9 and Figure 15 in comparison with the results in (Ihsan, 1995). The temperature dependence of the Gibbs free energy of the ZnO semiconductor F(T) is calculated using the formula (3.3.12) and the results are given in Figure 16 and Table 10 in comparison with source (Ihsan, 1995). Figure. 16 and Table 10. As can be seen from Figures 15, 16 and Tables 9, 10, the results obtained from the method proposed in this thesis are in agreement with the results obtained from theoretical and experimental sources.

4. DISCUSSION AND CONCLUSION

In the literature, many theoretical and experimental methods are used to calculate the thermodynamic properties of materials. In the early 20th century, after the emergence of quantum mechanics, which examines the physical properties of microsystems, the ability to accurately and precisely calculate all the physical properties of materials has enabled science and technology to develop to today's level. One of these developments is the Debye approach, which has made significant progress in the calculation of the thermodynamic properties of solids. The Debye approach has led to significant advances in the study of the thermal properties of conductive materials used in devices that form the basis of many modern technologies. Later, the Debye approximation has been improved by scientists, allowing more precise calculation of the thermodynamic properties of solid materials. One of these studies is the Einstein-Debye approach recently developed by (Cankurtaran, Askerov, 1994, 1996). In this study, the Einstein-Debye approach was first used, to investigate the temperature dependence of the free energy and entropy of InP, InAs, GeS and ZnO which are physical properties of semiconductors over a wide temperature range. Also in this study, new analytical formulas for the free energy (3.3.11) and entropy (3.3.15) are established using the Einstein-Debye approach. In the proposed thesis, the free energy and entropy of InP, InAs, GeS and ZnO semiconductors are investigated using the Einstein-Debye approximation and it is seen that the precision of the calculations is important to calculate analytically the n-dimensional Debye functions arising in the Einstein-Debye approximation. For the precise calculation of Debye functions, an efficient method recently proposed in the literature has been used.

The calculation results for the free energy and entropy of each of the InP, InAs, GeS and ZnO semiconductors according to the Einstein-Debye approximation are given in Fig. (8)-(15) and Table (5)-(10). As can be seen from Fig. (8)-(15) and Table (5)-(10), the calculation results are in agreement with the theoretical and experimental results in the references. In general, the calculation of free energy and entropy according to the theoretical and experimental approaches given in the references gives accurate results in limited temperature ranges. As seen from the results, the formulas for free energy and entropy using the Einstein-Debye approach are general and give accurate results in all temperature ranges. This is one of the important advantages of this work

and it is seen that it will contribute to the calculation of thermodynamic properties of other substances. This will allow us to calculate the free energy and entropy of semiconductors more precisely in all temperature ranges using the proposed method. In addition, it is seen from the results obtained from this thesis that it is possible to determine the free energy, entropy and other thermodynamic properties of other semiconductors. The theoretical developments on the free energy and entropy of solids using the Einstein-Debye approach and its applications to InP, InAs, GeS and ZnO semiconductors show that this theory is an important development for the precise calculation of the thermodynamic properties of other solids over a wide temperature range.

References

Abu-Eishah, S.I. Correlations for the Thermal Conductivity of Metals as a Function of Temperature, Inter. J. Thermophys. 22: 1855 (2001).

Anile, A. M., Allegretto, W., & Ringhofer, C. (2003). Mathematical problems in semiconductor physics: lectures given at the CIME Summer School held in Cetraro, Italy, June 15-22, 1998. Springer.

Askerov, B. M., & Cankurtaran, M. (1994). Isobaric specific heat and thermal expansion of solids in the Debye approximation. physica status solidi (b), 185(2), 341-348.

Askerov, B. M., & Figarova, S. (2009). Thermodynamics, Gibbs method and statistical physics of electron gases (Vol. 57). Springer Science & Business Media.

Aspnes, D. E. (1988, August). Analysis of semiconductor materials and structures by spectroellipsometry. In Spectroscopic Characterization Techniques for Semiconductor Technology III (Vol. 946, pp. 84-97). SPIE.

Avsec, J. and Marcic, M. Calculation of Elastic Modulus and Other Thermophysical Properties for Molecular Crystals, J. Thermophys. Heat. Transfer. 16, 463 (2002).

Balkanski, M., Wallis, R. F., & Wallis, R. F. (2000). Semiconductor physics and applications (Vol. 8). Oxford University Press.

Blancon, J. C., Even, J., Stoumpos, C., Kanatzidis, M., & Mohite, A. D. (2020). Semiconductor physics of organic-inorganic 2D halide perovskites. Nature nanotechnology, 15(12), 969-985.

Burns, G. (2016). Solid state physics. Academic press.

Calow, J. T., Deasley, P. J., Owen, S. J. T., & Webb, P. W. (1967). A review of semiconductor heterojunctions. Journal of Materials Science, 2(1), 88-96.

Cankurtaran, M. Askerov, B. M. Isobaric Specific Heat and Thermal Expansion of Solids in the Debye Approximation, Phys Stat Sol (b), 185, 341 (1994).

Cankurtaran, M. Askerov, B.M. Equation of state, isobaric specific heat, and thermal expansion of solids with polyatomic basis in the Einstein-Debye approximation. Phys Stat Sol B, 194, 499 (1996).

Cankurtaran, M., & Askerov, B. M. (1996). Equation of state, isobaric specific heat, and thermal expansion of solids with polyatomic basis in the Einstein- Debye approximation. physica status solidi (b), 194(2), 499-507.

Castro, A., Appel, H., Oliveira, M., Rozzi, C. A., Andrade, X., Lorenzen, F., ... & Rubio, A. (2006). basic solid state physics. phys. stat. sol.(b), 243(11), 2465-2488.

Cohen-Tannoudji, C., Diu, B., & Laloe, F. (1986). Quantum Mechanics, Volume 1. Quantum Mechanics, 1, 898.

Dabhi, S. D., & Jha, P. K. (2016). First-principles study for thermodynamic properties of wurtzite indium pnictides. Journal of Thermal Analysis and Calorimetry, 124(3), 1341-1347.

Debye, P. (1912). The Debye theory of specific heat. Ann. Phys.(Leipzig), 4(39), 789-803.

Demkov, A. A., Zhang, X., & Drabold, D. A. (2001). Towards a first-principles simulation and current-voltage characteristic of atomistic metal-oxide-semiconductor structures. Physical Review B, 64(12), 125306.

Ehrenreich, H., & Spaepen, F. (2001). Solid state physics. Academic Press.

Eınsteın, A. Planck's theory of radiation and the theory of specific heat, Ann. Phys., Lpz., 22 (1907) 180.

Elliott, S. R., & Franz, M. (2015). Colloquium: Majorana fermions in nuclear, particle, and solid-state physics. Reviews of Modern Physics, 87(1), 137.

Eymet, V. Brasil, A.M. El Hafi, M. Farais, T.L. and Coelho, P.J. Numerical investigation of the effect of soot aggregation on the radiative properties in the infrared region and radiative heat transfer , JQSRT, 74, 697 (2002).

Galindo, A., & Pascual, P. (2012). Quantum mechanics I. Springer Science & Business Media.

Gaur, U. Mehta, A. and Wunderlich, B. Heat capacity measurements by computerinterfaced DSC, J Thermal. Anal. Caorim. 13, 71 (1978).

Gradsteyn IS, Ryzhik IM (1980) Tables of Integrals, Sums, Series and Product, 4th edn. Academic Press, New York, USA.

Grahn, H. T. (1999). Introduction to semiconductor physics. World Scientific Publishing Company.

Grimvall, G. Thermophysical Properties of Materials, (North- Holland, Amsterdam, 1986).

Grosso, G., & Parravicini, G. P. (2013). Solid state physics. Academic press.

Guillot, J. C. (1990). Global existence of solutions for the nonlinear Boltzmann equation of semiconductor physics. Revista matemática iberoamericana, 6(1), 43- 59.

Guseinov, I.I. Mamedov, B.A. Calculation of Integer and Noninteger n-Dimensional Debye Functions Using Binomial Coefficients and Incomplete Gamma Functions. Int. J. Thermophys. 28, 1420 (2007).

Haug, A. (2016). Theoretical Solid State Physics: International Series in Natural Philosophy, Volume 1 (Vol. 1). Elsevier.

Hoffmann, R. (1987). How chemistry and physics meet in the solid state. Angewandte Chemie International Edition in English, 26(9), 846-878.

Hu, X., Li, G., & Yu, J. C. (2010). Design, fabrication, and modification of nanostructured semiconductor materials for environmental and energy applications. Langmuir, 26(5), 3031-3039.

Huang, K. (2009). Introduction to statistical physics. Chapman and Hall/CRC.

Huang, K. (2009). Introduction to statistical physics. Chapman and Hall/CRC.

Huang, X., Ji, D., Fuchs, H., Hu, W., & Li, T. (2020). Recent progress in organic phototransistors: Semiconductor materials, device structures and optoelectronic applications. ChemPhotoChem, 4(1), 9-38.

Hutten, E. H., & Hutten, E. H. (1956). The language of modern physics: an introduction to the philosophy of science. London: Allen & Unwin.

Ibach, H., & Lüth, H. (2009). Solid-state physics: an introduction to principles of materials science. Springer Science & Business Media.

Ihsan Barin, Thermochemical Data of Pure Substances, VCH Verlagsgesellschaf, Germany, 1995

Jammer, M. (1997). Concepts of mass in classical and modern physics. Courier Corporation.

Jones, W., & March, N. H. (1985). Theoretical solid state physics (Vol. 35). Courier Corporation.

Kapon, E. (1999). Semiconductor Lasers II: Materials and Structures. Elsevier.

Kittel et al., 1996; Jones and March, 1985; Mandl, 1991; Huang, 2009

Kittel, C., & McEuen, P. (2018). Introduction to solid state physics. John Wiley & Sons.

Kittel, C., McEuen, P., & McEuen, P. (1996). Introduction to solid state physics (Vol. 8, pp. 105-130). New York: Wiley.

Kittel, C., McEuen, P., & McEuen, P. (1996). Introduction to solid state physics (Vol. 8, pp. 105-130). New York: Wiley.

Kramers, H. A. (2018). Quantum mechanics. Courier Dover Publications.

Landsberg, P.T. Problems in Thermodynamics and Statistical Physics, (PION, London, UK, 1971).

Landsberg, P.T. Problems in Thermodynamics and Statistical Physics, (PION, London, UK, 1971).

Li, M. F. (1995). Modern semiconductor quantum physics. World scientific.

Li, Z., Tan, H. H., Jagadish, C., & Fu, L. (2018). III-V semiconductor single nanowire solar cells: a review. Advanced Materials Technologies, 3(9), 1800005.

Liu, G., Tuttle, B. R., & Dhar, S. (2015). Silicon carbide: A unique platform for metaloxide-semiconductor physics. Applied Physics Reviews, 2(2), 021307.

Lu Lai-Yu, Chenga Yan, Chena Xiang-Rong, J. Zhu, Thermodynamic properties of MgO under high pressure from first-principles calculations, Physica B 370, 236 (2005).

Ludwig, G. (2012). Foundations of quantum mechanics I. Springer Science & Business Media.

Magomedov, M.N. Thermodynamically Consistent Calculation of the Debye Temperature Using Thermophysical Data, High Temp. 40, 542 (2002).

Mandl, F. (1991). Statistical physics (Vol. 14). John Wiley & Sons.

Marko, I. P., & Sweeney, S. J. (2015). Optical and electronic processes in semiconductor materials for device applications. In Excitonic and Photonic Processes in Materials (pp. 253-297). Springer, Singapore.

McKinley, J. T., Albridge, R. G., Barnes, A. V., Baudat, P. A., Chen, G. C., Coluzza, C., ... & Tolk, N. (1994). Free-electron lasers and semiconductor physics: first results on nonlinear optics, interfaces, and desorption. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 341(1-3), 156-161.

Melissinos, A. C., & Napolitano, J. (2003). Experiments in modern physics. Gulf Professional Publishing.

Mil'vidskij, M. G. (1986). Semiconductor materials in modern electronics.

Mishra, U. K., & Singh, J. (2008). Semiconductor device physics and design (Vol. 83). Dordrecht: Springer.

Neamen, D. A. (2003). Semiconductor physics and devices: basic principles. McGraw-hill.

Neumann, H. High-temperature heat capacity and lattice anharmonicity of LiGaO2 , Cryst. Res. Technol. 39, 245 (2004).

Olla, P. (2015). An Introduction to Thermodynamics and Statistical Physics. Springer International Publishing.

Pankratz , L. B. Thermodynamıc Properties Of Carbıdes , Nıtrıdes , And Other Selected Substances , Bulletin 696, , 1994

Pathak, P.D. Pandya, N.M. Debye temperatures of KI and RbI and the anharmonic parameters of their potential functions, Acta Cryst. A, A31, 185 (1975).

Peter, Y. U., & Cardona, M. (2010). Fundamentals of semiconductors: physics and materials properties. Springer Science & Business Media.

Peverati, R., & Truhlar, D. G. (2012). Screened-exchange density functionals with broad accuracy for chemistry and solid-state physics. Physical Chemistry Chemical Physics, 14(47), 16187-16191.

Pyda, M. Bartkowiak, M. and Wunderlich, B. Computation of Heat Capacities of Solids Using a General Tarasov Equation, J. Therm. Anal. Calorim. 52, 631 (1988).

Ravindra, N. M., Abedrabbo, S., Chen, W., Tong, F. M., Nanda, A. K., & Speranza, A. C. (1998). Temperature-dependent emissivity of silicon-related materials and structures. IEEE Transactions on semiconductor manufacturing, 11(1), 30-39.

Schmidt, G., & Molenkamp, L. W. (2002). Spin injection into semiconductors, physics and experiments. Semiconductor science and technology, 17(4), 310.

Seeger, K., (1999). Semiconductor Physics An Introduction. Springer.

Serway, R. A., Moses, C. J., & Moyer, C. A. (2004). Modern physics. Cengage Learning.

Shi, X. L., Zou, J., & Chen, Z. G. (2020). Advanced thermoelectric design: from materials and structures to devices. Chemical Reviews, 120(15), 7399-7515.

Stradling, R. A. (1991). Novel semiconductor materials and structures produced by MBE and MOCVD. Physica Scripta, 1991(T35), 237.

Tamargo, M. C. (2002). II-VI semiconductor materials and their applications (Vol. 12). CRC Press.

Thornton, S. T., & Rex, A. (2012). Modern physics for scientists and engineers. Cengage Learning.

Tipler, P. A., & Llewellyn, R. A. (2012). Modern physics. WH Freeman and Co.

Walecka, J. D. (2008). Introduction to modern physics: theoretical foundations. World Scientific Publishing Company.

Wang, C., Wang, C., Huang, Z., & Xu, S. (2018). Materials and structures toward soft electronics. Advanced Materials, 30(50), 1801368.

Windsor, C.G. and Sinclair, R.N. The Debye-Waller factor of nickel measured at high scattering vectors by pulsed neutron powder diffraction, Acta Cryst A, A32, 395 (1976).

Young, H. D., Freedman, R. A., & Ford, A. L. (2013). University Physics with Modern Physics Technology Update. Pearson Education.

Zak, J. (1967). Finite translations in solid-state physics. Physical Review Letters, 19(24), 1385.

Ziman, J.M. Principles of the Theory of Solids, (Cambridge University Press, UK, 1965).