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Physics

INVESTIGATION OF THERMODYNAMIC QUANTITIES OF THE CUBIC ZIRCONIA BY STATISTICAL MOMENT METHOD

Vu Van Hung, Le Thi Mai Thanh

Hanoi National Pedagogic University

Nguyen Thanh Hai

Hanoi University of Technology

Abstract. We have investigated the thermodynamic properties of the cubic zirconia ZrO_2 using the statistical moment method in the statistical physics. The free energy, thermal lattice expansion coefficient, specific heats at the constant volume and those at the constant pressure, C_V and C_P, are derived in closed analytic forms in terms of the power moments of the atomic displacements. The present analytical formulas including the anharmonic effects of the lattice vibrations give the accurate values of the thermodynamic quantities, which are comparable to those of the *ab initio* calculations and experimental values. The calculated results are in agreement with experimental findings. The thermodynamic quantities of the cubic zirconia are predicted using two different inter-atomic potential models. The influence of dipole polarization effects on the thermodynamic properties for cubic zirconia have been studied.

1. INTRODUCTION

Zirconia (ZrO_2) with a fluorite crystal structure is a typical oxygen ion conductor. In order to understand the ionic conduction in ZrO_2, careful should be to study the local behavior of oxygen ions close to the vacancy and the thermodynamic properties of zirconia. ZrO_2 is an important industrial ceramic combining high temperature stability and high strength [1]. Zirconia is also interesting as a structural material: It can form cubic, tetragonal and monoclinic or orthorhombic phases at high pressure. Pure zirconia undergoes two crystallographic transformations between room temperature and its melting point: monoclinic to tetragonal at $T \approx 1443$ K and tetragonal to cubic at $T \sim 2570$ K. The wide range of applications (for use as an oxygen sensor, technical application and basic research), particularly those at hightemperature, makes the derivation of an atomistic model especially important because experimental measurements of material properties at high temperatures are difficult to perform and are susceptible to errors caused by the extreme environment [2]. In order to understand properties of zirconia and predict them there is a need for atomic scale simulation. Molecular dynamics (MD) has recently been applied to the study of oxide ion diffusion in zirconia systems [3-5] and the effect of grain boundaries on the oxide ion conductivity of zirconia ceramic [6]. Such a model of atomic scale simulation should be required a reliable model for the energy and interatomic forces. First principles, or *ab initio* calculations give the most reliable information about properties, but they are only possible for very simple structures involving a few atoms per unit cell. More *ab initio* data are available concentrate on zero K structure information while experimental information is available at high temperatures (for example in the case of zirconia, > 1200°C [7]). In this respect, therefore, the *ab initio* and experimental data can be considered as complementary. Recently, it has been widely recognized that the thermal lattice vibrations play an important role in determining the properties of materials. It is of great importance to take into account the anharmonic effects of lattice vibrations in the computations of the thermodynamic quantities of zirconia. So far, most of the theoretical calculations of thermodynamic quantities of zirconia have been done on the basis of harmonic or quasi- harmonic (QH) theories of lattice vibrations, and anharmonic effects have been neglected.

The purpose of the present study is to apply the statistical moment method (SMM) in the quantum statistical mechanics to calculate the thermodynamic properties and Debye-Waller factor of the cubic zirconia within the fourth-order moment approximation. The thermodynamic quantities as the free energy, specific heats C_V ans C_P, bulk modulus, are calculated taking into account the anharmonic effects of the lattice vibrations. We compared the calculated results with the previous theoretical calculations as well as the experimental results. In the present study, the influence of dipole polarization effects on the thermodynamic properties have been studied. We compared the dependence of the results on the choice of interatomic potential models.

2. CALCULATING METHOD

2.1. Anharmonicity of lattice vibrations

First, we derive the expression of the displacement of an atom Zr or O in zirconia, using the moment method in statistical dynamics.

The basic equations for obtaining thermodynamic quantities of the crystalline materials are derived in the following manner. We consider a quantum system, which is influenced by supplemental forces a_i in the space of the generalized coordinates Q_i. The Hamiltonian of the lattice system is given as

$$H = H_0 - \sum_i a_i Q_i \tag{1}$$

where H_0 denotes the Hamiltonian of the crystal without forces a_i. After the action of the suplemental forces a_i, the system passes into a new equilibrium state. From the statistical average of a thermodynamic quantity $\langle Q_k \rangle$, we obtain the exact formula for the correlation. Specifically, we use a recurrence formula [8-10]

$$\langle K_{n+1} \rangle_a = \langle K_n \rangle_a \langle Q_{n+1} \rangle_a + \theta \frac{\partial \langle K_n \rangle_a}{\partial a_{n+1}} - \theta \sum_{m-0}^{\infty} \frac{B_{2m}}{(2m)!} \left(\frac{i\hbar}{\theta} \right)^{2m} \left\langle \frac{\partial K_n^{(2m)}}{\partial a_{n+1}} \right\rangle_a \tag{2}$$

where $\theta = k_B T$ and K_n is the correlation operator of the n-*th* order

$$K_n = \frac{1}{2^{n-1}} [\ldots [Q_1, Q_2]_+ Q_3]_+ \ldots]_+ Q_n]_+ \tag{3}$$

In Eq. (2), the symbol $\langle ... \rangle_a$ expresses the thermal averaging over the equilibrium ensemble, H represents the Hamiltonian, and B_{2m} denotes the Bernunlli numbers.

The general formula (Eq. (2)) enables us to get all of the moments of the system and to investigate the nonlinear thermodynamic properties of the materials, taking into account the anharmonicity effects of the thermal lattice vibration. In the present study, we apply this formula to find the Helmholtz free energy of zirconia (ZrO_2).

First, we assume that the potential energy of the system zirconia composed of N_1 atoms Zr and N_2 atoms O can be written as

$$\begin{aligned} U &= \frac{N_1}{2}\sum_i \varphi_{io}^{Zr}(|r_i+u_i|) + \frac{N_2}{2}\sum_i \varphi_{io}^{O}(|r_i+u_i|) \\ &\equiv C_{Zr}U_0^{Zr} + C_O U_0^O \end{aligned} \tag{4}$$

where U_0^{Zr}, U_0^O represent the sum of effective pair interaction energies between the zero-*th* Zr and i-*th* atoms, and the zero-*th* O and i-*th* atoms in zirconia, respectively. In the Eq. (4), r_i is the equilibrium position of the i-*th* atom, u_i its displacement, and φ_{io}^{Zr}, φ_{io}^{O}, the effective interaction energies between the zero-*th* Zr and i-*th* atoms, and the zero-*th* O and i-*th* atoms, respectively. We consider the zirconia ZrO_2 with two concentrations of Zr and O (denoted by $C_{Zr} = \frac{N_1}{N}, C_O = \frac{N_2}{N}$, respectively).

First of all let us consider the displacement of atoms Zr in zirconia. In the fourth-order approximation of the atomic displacements, the potential energy between the zero-*th* Zr and i-*th* atoms of the system is written as

$$\begin{aligned} \varphi_{io}^{Zr}(|r_i+u_i|) = \varphi_{io}^{Zr}(|r_i|) &+ \frac{1}{2}\sum_{\alpha,\beta}\left(\frac{\partial^2 \varphi_{io}^{Zr}}{\partial u_{i\alpha}\partial u_{i\beta}}\right)_{eq} u_{i\alpha}u_{i\beta} \\ &+ \frac{1}{6}\sum_{\alpha,\beta,\gamma}\left(\frac{\partial^3 \varphi_{io}^{Zr}}{\partial u_{i\alpha}\partial u_{i\beta}\partial u_{i\gamma}}\right)_{eq} u_{i\alpha}u_{i\beta}u_{i\gamma} \\ &+ \frac{1}{24}\sum_{\alpha,\beta,\gamma,\eta}\left(\frac{\partial^4 \varphi_{io}^{Zr}}{\partial u_{i\alpha}\partial u_{i\beta}\partial u_{i\gamma}\partial u_{i\eta}}\right)_{eq} u_{i\alpha}u_{i\beta}u_{i\gamma}u_{i\eta} + ... \end{aligned} \tag{5}$$

In Eq. (5), the subscript *eq* means the quantities calculated at the equilibrium state.

The atomic force acting on a central zero-*th* atom Zr can be evaluated by taking derivatives of the interactomic potentials. If the zero-*th* central atom Zr in the lattice is affected by a supplementary force a_β, then the total force acting on it must be zero, and one can obtain the relation

$$\begin{aligned} &\frac{1}{2}\sum_{i,\alpha}\left(\frac{\partial^2 \varphi_{io}^{Zr}}{\partial u_{i\alpha}\partial u_{i\beta}}\right)_{eq} < u_{i\alpha} > + \frac{1}{4}\sum_{i,\alpha,\gamma}\left(\frac{\partial^3 \varphi_{io}^{Zr}}{\partial u_{i\alpha}\partial u_{i\beta}\partial u_{i\gamma}}\right)_{eq} < u_{i\alpha}u_{i\gamma} > \\ &+ \frac{1}{12}\sum_{i,\alpha,\gamma,\eta}\left(\frac{\partial^4 \varphi_{io}^{Zr}}{\partial u_{i\alpha}\partial u_{i\beta}\partial u_{i\gamma}\partial u_{i\eta}}\right)_{eq} < u_{i\alpha}u_{i\gamma}u_{i\eta} > -a_\beta = 0 \end{aligned} \tag{6}$$

The thermal averages on the atomic displacements (called second- and third-order moments) $< u_{i\alpha}u_{i\gamma} >$ and) $< u_{i\alpha}u_{i\gamma}u_{i\eta} >$ can be expressed in terms of $< u_{i\alpha} >$ with the aid of Eq. (2). Thus, Eq. (6) is transformed into the form

$$\gamma\theta^2\frac{d^2y}{da^2} + 3\gamma\theta y\frac{dy}{da} + \gamma y^3 + ky + \gamma\frac{\theta}{k}(x\coth x - 1)y - a = 0 \tag{7}$$

with $\beta \neq \gamma = x, y, z.$ and $y \equiv < u_i >$
where

$$k = \frac{1}{2}\sum_i \left(\frac{\partial^2\varphi_{io}^{Zr}}{\partial u_{i\alpha}^2}\right)_{eq} \equiv m^*\omega_{Zr}^2 \text{ and } x = \frac{\hbar\omega_{Zr}}{2\theta} \tag{8}$$

$$\gamma = \frac{1}{12}\sum \left[\left(\frac{\partial^4\varphi_{io}^{Zr}}{\partial u_{i\alpha}^4}\right)_{eq} + 6\left(\frac{\partial^4\varphi_{io}^{Zr}}{\partial u_{i\beta}^2\partial u_{i\gamma}^2}\right)_{eq}\right] \tag{9}$$

In deriving Eq. (7), we have assumed the symmetry property for the atomic displacements in the cubic lattice:

$$< u_{i\alpha} > = < u_{i\gamma} > = < u_{i\eta} > \equiv < u_i > \tag{10}$$

Equation (7) has the form of a nonlinear differential equation, and , since the external force a is arbitrary and small, one can find the approximate solution in the form

$$y = y_0 + A_1a + A_2a^2 \tag{11}$$

Here, y_0 is the displacement in the case of absence of external force a. Hence, one can get the solution of y_0 as

$$y_0^2 \approx \frac{2\gamma\theta^2}{3k^3}A \tag{12}$$

In an analogical way as for finding Eq. (7), for the atoms O in zirconia ZrO_2, equation for the displacement of a central zero-*th* atom O has the form

$$\gamma\theta^2\frac{d^2y}{da^2} + 3\gamma\theta y\frac{dy}{da} + ky + \gamma\frac{\theta}{k}(x\coth x - 1)y + \beta\theta\frac{dy}{da} + \beta y^2 - a = 0 \tag{13}$$

with $\langle u_i\rangle_a \equiv y$; $x = \frac{\hbar\omega_O}{2\theta}$

$$k = \frac{1}{2}\sum_i \left(\frac{\partial^2\varphi_{io}^{O}}{\partial u_{i\alpha}^2}\right)_{eq} \equiv m^*\omega_O^2 \tag{14}$$

$$\gamma = \frac{1}{12}\sum_i \left[\left(\frac{\partial^4\varphi_{io}^{O}}{\partial u_{i\alpha}^4}\right)_{eq} + 6\left(\frac{\partial^4\varphi_{io}^{O}}{\partial u_{i\beta}^2\partial u_{i\gamma}^2}\right)_{eq}\right] \tag{15}$$

and

$$\beta = \frac{1}{2}\sum_i (\frac{\partial^3\varphi_{io}^{O}}{\partial u_{i\alpha}\partial u_{i\beta}\partial u_{i\gamma}})_{eq} \tag{16}$$

Hence, one can get the solution of y_0 of the atom O in zirconia as

$$y_0 \approx \sqrt{\frac{2\gamma\theta^2}{3K^3}A} - \frac{\beta}{3\gamma} + \frac{1}{K}(1 + \frac{6\gamma^2\theta^2}{K^4})[\frac{1}{3} + \frac{\gamma\theta}{3k^2}(x\coth x - 1) - \frac{2\beta^2}{27\gamma k}] \tag{17}$$

where the parameter K has the form

$$K = k - \frac{\beta^2}{3\gamma} \tag{18}$$

2.2. Helmholtz free energy of zirconia

We consider the zirconia $\mathrm{ZrO_2}$ with two concentrations of Zr and O (denoted by $C_{Zr} = \frac{N_1}{N}$, $C_O = \frac{N_2}{N}$, respectively). The atomic mass of zirconia is simply assumed to be the average atoms of $m^* = C_{Zr}m_{Zr} + C_O m_O$. The free energy of zirconia is then obtained by taking into account the configurational entropies S_c, via the Boltzmann relation, and written as

$$\psi = C_{Zr}\psi_{Zr} + C_O\psi_O - TS_c \tag{19}$$

where ψ_{Zr} and ψ_O denote the free energy of atoms Zr and O in zirconia, respectively. Once the thermal expansion y_0 of atoms Zr or O in the lattice zirconia is found, one can get the Helmholtz free energy of system in the following form:

$$\psi_{Zr} = U_0^{Zr} + \psi_0^{Zr} + \psi_1^{Zr} \tag{20}$$

where ψ_0^{Zr} denotes the free energy in the harmonic approximation and ψ_1^{Zr} the anharmonicity contribution to the free energy [11-13]. We calculate the anharmonicity contribution to the free energy ψ_1^{Zr} by applying the general formula

$$\psi_{Zr} = U_0^{Zr} + \psi_0^{Zr} + \int\limits_0^{\lambda} < \hat{V} >_\lambda d\lambda \tag{21}$$

where $\lambda\hat{V}$ represents the Hamiltonian corresponding to the anharmonicity contribution. It is straightforward to evaluate the following integrals analytically

$$I_1 = \int\limits_0^{\gamma_1} < u_i^4 > d\gamma_1, \quad I_2 = \int\limits_0^{\gamma_2} < u_i^2 >^2_{\gamma_1=0} d\gamma_2 \tag{22}$$

Then the free energy of the system is given by

$$\begin{aligned}\Psi_{Zr} \approx {}& \left\{U_0^{Zr} + 3N\theta[x + \ln(1-e^{-2x})]\right\} + \frac{3N\theta^2}{k^2}\left\{\gamma_2 x^2\coth^2 x - \frac{2\gamma_1}{3}\left(1 + \frac{x\coth x}{2}\right)\right\} \\ & + \frac{3N\theta^3}{k^4}\left\{\frac{4}{3}\gamma_2^2 x\coth x(1 + \frac{x\coth x}{2}) - 2(\gamma_1^2 + 2\gamma_1\gamma_2)(1 + \frac{x\coth x}{2})(1 + x\coth x)\right\}\end{aligned} \tag{23}$$

where U_0^{Zr} represents the sum of effective pair interaction energies between zero-*th* Zr and i-*th* atoms, the first term of Eq. (23) given the harmonicity contribution of thermal lattice vibrations and the other terms in the above Eq. (23) given the anharmonicity contribution of thermal lattice vibrations and the fourth-order vibrational constants γ_1, γ_2 defined by

$$\gamma_1 = \frac{1}{48}\sum_i \left(\frac{\partial^4\varphi_{io}^{Zr}}{\partial u_{i\alpha}^4}\right)_{eq}, \quad \gamma_2 = \frac{6}{48}\sum_i \left(\frac{\partial^4\varphi_{io}^{Zr}}{\partial u_{i\alpha}^2\partial u_{i\beta}^2}\right)_{eq} \tag{24}$$

In an analogical way as for finding Eq. (23), the free energy of atoms O in the zirconia ZrO_2 is given as

$$
\begin{aligned}
\Psi_O \approx & \left\{U_0^O + 3N\theta[x + \ln(1 - e^{-2x})]\right\} + \frac{3N\theta^2}{k^2}\left\{\gamma_2 x^2 \coth^2 x - \frac{2\gamma_1}{3}\left(1 + \frac{x\coth x}{2}\right)\right\} \\
& + \frac{3N\theta^3}{k^4}\left\{\frac{4}{3}\gamma_2^2 x\coth x(1 + \frac{x\coth x}{2}) - 2(\gamma_1^2 + 2\gamma_1\gamma_2)(1 + \frac{x\coth x}{2})(1 + x\coth x)\right\} \\
& + 3N\theta[\frac{\beta^2 k}{6K^2\gamma} - \frac{\beta^2}{6K\gamma}] + 3N_2\theta^2[\frac{\beta}{K}(\frac{2\gamma}{3K^3}a_1)^{1/2} - \frac{\beta^2 a_1}{9K^3} + \frac{\beta^2 k a_1}{9K^4} + \frac{\beta^2}{6K^2 k}(x\coth x - 1)].
\end{aligned}
\tag{25}
$$

Note that the parameters γ_1, γ_2 in the above Eq. (25) have the form analogous to (24), but φ_{io}^O, the effective interaction energies between the zero-*th* O and i-*th* atoms, respectively.

With the aid of the free energy formula $\psi = E - TS$, one can find the thermodynamic quantities of zirconia. The specific heats at constant volume C_V^{Zr}, C_V^O are directly derived from the free energy of the system ψ_{Zr}, ψ_O (23), (25), respectively, and then the specific heat at constant volume of the cubic zirconia is given as

$$C_V = C_{Zr}C_V^{Zr} + C_O C_V^O \tag{26}$$

We assume that the average nearest-neighbor distance of the cubic zirconia at temperature T can be written as

$$r_1(T) = r_1(0) + C_{Zr}y_0^{Zr} + C_O y_0^O \tag{27}$$

in which y_0^{Zr}(T) and $y_0^O(T)$are the atomic displacements of Zr and O atoms from the equlibrium position in the fluorite lattice, and $r_1(0)$ is the distance r_1 at zero temperature. In the above Eq. (27), y_0^{Zr} and y_0^O are determined from Eqs. (12) and (17), respectively. The average nearest-neighbor distance at $T = 0$ K can be determined from experiment or the minimum condition of the potential energy of the system of the cubic zirconia composed of N_1 atoms Zr and N_2 atoms O

$$
\begin{aligned}
\frac{\partial U}{\partial r_1} &= \frac{\partial U_0^{Zr}}{\partial r_1} + \frac{\partial U_0^O}{\partial r_1} \\
&= \frac{N_1}{2}\frac{\partial}{\partial r_1}\left(\sum_i \varphi_{io}^{Zr}(|r_i|)\right) + \frac{N_2}{2}\frac{\partial}{\partial r_1}\left(\sum_i \varphi_{io}^O(|r_i|)\right) = 0.
\end{aligned}
\tag{28}
$$

From the definition of the linear thermal expansion coefficient, it is easy to derive the result

$$\alpha_T = C_{Ce}\alpha_T^{Ce} + C_O\alpha_T^O, \tag{29}$$

where

$$\alpha_T^{Zr} = \frac{k_B}{r_1(0)}\frac{\partial y_0^{Zr}}{\partial \theta}, \quad \alpha_T^O = \frac{k_B}{r_1(0)}\frac{\partial y_0^O}{\partial \theta} \tag{30}$$

The bulk modulus of the cubic zirconia is derived from the free energy of Eq. (19) as

$$\begin{aligned} B_T &= -V_0\left(\frac{\partial P}{\partial V}\right)_T \\ &= -V_0\left(\frac{\partial^2\Psi}{\partial V^2}\right)_T = C_{Zr}B_T^{Zr} + C_O B_T^O \end{aligned} \tag{31}$$

where P denotes the pressure, V_0 is the lattice volume of the cubic zirconia crystal at zero temperature, and the bulk moduli B_T^{Ce} and B_T^O are given by

$$B_T^{Zr} = -\frac{k_B}{3\alpha_T^{Zr}}\left(\frac{\partial^2\Psi_{Zr}}{\partial V\partial\theta}\right), \quad B_T^O = -\frac{k_B}{3\alpha_T^O}\left(\frac{\partial^2\Psi_O}{\partial V\partial\theta}\right) \tag{32}$$

Due to the anharmonicity, the heat capacity at constant pressure, C_P, is different from the heat capacity at constant volume, C_V. The relation between C_P and C_V of the cubic zirconia is

$$C_P = C_V - T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T = C_V + 9\alpha_T^2 B_T VT. \tag{33}$$

3. RESULTS AND DISCUSSIONS

3.1. Potential dependence of thermodynamic quantities

With the use of the moment method in the statistical dynamics, we calculated the thermodynamic properties of zirconia with the cubic fluorite structure. In discussing the thermodynamic properties of zirconia, the Buckingham potential has been very successful. The atomic interactions are described by a potential function which divides the forces into long-range interactions (described by Coulomb's Law and summated by the Ewald method) and short-range interactions treated by a pairwise function of the Buckingham form

$$\varphi_{ij}(r) = \frac{q_i q_j}{r} + A_{ij}\exp(-\frac{r}{B_{ij}}) - \frac{C_{ij}}{r^6} \quad , \tag{34}$$

where q_i and q_j are the charges of ions i and j respectively, r is thedistance between them and A_{ij}, B_{ij} and C_{ij} are the parameters particular to each ion-ion interaction. In the Eq. (34), the exponential term corresponds to the electron cloud overlap and the C_{ij}/r^6 term any attractive dispersion or Van der Waal's force. Potential parameters A_{ij}, B_{ij} and C_{ij} have most commonly been derived by the procedure of 'empirical fitting', i.e., parameters are adjusted, usually by a least-squares fitting routine, so as to achieve the best possible agreement between calculated and experimental crystal properties. The potential parameters used in the present study were taken from Lewis and Catlow [14] and from Ref. [29].

The potential parameters are listed in Tables 1 and 2 compares the zero K lattice parameter predicted by *ab initio* calculations with previous calculations and two experimental values. The experimental values are derived from the high temperature neutron scattering data [7] and to zero impurity in the cubic stabilized structure [19]. We summarized here the results of different *ab initio* calculations and compare them to experimental

Table 1. *Short range potential parameters*

Interaction	A/eV	B/Å	C/eVÅ^6	
$O^{2-} - O^{2-}$	9547.92	0.2192	32.00	potential 1
$Zr^{4+} - O^{2-}$	1453.8	0.35	25.183	
$Zr^{4+} - Zr^{4+}$			9.274	
$O^{2-} - O^{2-}$	1500	0.149	27.88	potential 2
$Zr^{4+} - O^{2-}$	1453.8	0.35	25.183	
$Zr^{4+} - Zr^{4+}$			9.274	

Table 2. *Ab initio 0 K flourite lattice parameters of zirconia compared with present results and experimental values.*

Method	a_0(Å)	V(AA^3)	Ref.
CLUSTER	4.90	30.14	15
CRYSTAL	5.154	34.23	15
FLAPW-DFT	5.03	32.27	16
Hartree-Fock	5.035	31.91	17
Potential-induced breathing	5.101	33.19	18
LMTO	5.04	32.90	2
RIP	5.162	34.39	2
PWP-DFT	5.134	33.83	22
SMM (0 K)	5.0615	32.417	current work
SMM (2600 K)	5.2223	35.606	current work
Expt.	5.090	32.97	7
Expt.	5.127	33.69	19

ones. It is noted that the *ab initio* calculations of lattice paramerters at zero K, but present results by SMM at temperatures $T = 0$ K and $T = 2600$ K, while experimental values at high temperatures ($> 1500K$) [7]. The full-potential linearized augmented-plane-wave (FLAPW) *ab initio* calculation of Jansen [16], based on the density functional theory in the local-density approximation (LDA), give $a_0(A^0)$= 5.03, while Hartre-Fock calculations (the CRYSTAL code) give $a_0(A^0)$= 5.035 (both at zero K). The linear muffin-tin orbital (LMTO) *ab initio* calculations of lattice parameters are larger than both experimental values and are in best agreement with the Hartree-Fock calculation [17]. The potential-induced breathing model [18] (PIB) augments the effective pair potential (EPP) by allowing for the spherical relaxation (‘’breathing”) of the oxide anion charge density, calculated by using a Watson sphere method, give a_0(Å)= 5.101 (at $T = 0$ K). The density functional theory (DFT) within the plane-wave pseudopotential (PWP) [22] and RIP give a_0(Å) = 5.134, and a_0 (Å) = 5.162. These results and the CRYSTAL calculation [15] are larger than the experimental values. Our SMM calculations give a lattice parameter a =5.0615(Å) and unit cell volume V(Å^3) = 32.417 at zero temperature and are in best agreement with the experimental values [7] and FLAPW-DFT, LMTO and Hartree-Fock calculations.

Table 3 lists the thermodynamic quantities of the cubic fluorite zirconia calculated by the present SMM using potential 1. The experimental nearest-neighbor anion-anion separations r_2^{O-O} lie in the range $2.581 - 2.985$Å[21], while the current SMM give 2.5931 Å (without dipole polarization effects) and 2.6031Å (with dipole polarization effects) at $T =$ 2600 K, and are in best agreement with the *ab initio* calculations [2]. These calculations [2] used a potential fitted to *ab initio* calculations using the oxide anion electron the density appropriate to the equilibrium lattice parameter give 2.581 Å as the fluorite analog for all nearest-neighbor pairs. The nearest-neighbor cation-anion separations r_1^{Zr-O} calculated by SMM lie in the range 2.2543-2.2669Å (with dipole polarization effects) and $2.2457 \div 2.2557$ Å(without dipole polarization effects) corresponding to the temperature range $T = 2600 \div$ 3000 K and being in best agreement with the first-principles calculations give 2.236 Å in cubic zirconia [23]. We also calculated the bulk modulus B_T of the cubic zirconia as function of the temperature T. We have found that the bulk modulus B_T depends strongly on the temperature and is a decreasing function of T. The decrease of B_T with increasing temperature arises from the thermal lattice expansion and the effects of the vibration entropy. At zero temperature, the EPP (EPP- OO) in which the $O^{2-} - O^{2-}$ short-range term is neglected, gives the bulk modulus $B_T = 201(GPa)$, and the CIM calculations of the short-range anion-cation interactions with and without full dipolar and quadruppolar polarization effects, give the bulk modulus $B_T = 204(GPa)$ [2], while the experimental results of the bulk modulus $B_T = 194(GPa)$ [20]. The two bulk modulus calculated by CIM (no polarization and full polarization) for the fluorite structure are equal and greater than the experimental values while the SMM results of the bulk modulus at high temperature ($T = 2600$ K) are smaller than the experimental ones. At lower temperatures the SMM calculations of the bulk modulus give a much better agreement with experiment, because the bulk modulus are the decreasing functions of the temperature. Above about 2570 K (up to the melting point at 2980 K), the zirconia is assumed to have the cubic fluorite structure. In this phase the thermodynamic quantities as the lattice parameter, a, specific heats at constant volume and pressure, C_V, C_P, and the bulk modulus, B_T,... are calculated by the present SMM using potentials 1 and 2. Table 4 lists the thermodynamic quantities of the cubic fluorite zirconia calculated by the present SMM using potential 2. Tables 3 and 4 show the thermodynamic quantities, a, C_V, C_P and B_T, for the cubic phase of the bulk zirconia as functions of the temperature T. The variations in temperature of the specific heats at constant volume and pressure C_V, C_P, reported in Fig. 1, show that the specific heat C_V depends slightly on the temperature, but the specific heat C_P depends strongly on T. Similarly, Figs. 2 and 3, and Tables 3 and 4 show that the linear thermal expansion coefficient, α, and the bulk modulus, B_T, depend strongly on the temperature. The linear thermal expansion coefficient α determined experimentally by Terreblanche [24], i. e. $\alpha = 10.5 \times 10^{-6} K^{-1}$, a value which is practically independent of the yttria content and also close to the thermal expansion coefficient of the tetragonal phase [25]. This experimental value is also close to the value calculated in the present study using potential 1 for the cubic phase of bulk zirconia at the temperature $T = 2600$ K. For the specific heat capacity C_P of the cubic zirconia, the reference data reported by Chase [26] give $C_P \sim 640$ J/(kg.K) at $T \sim 1400$ K, while the current SMM using potential 1 gives $C_P = 9.4316$ cal/(mol.K) (with dipole polarization effects) and $C_P = 8.8674)$ cal/(mol.K) (without dipole polarization effects) at T = 2600 K. The lattice specific heats C_V and C_P at constant volume and at constant pressure are calculated using Eqs. (26) and (33), respectively. However, the evaluations by Eqs. (26) and (33) are the lattice contributions, and we do not include the contributions of lattice vacancies and electronic parts of the specific heats C_V. The calculated values of the lattice specific heats C_V and C_P by the present SMM may not be directly compared with the corresponding experimental values for high temperature region (from T = 2600 K to the melting temperature), but the temperature dependence (curvature) of C_P for the cubic phase of the bulk zirconia is in agreement with the experimental results.

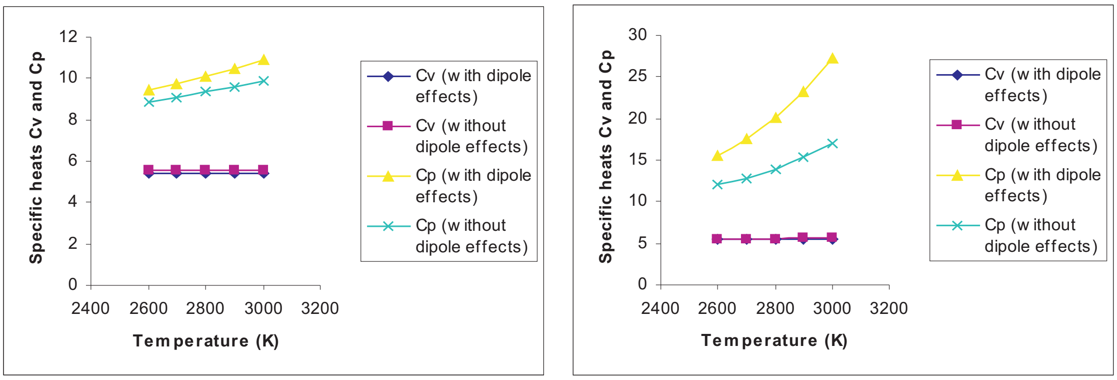

Fig. 1. Temperature dependence of specific heats Cv and Cp (in cal/ mol.K) for zirconia: using potential 1 ; b) using potential 2

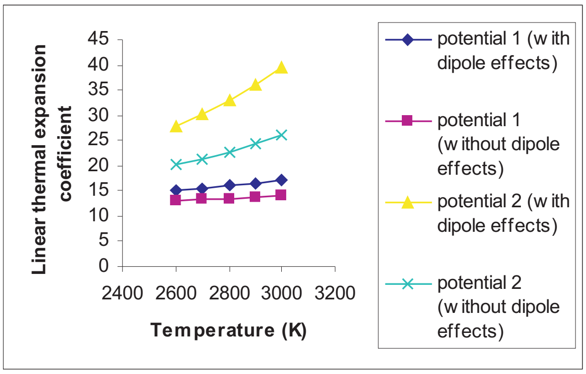

Fig. 2. Temperature dependence of the linear thermal expansion coefficient (in $10^{-6}K^{-1}$) for the cubic zirconia

Table 3. *Calculated thermodynamic quantities of the cubic zirconia using potential 1*

T (K)		2600	2700	2800	2900	3000
r_1^{Zr-O}(Å)	+with dipole	2.2543	2.2572	2.2603	2.2636	2.2669
	+without dipole	2.2457	2.2481	2.2506	2.2531	2.2557
r_2^{O-O}(Å)	+with dipole	2.6031	2.6065	2.6101	2.6138	2.6177
	+without dipole	2.5931	2.5959	2.5987	2.6016	2.6047
a(Å)	+with dipole	5.2061	5.2130	5.2201	5.2276	5.2353
	+without dipole	5.1863	5.1918	5.1975	5.2033	5.2093
$\alpha(10^{-6}K^{-1})$	+with dipole	15.135	15.559	16.017	16.535	17.121
	+without dipole	12.948	13.230	13.527	13.854	14.215
C_V (cal/mol.K)	+ with dipole	5.4374	5.4390	5.4405	5.4421	5.4436
	+without dipole	5.5353	5.5407	5.5461	5.5515	5.5568
C_P (cal/mol.K)	+with dipole	9.4316	9.7435	10.0836	10.4669	10.8915
	+without dipole	8.8673	9.0985	9.3440	9.6106	9.9026
$B_T(GPa)$	+with dipole	146.136	142.938	139.723	136.402	132.975
	+without dipole	168.498	165.410	162.335	159.179	155.932
$V(A^{o3})$	+with dipole	35.2759	35.4163	35.5612	35.7147	35.8728
	+without dipole	34.8742	34.9856	35.1003	35.2185	35.3409

Fig. 4 shows the lattice parameter, a, for cubic zirconia is calculated by the present SMM using potentials 1 and 2 as functions of the temperature T. The difference between the SMM calculated results using potentials 1 and 2 for the lattice parameter is very small. This difference is related to the effect of the oxygen-oxygen interactions, since the Coulombic contribution and the zirconium-oxygen potential are the same for the SMM calculations using potentials 1 and 2. Fig. 4 shows that potential 1 gives a low theoretical value for the lattice parameter. The values of the lattice parameters calculated by two potentials are very slightly different, i. e. the choice of potential has very little effect upon the lattice parameter, but it does play a important role in determining the bulk modulus and the thermal expansion coefficient. Tables 3 and 4 and Figs. 2 and 3 show the bulk modulus, B_T, and the linear thermal expansion coefficient, α, of the cubic zirconia depends strongly both on the temperature and the potential sets. Potential 1 gives the highest values for the bulk modulus, B_T, and the lowest values for the linear thermal expansion coefficient, α, while the potential 2 gives the lowest values for B_T, and the highest values for α. Potential 2 gives the lower bulk modulus and higher thermal expansion coefficient

Table 4. *Calculated thermodynamic quantities of the cubic zirconia using potential 2*

T (K)		2600	2700	2800	2900	3000
r_1^{Zr-O}(Å)	+with dipole	2.2794	2.2859	2.2931	2.3143	2.3350
	+without dipole	2.2613	2.2655	2.2699	2.2749	2.2803
r_2^{O-O}(Å)	+with dipole	2.6321	2.6395	2.6479	2.6571	2.6675
	+without dipole	2.6112	2.6160	2.6212	2.6269	2.6331
a(Å)	+with dipole	5.2642	5.2791	5.2957	5.3143	5.3350
	+without dipole	5.2223	5.2319	5.2423	5.2537	5.2662
$\alpha(10^{-6}K^{-1})$	+with dipole	27.767	30.171	32.916	36.070	39.659
	+without dipole	20.253	21.458	22.832	24.426	26.262
C_V (cal/mol.K)	+with dipole	5.4147	5.4153	5.4160	5.4166	5.4172
	+without dipole	5.5658	5.5723	5.5788	5.5853	5.5918
C_P (cal/mol.K)	+with dipole	15.6333	17.6243	20.1202	23.2843	27.2901
	+without dipole	11.9906	12.8899	13.9706	15.2774	16.9262
$B_T(GPa)$	+with dipole	107.447	103.821	100.348	97.019	93.871
	+without dipole	130.059	126.382	122.705	119.004	115.331
$V(A^{o3})$	+with dipole	36.4691	36.7806	37.1293	37.5205	37.9606
	+without dipole	35.6062	35.8029	36.0168	36.1833	36.5117

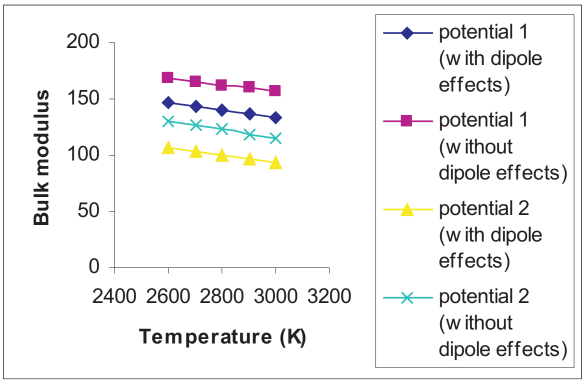

Fig. 3. Temperature dependence of the bulk modulus (in GPa) for the cubic zirconia

than the potential 1, since potential 2 is based on a different oxygen-oxygen potential. It would be reasonable to conclude that the low bulk modulus and high thermal expansion

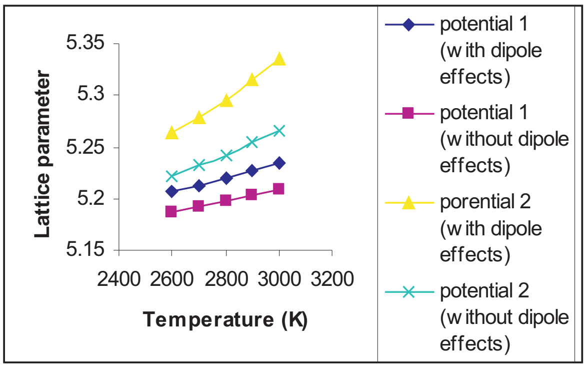

Fig. 4. Temperature dependence of the lattice paramater (in Å) for the cubic zirconia

coefficient predicted by potential 2 are due to the effect of the oxygen-oxygen interactions. Fig. 1 and Tables 3 and 4 show also that the deference between the SMM calculated results using potentials 1 and 2 for the specific heat C_V is very small, but the specific heat C_P depends strongly on the choice of the potential. The potential 2 gives the higher thermal expansion coefficient and lattice parameter than the potential 1, therefore the specific heat C_P has the higher values. We see that the large difference in $O^{2-} - O^{2-}$ interatomic potential of potentials 1 and 2 (the exponential term corresponds to the electron cloud overlap term,$A\exp(-r/B)$, and the attractive term, C_{ij}/r^6,) determined the role of the various contributions to the thermodynamic properties of the cubic zirconia.

3.2. Dipole polarization effects

We have investigated here the influence of the dipole polarization effects on the thermodynamic properties of the cubic zirconia. The calculated lattice constants by the present SMM with dipole polarization effects are greater than those of calculations using the SMM without dipole polarization effects. But the present SMM calculations with dipole polarization effects for the bulk modulus using all two potentials give the smaller values. The lattice constants increase due to the effect of the dipole interaction term (C/r^6) in the two potentials, therefore the bulk modulus becomes smaller. The contribution of the dipole polarization effects on the lattice constants and the specific heat C_V is approximately $\sim$1 %, and $\sim$ 2 %, respectively, while this contribution $\sim$ 13-15 % (for potential 1) and $\sim 15 - 17$ % (for potential 2) for the bulk modulus, B_T. For the thermal expansion coefficient, α, and the specific heat at constant pressure, C_P, the contribution of the dipole polarization effects is larger, approximately $\sim$ 20 % (using potential 1) and $\sim$37-50 % (using potential 2) for α, and approximately $\sim$ 10 % (using potential 1) and $\sim$30-60 % (using potential 2) for C_P, respectively. The effect of the dipole polarization is to increase the temperature and stronger for the potential 2. The small dipoles that do arise do so as a result of small displacement of the anions from the ideal lattice sites. The dipole polarization effects are small to the lattice constants and the specific heat C_V, but large enough to the bulk modulus, B_T, thermal expansion coefficient, α, and specific heat at constant pressure, C_P.

The dipolar part of the potential model is much better defined because it has been obtained from *ab initio* calculations [2]. When both dipole and quadruppole effects are added the calculations of the some thermodynamic properties for the cubic zirconia (for example the cubic equilibrium volume, . . .) give a much better agreement with the experimental results [2]. However, in cubic fluorite zirconia $\mathrm{ZrO_2}$ the polarization energies are small and in the crystalline environment the high symmetry of the anion site may more effectively cancel the induced quadruppole effects.

4. CONCLUSIONS

We have presented an analytic formulation for obtaining the thermodynamic quantities of the cubic zirconia $\mathrm{ZrO_2}$ based on the statistical moment method in the statistical physics. The present formalism takes into account the higher-order anharmonic terms in the atomic displacements and it enables us to derive the various thermodynamic quantities of the cubic zirconia for a wide temperature range (the cubic phase of zirconia is stable between 2570 K and the melting temperature at 2980 K [28]. The analytic formulae can be used not only for the cubic zirconia but also for other oxide materials with the cubic fluorite structure. The calculated thermodynamic quantities of the cubic zirconia are in good agreement with the experimental results as well as with those by *ab initio* calculations (in some cases, better results by the present method).

The two inter-atomic potentials (potentials 1 and 2) used in this study give small differences in the lattice parameter, specific heat C_V, but give the larger differences in the linear thermal expansion coefficient, α, bulk modulus, B_T, specific heat at constant pressure, C_P,. This is mainly due to the large difference between the $O^{2-} - O^{2-}$ potential interactions of potentials 1 and 2. In the present study, the influence of the dipole polarization effects on the thermodynamic peoperties of the cubic zirconia have been studied. The SMM calculation with the dipolar term is necessary in order to explain all the data we have from experiments and simulation calculations.

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