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Study of Thermodynamic Properties of Zircon Based on the Debye Model

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Abstract The work we present here is intended as a contribution to the study of the thermodynamic properties of zircon. For this purpose, we have implemented the quasi-harmonic Debye model, in which the vibrations of the network of atoms are taken into account. This study has a dual objective, first to calculate the thermodynamic quantities of zircon for different temperatures and to test the validity of the model with the data available in the literature. In addition, due to the structural complexity of the zircon equation of state, we have developed a Matlab code in deterministic mode to perform the calculations. At the end of the study, the results obtained are consistent and meaningful. Overall, the results indicate that heat capacity, internal energy and entropy increase with temperature. This growth is more marked with the internal energy than with the entropy and the thermal capacity which tends towards the limit value of Dulong-Petit. In addition, the results of our simulations are in excellent agreement with others reported in the literature. These studies clearly demonstrate that zircon can be categorized as hard materials due to their high Debye temperature. We hope that this study could stimulate experimental studies about zircon ($ZrSiO_4$) characterization in Senegal.

Keywords Zircon morphology, Debye function, Debye model, Thermal properties, Vibrational properties, Specific heat capacity

1. Introduction

Nowadays, understanding the thermodynamic properties of a material is one of the major concerns of the scientific community [1]. This understanding necessarily goes through the resolution of the problems of quantum mechanics allowing to describe the quantum system studied [2]. According to [3], the study of the thermodynamic properties of materials makes it possible to predict the stability of materials and to evaluate their possible applications. In the opinion of [4], the study of these properties is motivated by an understanding of the chemical bonds and the cohesion of these materials [5]. These are often used at different pressures and temperatures [6]. The influences of these parameters on these materials can provide important information for understanding phase transitions and phase diagrams [4,7]. Because of their various industrial applications and their remarkable physical properties, the study of the thermodynamic properties of solids has attracted the attention of several researchers all over the world [8,9,10]. Among the latter, we can cite the works of [6,11,12,13,14,15,16,17,18,19]. The results obtained are in excellent agreement with those experimental and theoretical available in the literature. Through the various works consulted, the materials used are numerous and multifaceted; they are more or less complex structures. We find in others: zincite (ZnO), periclase (MgO), sphalerite (ZnS), covellite (CuS), realgar (AsS), cinnabar (HgS), galena (PbS), sylvine (KCl), halite (NaCl), clausthalite (PbSe), pyrite (FeS_2), brookite (TiO_2), cassiterite (SnO_2), quartz (SiO_2), chalcocite (Cu_2S), argentite (Ag_2S), fluorite (CaF_2), goethite ($HFeO_2$), nitre (KNO_3), nitronatrite ($NaNO_3$), cerusite ($PbCO_3$), rhodochrosite ($MnCO_3$), magnesite ($MgCO_3$), siderite ($FeCO_3$), smithsonite ($ZnCO_3$), nitronatrite ($NaNO_3$), calcite ($CaCO_3$), ilmenite (Fe_3) corindon (AlO_3), hematite (Fe_2O_3), stibnite (Sb_2S_3), anglesite ($PbSO_4$), anhydrite ($CaSO_4$), barite ($BaSO_4$), celestine ($SrSO_4$), scheelite ($CaWO_4$), crocoite ($PbCrO_4$), magnetite (Fe_2SiO_5), zircon ($ZrSiO_4$), etc. Scientists are interested in these materials because of their extraordinary magnetic properties and their industrial applications [20]. In the literature, many studies seem to be oriented towards zircon ($ZrSiO_4$) like the authors: [8,9,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35, 36,37,38,39,40,41,42,43,44,45]. The topics covered are essentially articulated around: electronic properties, physical properties, thermal properties, structural changes, swelling effects, partition coefficients, phase transition, external morphology, internal structures, effects

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temperature, morphological characteristics, thermometric measurement, impact dating, electron irradiation, thermochemical constraints, textural classification, neoblast formation, geochemistry, origin of magma, chemical composition, surveys detrital, etc. This wealth of literature testifies to the obvious interest that scientists place in zircon. Thus, according to [8] zircon can retain chemical and radioisotopic information of trace radioactive elements. As such, it is applied in the dating of the age and the limitation of the thermal history of geological formations [30]. According to [8,46,47] this mineral has been widely studied as a ceramic model for the immobilization of high activity nuclear waste due to its multiple properties [21,23] add that zircon is a host mineral for the element's radioactive uranium and thorium in the earth's crust and is a natural candidate for use as a nuclear waste storage material. Its low thermal conductivity and high melting point make it attractive for industrial applications [24]. Among the thermodynamic properties studied, heat capacity is the property that has captured the most attention of researchers [48]. It is an important parameter of condensed matter physics; in that it not only provides a fundamental overview of their vibrational properties, but it is also mandatory for many applications [3]. Which means [49] that thermal capacity has a significant technological and scientific impact. [46,50] argue that it is crucial to determine the onset of phase transitions, to build thermodynamic databases [47], to evaluate magnetocaloric effects [51,52] for applications in microelectronics [53] and in modern battery materials [54]. According to [6] the influences of temperature on the heat capacity are much greater than that of the pressure exerted on it. Knowledge of heat capacity allows other thermodynamic properties to be calculated such as internal energy, entropy, coefficient of thermal expansion and Debye temperatures. In the literature, there is a lot of work devoted to the determination of the thermal capacity of materials in general and of zircon in particular like [8,22,55,56,57]. Nowadays, there are several expressions in the literature for functions important in the equations of state of materials. Among these functions, we have that of Debye. This function appeared for the first time in a model proposed by Debye [58]. This model is an explanation, developed by Peter Debye in 1912, of the behavior of the heat capacity of solids as a function of temperature. It consists in studying the vibrations of the network of atoms forming the solid, in other words, the phonons [59]. In this sense, [4] state that the thermal properties of three-dimensional solids can be unambiguously determined from this model. In this article, we propose to calculate the thermodynamic properties of zircon ZrSiO4 on the basis of the Debye numerical method and to study the effect of temperature. In addition, due to the structural complexity of Debye functions, the zircon equation of state was solved using MATLAB software in deterministic mode. Indeed, our country is rich in mineral resources and since a certain year, one extracts zircon in great quantity. Paradoxically, despite the impact of zircon on the country's economy, to our knowledge, there is no experimental or theoretical work exploring the thermodynamic properties of this material. So, this article is intended as part of the answer to this concern. The results of our simulations will be discussed and compared to the experimental and theoretical results available in the literature for a need for validation.

2. Materials and Methods

2.1. Zircon Crystal Structure

Zircon ($ZrSiO_4$) is a heavy mineral found in geological formations [60]. It is a common accessory extracted from rocks and sediments [24]. It is a host material for radioactive elements of uranium and thorium in the earth's crust. Zircon is a chemically inert mineral that can survive weathering, physical abrasion, transport, diagenesis, metamorphism, and crustal fusion [61]. The widespread distribution of zircon in the continental crust, its tendency to concentrate trace elements (lanthanides and actinides), its use in age dating and its resistance to chemical and physical degradation have made zircon probably the mineral the more useful in geological studies [8]. At low pressure, the crystal structure of zircon ($ZrSiO_4$) is of tetragonal symmetry [62]. It is composed of a tetrahedral arrangement of SiO4 and dodecahedral of ZrO_8 [22]. The tetragonal lattice is also body-centered with 12 atoms in a unit cell that contains four groups of $SiO4^{-4}$ and ZrO_8^{-12}. The four groups in each set have the same geometry and different orientations. SiO_4^{-4} groups are deformed tetrahedra elongated along a double z axis parallel to the crystallographic axis c. The eight oxygen atoms coordinated with a zirconium atom have the geometry of a triangular dodecahedron. Four of them are arranged in a deformed tetrahedron elongated along a double axis z also parallel to the crystallographic axis c. The other four oxygen are arranged in a deformed tetrahedron compressed along the same z axis and rotated 90° with respect to the previous one. The overall symmetries of the SiO_4^{-4} and ZrO_8^{-12} groups are identical [22,61]. Figures 1a and 1b show the structure of zircon in its phase and an example image of the zircon crystal.

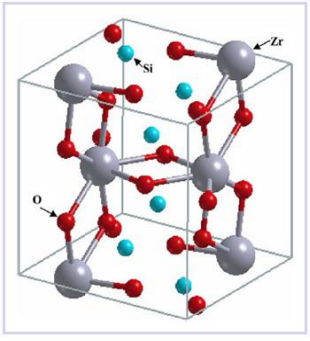

Figure 1a. Sructure of zircon [22]

Figure 1b. Zircon crystal of *Afghanistan*

https://mineral-s.com/wp-content/uploads/2020/05/zircon-afganistan-6-1017915-300x300.jpg

2.2. Debye's Model

2.2.1. Mathematical Formulation

Debye functions are widely used in the study of many physical problems, in particular in the evaluation of the heat capacity of solids [56]. In the literature, various efficient numerical methods have been proposed to improve the evaluation of these Debye functions [48,63]. In this study, the Debye model is used. Debye modeled vibrations in a solid as normal mode vibrations of a continuous elastic body, which works well for long wavelength vibrations that do not depend on the detailed atomic character of the solid [64]. Debye's model is commonly used to describe the temperature dependence of the heat capacity of materials. This model gives the thermal capacity according to the relation (1) [57]

$$C_V = 3nNk_B \int_0^{\omega_{\max}} \left(\frac{\hbar\omega}{2k_BT}\right)^2 \operatorname{csch}^2\left(\frac{\hbar\omega}{2k_BT}\right) g(\omega)d\omega \quad (1)$$

Where n is the number of atoms in the material; N the Avogadro number, k_B the Boltzmann constant, ω_{max} the maximum frequency, T the temperature, ħ the Planck constant, ω the frequency and g (ω) the density of states of a compound of volume V given by equation (2)

$$g(\omega) = \frac{V\omega^2}{\pi^2 v^3} \quad (2)$$

With v the speed of light in the material; the normalization of this density of state, leads to relation (3) which also allows us to have the maximum frequency according to equation (4)

$$\int_0^{\omega_{\max}} g(\omega)d\omega = 1 \quad (3)$$

$$\omega_{\max}{}^3 = \frac{3\pi^2 v^3}{V} \quad (4)$$

By setting the variable x according to relation (5), we can establish the frequency ω according to equation (6)

$$x = \frac{\hbar\omega}{k_BT} \quad (5)$$

$$\omega = \frac{xk_BT}{\hbar} \quad (6)$$

If ω tends to zero, x also tends to zero; similarly, if ω tends towards $\omega_{max,}$ x also tends towards a value x_D defined by equation (7) which can also be put in the form given by relation (8)

$$x_D = \frac{\hbar\omega_{\max}}{k_BT} \quad (7)$$

$$x_D = \frac{\theta_D}{T} \quad (8)$$

With θ_D the Debye temperature given by expression (9)

$$\theta_D = \frac{\hbar\omega_{\max}}{k_B} \quad (9)$$

We define the square of the hyperbolic cosine of an angle x by the relation (10)

$$\operatorname{csch}^2\left(\frac{x}{2}\right) = \frac{4e^x}{\left(e^x - 1\right)^2} \quad (10)$$

Taking into account equations (2) to (10), equation (1) can be expressed by equation (11) whose integration by part leads to equation (12)

$$C_V = 9nNk_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{4e^x}{\left(e^x - 1\right)^2} dx \quad (11)$$

$$C_V = 9nNk_B\left(\frac{T}{\theta_D}\right)^3 \left[\frac{-x_D{}^4}{e^{x_D} - 1} + 4\int_0^{x_D} \frac{x^3}{e^x - 1} dx\right] \quad (12)$$

By setting the parameter A according to equation (13), we can rewrite it according to equation (14)

$$A = \int_0^{x_D} \frac{x^3}{e^x - 1} dx \quad (13)$$

$$A = \int_0^{x_D} \frac{x^3 e^{-x}}{1 - e^{-x}} dx \quad (14)$$

The development in integer series of the usual functions given by equation (15), makes it possible to reduce equation (14) to (16) then to (17)

$$\frac{1}{1 - e^{-x}} = \sum_{\ell=1}^{\infty} e^{-\ell x} \quad (15)$$

$$A = \sum_{m=1}^{\infty} \int_0^{x_D} x^3 e^{-mx} dx \quad (16)$$

$$A = \lim_{M\to\infty} \sum_{m=1}^{M} \int_0^{x_D} \frac{3!}{m^4} \left\{1 - e^{-mx_D} p(m, x_D)\right\} \quad (17)$$

Where p(m, x_D) is a function given by equation (18)

$$p(m, x_D) = 1 + \frac{mx_D}{1!} + \frac{(mx_D)^2}{2!} + \frac{(mx_D)^3}{3!} \quad (18)$$

Finally, the heat capacity according to the Debye model presented by equation (19) then reduces to equation

$$C_V = 3nNk_B\left[4D - \frac{3x_D}{e^x - 1}\right] \quad (19)$$

With D the Debye function given by equation (20)

$$D = \frac{3}{x_D{}^3} A \quad (20)$$

2.2.2. Numerical Procedure

In this study, we propose to calculate the thermodynamic properties of zircon (ZrSiO4); using the Debye quasi-harmonic model. Within this framework, Debye considered the vibrational modes of a medium. This is to describe the temperature dependence of the heat capacity of (ZrSiO4) and draw the consequences. Since the Debye model is not analytical, the base equations of state were implicitly linearized and solved numerically by the finite element method using Matlab software. This resolution is done in an iterative manner following 7 steps:

i) we chose a temperature interval;
ii) we determine a dimensionless quantity x_D;
iii) we calculate the Debye function D;
iv) we compare this value with those taken from the literature, if there is compatibility, we continue the process, otherwise start the cycle again;
v) if there is compatibility, we calculate the specific heat Cv;
vi) the internal energy is then calculated;
vii) we finally compute the entropy and stop the process.

The algorithm below schematizes the different stages of our programming in Matlab (see figure 2).

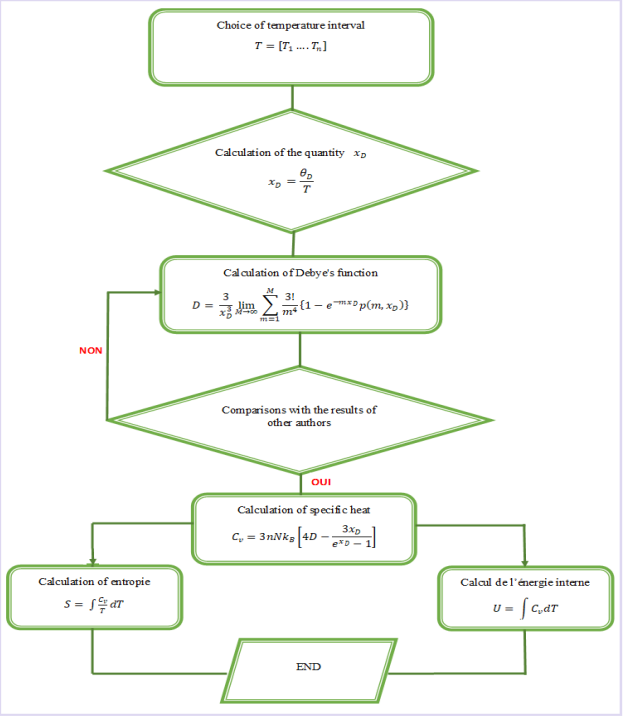

Figure 2. Iterative process used in solving zircon equations of state according to Debye's philosophy

3. Results and Discussion

Debye functions are widely used in the study of many physical problems, especially in the study of thermodynamic properties of solids. In the present study, we have a dual objective, first to collect more information on the physical properties of zircon and then to test the validity of the Debye quasi-harmonic model through good agreement with the data available in the literature. The results considered relate to specific heat, internal energy and entropy.

3.1. Validation Procedure

Table 1 tests the validity of our results relating to Debye's function compared to previous results available in the literature. We note that there is a fairly good agreement between the results.

Table 1. Comparison of our results with those of reference [65] for the Debye function

x_D	D Our results	D Results of reference [65]
0.1	0.962998	0.963000
0.5	0.824963	0.824963
1.0	0.674416	0.674416
2.0	0.441128	0.441129
3.0	0.283580	0.283580
4.0	0.181737	0.181737
5.0	0.117597	0.117597
6.0	0.077581	0.077581
7.0	0.052506	0.052506
8.0	0.036560	0.036560

3.2. Heat Capacity

The effect of temperature on the heat capacity of zircon is shown in Figure 3 and compared to experimentally available data. It can be seen that the heat capacity increases with temperature up to 500 K. Below this temperature; the heat capacity gradually approaches a linear increase. At this level, it seems to tend towards a limit value given by the Dulong-Petit formula. Generally speaking, the heat capacity of zircon increases with temperature. The agreement between our results and those of [8] and [22] was found to be quite good.

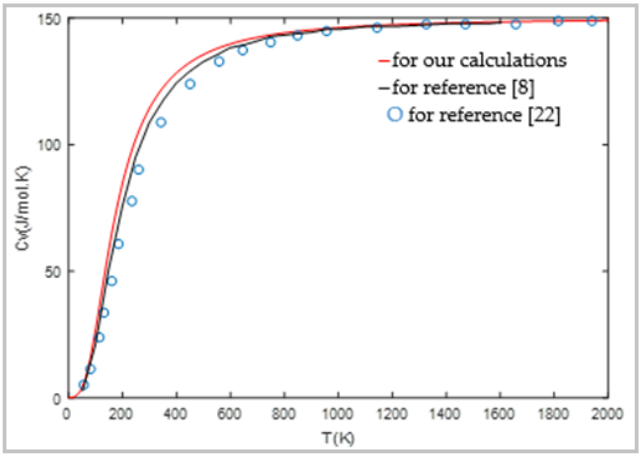

Figure 3. Temperature dependence of heat capacity of ZrSiO4

3.3. Internal Energy

Figure 4 illustrates the effect of temperature on the internal energy of zircon. The internal energy is almost zero for temperature values between 0K and 200 K. Beyond this

value, it increases monotonically with temperature. In short, internal energy is also an increasing function of temperature.

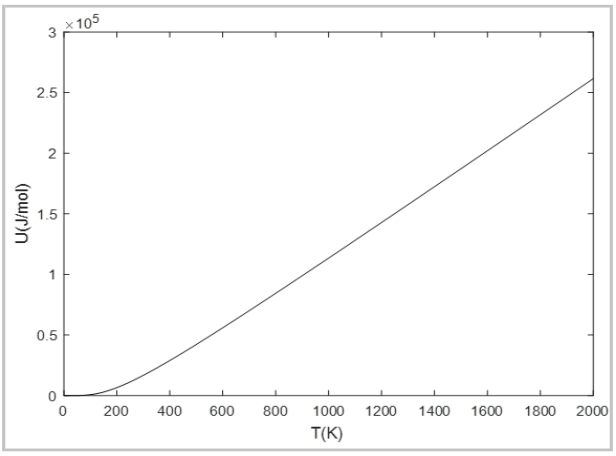

Figure 4. Temperature dependence of internal energy of ZrSiO4

3.4. Entropy

Figure 5 describes the effect of temperature on the entropy of zircon and compared to the experimentally available data. The curve indicates that the entropy is practically zero for the temperature values between 0K and 100 K and becomes moderately increasing beyond this temperature. Generally speaking, the entropy of zircon also increases with temperature. In addition, the agreement with reference [66] is considered excellent.

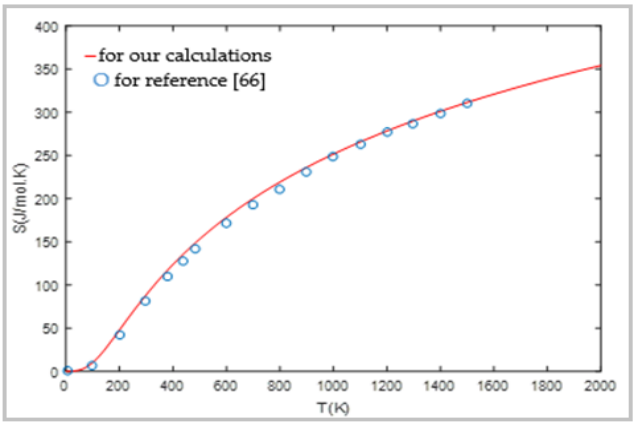

Figure 5. Temperature dependence of entropy of ZrSiO4

3.5. Comparaison

Figure 6 highlights the effect of temperature on the thermodynamic quantities of zircon. We can see that overall, all three quantities increase with temperature. In addition, we can see that up to 400 K, the thermal capacity is above the entropy which is above the internal energy. For temperature values between 400K and 1300K, entropy takes precedence over internal energy, which takes precedence over heat capacity. 400 K stands out as the common temperature between heat capacity and entropy; 1300 K is the common temperature between thermal capacity and internal energy. The salient fact is that there is no common temperature between entropy and internal energy.

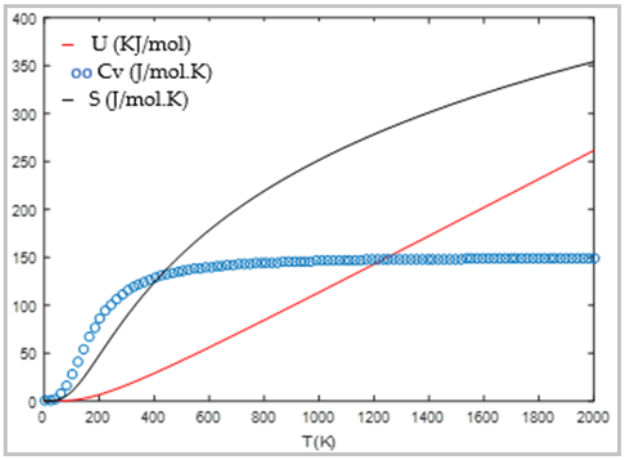

Figure 6. Temperature dependence of thermodynamic grandeur of ZrSiO4

4. Conclusions

Since the 1970s, understanding the thermodynamic properties of solids has become the focus of interest for researchers in quantum physics. This understanding necessarily requires a rational explanation of the behavior of the characteristics of the material studied as a function of temperature. The study that we present through this article follows this same logic. It is intended as a contribution to a theoretical study on the thermodynamic properties of zircon using the Debye quasi-harmonic model in which the vibrations of the network of atoms forming the solid are taken into account. This model has the advantage of being robust, faithful, precise and concise. These qualities make it the best suited tool for understanding the physical properties of materials. However, due to the structural complexity of Debye functions, we have developed a Matlab code in deterministic mode to calculate specific heat, internal energy and entropy. Our values are then compared to previous experimental and theoretical data available in the literature. At the end of the study, the results obtained are consistent and meaningful. The thermal capacity increases with temperature up to 500 K. Beyond this value, it tends to be linear with temperature. At this level, it seems to tend towards a limit value given by the Dulong-Petit formula. As for internal energy, it is almost zero for temperature values between 0K and 200 K. Beyond that, it increases monotonically with temperature. As for entropy, it is practically zero for temperature values between 0K and 100 K and becomes moderately increasing beyond this temperature. In general, the various calculated thermodynamic parameters systematically increase with temperature even if this growth is not identical. In addition, the agreement between our results and previous experimental and theoretical data was found to be quite good. This good agreement between the calculations sufficiently demonstrates that the Debye model gives a reasonable description of the behavior of the thermodynamic quantities of zircon as a function of temperature. Despite its success,

Debye's model has limits: it is not analytical, it considers the vibrations of the network of atoms forming the solid. However, it is useful to have analytical expressions for important functions in the equations of state of materials such as zircon. Thus, to give this study all its relevance, it is imperative to validate our results by exploiting other methods such as the Einstein model which is both analytical and numerical and based on the vibrations of independent atoms unlike the model. by Debye.

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Competing Interests

There is no conflict of interest related to this work.

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