

# Thermodynamical functions for crystals with large unit cells such as zircon, coffinite, fluorapatite, and iodoapatite from *ab initio* calculations

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We derive thermodynamical functions for some large unit cell ionocovalent crystals from the well known quasiharmonic free energy model with the help of *ab initio* calculations. In order to keep the computation time within reasonable bounds the *ab initio* assessment applies only to the cohesive energy as a function of volume, Poisson's ratio, and the harmonic vibration frequencies at the  $\Gamma$  point for the unit cell at zero static pressure. These quantities are obtained by solving the electronic Schrödinger equation in the framework of the electronic density functional theory using available packages. Thermal contributions are estimated using the Debye model for acoustic modes and the extended Grüneisen method for optical modes. We have estimated in this way the thermodynamical functions of some crystals relevant to radioactive waste management such as zircon, coffinite, fluorapatite, and, in the end, iodoapatite, which is able to immobilize  $^{129}\text{I}$ . For zircon, coffinite, and fluorapatite for which the main thermodynamical functions are experimentally known, the enthalpy of formation in standard conditions is determined within 6% of the experimental value, and heat capacities at constant pressure are well reproduced, within 5%, at any temperature up to the dissociation temperature. For iodoapatite there are as yet no published experimental thermochemical data to compare to the present theoretical results.

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## I. INTRODUCTION

Knowledge of thermodynamical functions is essential to study crystal stability and chemical reactivity. They are not always experimentally known. In this paper, we calculate these functions for a ionocovalent crystal starting from the free energy modeled at the quasiharmonic approximation level recalled in Sec. II and with the help of *ab initio* calculations,<sup>1</sup> in the sense that no adjustable or experimental parameters enter the calculation. Though theoretically possible, a full *ab initio* calculation is not realistic when the unit cell contains many atoms because the calculation time becomes rapidly too large. We have therefore simplified this free energy model in order to reduce the overall calculation time. Simplifications, presented in Sec. III, consist of calculating the thermal contributions using a Debye model for the acoustic modes and the extended Grüneisen method for optical modes. The *ab initio* calculation part is reduced to the energy of the static lattice (i.e., each atom occupies its mean position) as a function of volume  $E(V)$  and, for equilibrium structure at zero static pressure (denoted with a superscript 0) normal-mode frequencies  $\nu_i^0(\Gamma)$  calculated at the  $\Gamma$  point and Poisson's ratio for uniaxial stress  $\sigma^0$  along  $c$ . As described in Sec. IV, *ab initio* calculations are performed using the DMOL<sup>3</sup> code,<sup>2</sup> which solves the electronic Schrödinger equation within the electronic density functional theory in the local density approximation (LDA) and gradient corrected LDA versions.

We have calculated in this way the thermodynamical functions of zircon, coffinite, fluorapatite, and lead vanado-iodoapatite. Results are given in Sec. V. Zircon  $\text{ZrSiO}_4$  has been widely studied, in particular as a durable actinide-host matrix in the framework of radioactive waste management.<sup>3</sup> Its main thermodynamical functions are experimentally known<sup>4-6</sup> and we compare them with our theoretical calcu-

lations. According to the literature,<sup>7</sup> coffinite  $\text{USiO}_4$ , which is isostructural to zircon, is one of the mineral phases determining uranium solubility in accidental corrosion of nuclear fuel by geological groundwater. However, the thermodynamical functions<sup>8,9</sup> of this mineral are not known as well as those of zircon and therefore give rise to our interest. Apatites<sup>10</sup> constitute a family of compounds that are susceptible of incorporating many chemical elements and in particular some radionuclides after spent fuel reprocessing. Fluorapatite  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  is the best-known apatite from a thermodynamical point of view.<sup>11-13</sup> This makes possible a comparison between theory and experiment in the same way as for zircon. On the other hand, the thermodynamical functions of the lead vanado-iodoapatite  $\text{Pb}_{9.85}(\text{VO}_4)_6\text{I}_{1.7}$  synthesized in order to immobilize iodine-129,<sup>14-16</sup> studied here in its stoichiometric composition  $\text{Pb}_5(\text{VO}_4)_3\text{I}$ , have only partially been measured<sup>17</sup> and thus only thermal conductivity, volume thermal expansion, and Young's modulus are experimentally known.

## II. THERMODYNAMICAL FUNCTIONS IN THE QUASIHARMONIC APPROXIMATION

In this section we recall essentials of the free energy model at the quasiharmonic approximation level. A crystal lattice, containing  $N$  cells of  $n$  atoms per cell, may be considered as an assembly of  $3Nn$  independent harmonic oscillators of frequencies  $\nu_i$  ( $i = 1, \dots, 3Nn$ ) associated with the normal-mode vibrations calculated with the harmonic approximation.<sup>18</sup> The free energy of the crystal may then be deduced from statistical mechanics of harmonic oscillators:

$$F = E + k_B T \sum_{i=1}^{3Nn} \left[ \frac{x_i}{2} + \ln(1 - e^{-x_i}) \right], \quad (1)$$

with  $x_i = h\nu_i/k_B T$ .  $T$  is the absolute temperature,  $k_B$  and  $h$  being Boltzmann's and Planck's constants, respectively. In Eq. (1)  $E$  is the energy of the static lattice in which each atom occupies its mean position. If the crystal is submitted to a pressure change at constant temperature or to a temperature change at constant pressure, we consider that the response of the crystal is only an isotropic change in its volume  $V$ . Therefore  $E$  and  $\nu_i$  are to be considered as functions of  $V$  in the quasiharmonic approximation.<sup>19</sup> From the free energy we deduce entropy  $S = -(\partial F/\partial T)_V$ , internal energy  $U = F + TS$ , and heat capacity at constant volume  $C_V = (\partial U/\partial T)_V$  as well as pressure  $p = -(\partial F/\partial V)_T$  and bulk modulus at constant temperature  $B = -V(\partial p/\partial V)_T$ . The total pressure is given by

$$p = -\frac{dE}{dV} + k_B T \sum_{i=1}^{3Nn} \frac{\gamma_i}{V} \left[ \frac{x_i}{2} + \frac{x_i}{e^{x_i} - 1} \right], \quad (2)$$

where  $\gamma_i$  is the dimensionless quantity called the Grüneisen parameter in the Mie-Grüneisen theory:

$$\gamma_i = -\frac{d \ln \nu_i}{d \ln V}. \quad (3)$$

In Eq. (2) the first term is defined as the static pressure, and the second one is the dynamic pressure equal to the sum of zero point vibrations and thermal pressures. Moreover, once  $B$  is known it is convenient to deduce the coefficient of thermal expansion at constant pressure  $\alpha$  from the product  $B\alpha = (\partial p/\partial T)_V$ . Finally, the heat capacity at constant pressure is obtained from

$$C_p = C_V + TVB\alpha^2. \quad (4)$$

In a crystal, the Born-von Kármán theory and the Bloch theorem lead to a classification of the  $3Nn$  vibration frequencies as  $3n$  branches  $\nu_i(\vec{k})$  ( $i = 1, \dots, 3n$ ) for  $N$  values of wave vector  $\vec{k}$  in the first Brillouin zone. These  $3n$  frequency dispersion branches are further divided into three acoustic branches  $\nu_{ac,i}(\vec{k})$  and  $3n - 3$  optical branches  $\nu_{op,i}(\vec{k})$ . In the free energy equation (1) and the derived quantities we may then replace the sum  $\sum_{i=1}^{3Nn}$  by the double sums  $\sum_{i=1}^3 \sum_{\vec{k}} + \sum_{i=4}^{3n} \sum_{\vec{k}}$ . Finally, for large  $N$  the sum over  $\vec{k}$  can be converted into an integral over the first Brillouin zone  $\sum_{\vec{k}} \rightarrow NV/(2\pi)^3 \int d^3k$ .

From this point and with an *ab initio* code for solid state materials with periodic structure it should be possible to calculate both the static energy and the  $3n$  frequency dispersion branches as a function of volume. From then on the Grüneisen parameter  $\gamma_i$  evaluation should be possible. In practice this is not feasible because for large  $n$  the calculation time for the frequency dispersion branches and their derivatives with respect to volume becomes prohibitive.

### III. SIMPLE TREATMENT OF THERMODYNAMICAL FUNCTIONS

In order to make *ab initio* computations tractable we must simplify the thermal part of the free energy model presented

in Sec. II. For this purpose we start by approximating the frequency dispersion branches for  $\vec{k} \neq \vec{0}$  by the Debye model<sup>20</sup> for the acoustic frequencies,

$$\nu_{ac,i}(\vec{k}) = (v_i/2\pi)k, \quad i = 1, 2, 3 \quad (5)$$

where  $v_i$  represents the phase velocity of the acoustic vibrations and  $k = |\vec{k}|$ , and by the Einstein model for the optical frequencies,

$$\nu_{op,i}(\vec{k}) = \nu_i(\Gamma), \quad i = 4, 3n \quad (6)$$

in which  $\nu_i(\Gamma)$  denotes the frequencies of vibration at the  $\Gamma$  point or zone center  $\vec{k} = \vec{0}$ . Subsequently, we replace  $v_1$ ,  $v_2$ , and  $v_3$  by a mean velocity  $\langle v \rangle$ . It is possible to show that due to Eq. (5) and the replacement of discrete sums over  $\vec{k}$  by integrals the mean velocity must be equal to

$$\frac{3}{\langle v \rangle^3} = \sum_{i=1}^3 \frac{1}{v_i^3}. \quad (7)$$

Next we assume that the first Brillouin zone polyhedron can be approximated by a sphere of radius  $k_{\max}$ . If  $V$  represents the unit cell volume, then  $k_{\max}$  is given by

$$k_{\max} = (6\pi^2/V)^{1/3}. \quad (8)$$

Consequently the Grüneisen parameters  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_3$  given by Eq. (3) are all equal to a value  $\gamma_{ac}$  called here the acoustic Grüneisen parameter:

$$\gamma_{ac} = -V \frac{d \ln(\langle v \rangle k_{\max})}{dV}. \quad (9)$$

As for the Grüneisen parameters  $\gamma_i$  for  $i = 4, \dots, 3n$ , they are all taken equal to a value  $\gamma_{op}$  or optical Grüneisen parameter, which will be determined later. To write the thermodynamical functions, it is convenient to separate the static quantities from the dynamic ones, the latter being frequency dependent:

$$F = F_{\text{sta}} + F_{\text{ac}} + F_{\text{op}}, \quad (10)$$

$$S = S_{\text{ac}} + S_{\text{op}}, \quad (11)$$

$$U = F_{\text{sta}} + F_{\text{ac}} + TS_{\text{ac}} + F_{\text{op}} + TS_{\text{op}}, \quad (12)$$

$$C_V = C_{V\text{ac}} + C_{V\text{op}}, \quad (13)$$

$$p = p_{\text{sta}} + \frac{\gamma_{ac}}{V}(F_{\text{ac}} + TS_{\text{ac}}) + \frac{\gamma_{op}}{V}(F_{\text{op}} + TS_{\text{op}}), \quad (14)$$

$$\begin{aligned} B = B_{\text{sta}} + & \left( \frac{\gamma_{ac}^2}{V} + \frac{\gamma_{ac}}{V} - \frac{d\gamma_{ac}}{dV} \right) (F_{\text{ac}} + TS_{\text{ac}}) - T \frac{\gamma_{ac}^2}{V} C_{V\text{ac}} \\ & + \left( \frac{\gamma_{op}^2}{V} + \frac{\gamma_{op}}{V} - \frac{d\gamma_{op}}{dV} \right) (F_{\text{op}} + TS_{\text{op}}) - T \frac{\gamma_{op}^2}{V} C_{V\text{op}}, \end{aligned} \quad (15)$$

$$B\alpha = \frac{\gamma_{ac}}{V} C_{V\text{ac}} + \frac{\gamma_{op}}{V} C_{V\text{op}}, \quad (16)$$

with

$$F_{\text{sta}} = E(V), \quad (17)$$

$$p_{\text{sta}} = - \frac{dE(V)}{dV}, \quad (18)$$

$$B_{\text{sta}} = V \frac{d^2 E(V)}{dV^2}, \quad (19)$$

$$F_{\text{ac}} = Nk_B T \left[ \frac{9}{8} x_D + 3 \ln(1 - e^{-x_D}) - D(x_D) \right], \quad (20)$$

$$F_{\text{op}} = Nk_B T \sum_{i=4}^{3n} \left[ \frac{x_i}{2} + \ln(1 - e^{-x_i}) \right], \quad (21)$$

$$S_{\text{ac}} = Nk_B [4D(x_D) - 3 \ln(1 - e^{-x_D})], \quad (22)$$

$$S_{\text{op}} = Nk_B \sum_{i=4}^{3n} \left[ \frac{x_i}{e^{x_i} - 1} - \ln(1 - e^{-x_i}) \right], \quad (23)$$

$$C_{\text{vac}} = Nk_B \left[ 12D(x_D) - 9 \frac{x_D}{e^{x_D} - 1} \right], \quad (24)$$

$$C_{\text{vop}} = Nk_B \sum_{i=4}^{3n} \left[ \frac{(x_i)^2 e^{x_i}}{(e^{x_i} - 1)^2} \right]. \quad (25)$$

In these equations  $x_i = h\nu_i(\Gamma)/k_B T$  and  $D(x_D)$  is the Debye function defined by

$$D(x_D) = \frac{3}{(x_D)^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx, \quad (26)$$

with  $x_D = \Theta_D/T$ .  $\Theta_D$  is the Debye temperature given by

$$\Theta_D = h\langle v \rangle k_{\text{max}} / 2\pi k_B. \quad (27)$$

To estimate the Debye temperature and the acoustic Grüneisen parameter, we consider an ideal isotropic crystal where two vibrations are transverse with the same velocity  $v_1 = v_2 = v_t$ , and the remaining vibration is longitudinal with velocity  $v_3 = v_l$ . The velocities  $v_t$  and  $v_l$  are given by<sup>21</sup>

$$v_l = \left( \frac{3B}{\rho} \frac{1 - \sigma}{1 + \sigma} \right)^{1/2}, \quad (28)$$

$$v_t = \left( \frac{3B}{2\rho} \frac{1 - 2\sigma}{1 + \sigma} \right)^{1/2}, \quad (29)$$

where  $\sigma$  is Poisson's ratio for uniaxial stress applied along the  $c$  axis,

$$\sigma = - \frac{d \ln a}{d \ln c}, \quad (30)$$

and  $\rho$  is the mass per unit volume given by

$$\rho = \sum_{j=1}^n m_j / \mathcal{N}V, \quad (31)$$

where  $m_j$  is the atomic mass of atom  $j$  and  $\mathcal{N}$  is Avogadro's number. In the following in order to calculate velocities  $v_t$  and  $v_l$  we use  $B_{\text{sta}}$  given by Eq. (19) in place of  $B$  and Poisson's ratio  $\sigma^0$ , calculated near the equilibrium structure at zero static pressure, in place of  $\sigma$ . We obtain

$$\Theta_D = \frac{h}{k_B} \left( \frac{9}{4\pi V} \right)^{1/3} \left( 3 \frac{B_{\text{sta}}}{\rho} \right)^{1/2} \left( \frac{1 - \sigma^0}{1 + \sigma^0} \right)^{1/2} \times \left[ 1 + 2 \left( \frac{2 - 2\sigma^0}{1 - 2\sigma^0} \right)^{3/2} \right]^{-1/3}, \quad (32)$$

$$\gamma_{\text{ac}} = \frac{3K_{\text{sta}} - 1}{6}, \quad (33)$$

with

$$K_{\text{sta}} = \frac{dB_{\text{sta}}}{dp_{\text{sta}}}. \quad (34)$$

To calculate the optical Grüneisen parameter we use an extension of Mie-Grüneisen theory<sup>22-24</sup> in which it is assumed that all optical frequencies are proportional to the square root of the second derivative of the static energy with respect to Wigner-Seitz radius. In this work we replace the latter by the cubic root of the unit cell volume. We obtain with these assumptions

$$\gamma_{\text{op}} = \frac{V}{4} \frac{d}{dV} \ln \frac{d^2 E(V)}{(dV^{1/3})^2} = \frac{9B_{\text{sta}}(K_{\text{sta}} - 1) + 2P_{\text{sta}}}{6(3B_{\text{sta}} - 2P_{\text{sta}})}. \quad (35)$$

The last important simplification pertains to the vibration frequencies at the  $\Gamma$  point. We calculate *ab initio* only those corresponding to the equilibrium unit cell volume  $V^0$  at zero static pressure, namely  $\nu_i^0(\Gamma)$ . To take into account the variation of these frequencies with respect to volume in the quasi-harmonic approximation we use the definition Eq. (3) of the optical Grüneisen parameter and its expression given by Eq. (35). We obtain

$$\nu_i(\Gamma) = \nu_i^0(\Gamma) \left( \frac{V}{V^0} \right)^{1/6} \left( \frac{B_{\text{sta}}}{B^0} \right)^{1/2} \left( 1 - \frac{2}{3} \frac{P_{\text{sta}}}{B_{\text{sta}}} \right)^{1/2}, \quad (36)$$

where  $B^0$  represents the bulk modulus Eq. (19) at zero static pressure.

The volume at given temperature and pressure is an input variable in the calculation of thermodynamical functions which can be computed by an iterative process. Knowing an analytical relationship for the total static energy as a function of volume  $E(V)$  from a fit to a few *ab initio* calculations we compute  $V^0$ ,  $E^0$ ,  $B^0$ , and  $K^0$  in an initial step. In the second step we compute  $\gamma_{\text{ac}}$ ,  $\gamma_{\text{op}}$ , and  $\Theta_D$  knowing  $\sigma^0$ , from which  $D(x_D)$ ,  $F_{\text{ac}}$ , and  $S_{\text{ac}}$  calculations are possible. Knowing  $\nu_i^0(\Gamma)$  we can calculate  $F_{\text{op}}$  and  $S_{\text{op}}$  and obtain finally a new value of  $V$  with Eq. (14). This second step is carried out

again until the unit cell volume calculation is converged. For this volume  $F$ ,  $S$ ,  $U$ ,  $C_V$ ,  $B$ ,  $\alpha$ , and  $C_p$  calculations are straightforward.

#### IV. *ab initio* CALCULATIONS

The *ab initio* calculations are carried out with the DMOL<sup>3</sup> code,<sup>2</sup> which is a first-principles quantum chemistry software. DMOL<sup>3</sup> calculates variational self-consistent solutions to the density functional theory equations (DFT), expressed in a numerical atomic orbitals basis given on an atom-centered set of grid points. The DMOL<sup>3</sup> method is described extensively elsewhere.<sup>25</sup> In the DMOL<sup>3</sup> code the total energy and forces acting on the atoms are calculated in the Perdew-Wang<sup>26</sup> local density approximation (LDA) for the exchange and correlation energy. In our applications, in order to reduce the computational cost and to take into account the relativistic effects that concern mostly the uranium, lead, and iodine atoms, calculations are carried out with the relativistic effective core potential method<sup>28</sup> in which the core electrons are gathered into a single analytical representation. DMOL<sup>3</sup> performs calculations using periodic boundary conditions. However, the one-particle Schrödinger equation is solved only for the  $\Gamma$  point and no information is available at all as to the band structure elsewhere in the Brillouin zone. Clearly this can be accurate only for large unit cells for which all wave vectors in the first Brillouin zone are sufficiently small. Otherwise a supercell containing several crystal unit cells must be used in the *ab initio* calculation.

The static energy for a given volume  $E(V)$  is obtained by minimizing the total energy of the proposed structures with respect to both atomic coordinates and cell parameters. Considering that the crystal systems studied are tetragonal for zircon and coffinite and hexagonal for the fluoapatites and iodoapatites we have performed these minimizations with respect to  $c/a$  and atom coordinates for a given unit cell volume. This step is repeated for a few values of the unit cell volume near the experimental equilibrium value. This method yields crystal parameters and atom coordinates as functions of the unit cell volume. We then fit these  $E(V)$  theoretical values to an integrated equation of state. The most common ones are those proposed by Murnaghan,<sup>29</sup> Birch,<sup>30</sup> and Vinet *et al.*<sup>31</sup> In this work we have used the latter,

$$E_{\text{coh}}(V) = E_{\text{coh}}^0 [1 - \eta(1-x)] \exp[\eta(1-x)], \quad (37)$$

where  $x = (V/V^0)^{1/3}$ . The cohesive energy  $E_{\text{coh}}(V)$  is obtained by subtracting from the static lattice energy  $E(V)$  the sum of atomic ground-state energies including spin polarization.  $E_{\text{coh}}^0$  is defined as the cohesive energy of the equilibrium structure at zero static pressure. In Eq. (37) the parameter  $\eta$  is related to  $B^0$  and  $K^0$  by

$$B^0 = \eta^2 \frac{E_{\text{coh}}^0}{9V^0}, \quad (38)$$

$$K^0 = \frac{2}{3} \eta + 1. \quad (39)$$

TABLE I. Standard enthalpies of formation (kcal/mol) (Ref. 4) of the chemical species in the gas state used in this work at 298.15 K and one atmosphere.

Chemical species	$\Delta_f H_{298.15 \text{ K}}^\circ$	Chemical species	$\Delta_f H_{298.15 \text{ K}}^\circ$
O	59.553	Si	108.9
P	75.20	Ca	42.6
V	122.90	Zr	145.5
I	25.535	Pb	46.6
U	128.0	F	18.88

Knowledge of  $V^0$ ,  $E_{\text{coh}}^0$ , and  $\eta$  is enough to construct the Vinet *et al.* integrated equation of state and to analytically derive the quantities given by Eqs. (17)–(19) and (32)–(36).

The  $\Gamma$  point harmonic vibrational frequencies are computed with the DMOL<sup>3</sup> code by diagonalizing the mass-weighted second-derivative Hessian matrix. The matrix elements are

$$\frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 \mathcal{E}}{\partial q_i \partial q_j}. \quad (40)$$

Here,  $\mathcal{E}$  is the total energy,  $q_i$  and  $q_j$  are two Cartesian coordinates of two atoms with masses  $m_i$  and  $m_j$ . The square roots of the eigenvalues of this matrix are the harmonic frequencies. DMOL<sup>3</sup> computes the second derivatives numerically by finite differences of the first derivatives obtained at displaced geometries and calculated analytically. Poisson's ratio  $\sigma^0$  is obtained by numerical differentiation according to Eq. (30) using  $a$  calculated as function of  $c$  by minimizing the total energy near equilibrium values  $a^0$  and  $c^0$  at zero static pressure. In fact it is not necessary to carry out new DMOL<sup>3</sup> runs, those made to obtain the equation of state being sufficient to evaluate numerically  $\sigma^0$ .

#### V. RESULTS AND DISCUSSION

In order to compare theory and experience we have calculated the thermodynamical functions at the reference pres-

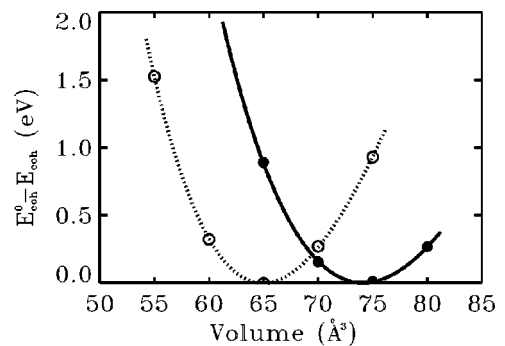


FIG. 1. Theoretical energy-volume relationship based on a fit with the Vinet *et al.* (Ref. 31) integrated equation of state for zircon (dotted line) and coffinite (solid line). The open circles for zircon and the closed circles for coffinite are the theoretically calculated values with the DMOL<sup>3</sup> code in DFT/LDA.  $E_{\text{coh}}^0$  is given in Table II.



TABLE II. Calculated parameters for zircon and coffinite at zero static pressure.

Parameters	Zircon	Coffinite
$E_{\text{coh}}^0$ (LDA) (eV/molecule)	47.8	47.9
$E_{\text{coh}}^0$ (GGA) (eV/molecule)	42.3	42.6
$V^0$ ( $\text{\AA}^3$ /molecule)	64.9	74.1
$\eta$	4.327	4.221
$B^0$ (GPa)	245.0	205.0
$K^0$	3.88	3.81
$a^0$ ( $\text{\AA}$ )	6.491	6.842
$c^0$ ( $\text{\AA}$ )	6.168	6.333
$v^0$	0.060	0.066
$w^0$	0.206	0.213
$\sigma^0$	0.270	0.337

sure of one atmosphere using the iterative process described at the end of Sec. III. Knowledge of the internal energy  $U$ , the  $pV$  term, and the entropy  $S$  leads to the enthalpy increment  $H_T^\circ - H_{298.15 \text{ K}}^\circ$  and the entropy increment  $S_T^\circ - S_{298.15 \text{ K}}^\circ$  between any temperature  $T$  and the reference temperature 298.15 K. Note that the free enthalpy increment  $G_T^\circ - G_{298.15 \text{ K}}^\circ$  can be deduced from the latter two and the  $S_{298.15 \text{ K}}^\circ$  value. In these expressions, the superscript  $\circ$  means that the substance is in its standard state. To calculate the standard enthalpy of formation  $\Delta_f H_T^\circ$  of the crystal we use Hess's law, which states that the overall enthalpy change in a chemical reaction is the same whether it takes place in one step or in several steps. Take zircon as an example. Besides the reaction of formation from its chemical components in their standard states we consider the reactions of sublimation for zirconium and silicon and dissociation of oxygen in atomic gas phase followed by the reaction of formation of zircon from these gases, which is the reversed reaction of sublimation:

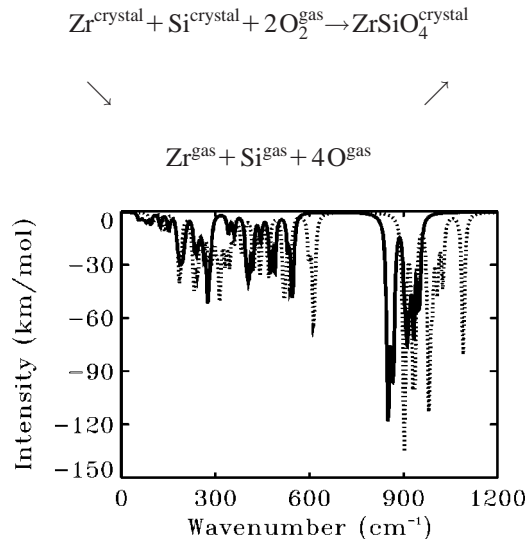
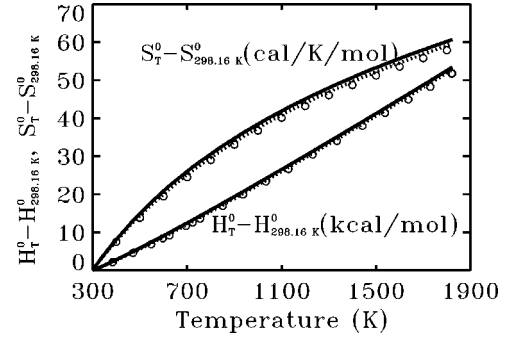
FIG. 2. Theoretical infrared spectrum for zircon (dotted line) and coffinite (solid line). The peak shape is Lorentzian. Widths have been arbitrarily set to  $10 \text{ cm}^{-1}$ .

FIG. 3. Theoretical enthalpy and entropy increment vs temperature for zircon (dotted line) and coffinite (solid line). The open circles are measurements for zircon (Ref. 5).

Applying Hess's law to these reactions, we obtain at temperature  $T$

$$\begin{aligned} \Delta_f H_T^\circ(\text{ZrSiO}_4) = & \Delta_{\text{subl}} H_T(\text{Zr}) + \Delta_{\text{subl}} H_T(\text{Si}) \\ & + 2\Delta_{\text{diss}} H_T(\text{O}_2) - \Delta_{\text{subl}} H_T(\text{ZrSiO}_4), \end{aligned} \quad (41)$$

where  $\Delta_{\text{subl}} H_T(\text{ZrSiO}_4)$  is the sublimation enthalpy of zircon defined by

$$\begin{aligned} \Delta_{\text{subl}} H_T(\text{ZrSiO}_4) = & H_T(\text{Zr}^{\text{gas}}) + H_T(\text{Si}^{\text{gas}}) + 4H_T(\text{O}^{\text{gas}}) \\ & - H_T(\text{ZrSiO}_4^{\text{crystal}}). \end{aligned} \quad (42)$$

Enthalpies of sublimation and dissociation of pure chemical components in their standard state are known<sup>4</sup> and reported in Table I at the reference temperature 298.15 K. To calculate  $\Delta_f H_T^\circ(\text{ZrSiO}_4)$  we only need  $\Delta_{\text{subl}} H_T(\text{ZrSiO}_4)$ , which can be obtained with the help of Eqs. (12) and (14), the  $E_{\text{coh}}(V)$  definition, and the properties of the calorically perfect gas. We find for  $\Delta_f H_T(\text{ZrSiO}_4)$  and in general for a crystal with  $n$  atoms per unit cell

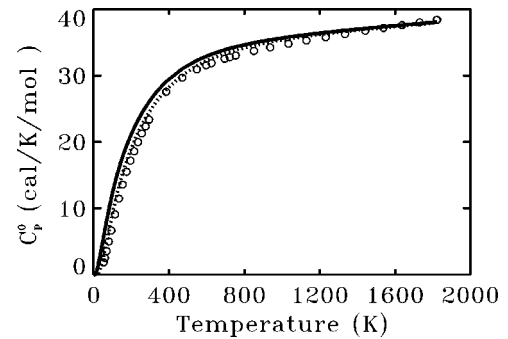


FIG. 4. Theoretical heat capacity at constant pressure vs temperature for zircon (dotted line) and coffinite (solid line). The open circles are measurements for zircon at low temperature (Ref. 6) and high temperature (Ref. 5).

TABLE III. Regression coefficients to fit with Eq. (45) the theoretical heat capacity at constant pressure of coffinite as shown in Fig. 4.

$k_0$	$k_1$	$k_2$	$k_3$	Relative error (%)
43.6460	-238.174	-426686.0	$2.91578 \times 10^7$	0.3 <sup>a</sup>

<sup>a</sup>Maximum absolute percent deviation of theoretical  $C_p^\circ$ .

$$\Delta_{\text{subl}} H_T = E_{\text{coh}} - p_{\text{sta}} V + \frac{5}{2} n N k_B T - N k_B T \times \left[ (\gamma_{\text{ac}} + 1) \left( \frac{9}{8} x_D + 3 D(x_D) \right) + (\gamma_{\text{op}} + 1) \sum_{i=4}^{3n} \left( \frac{x_i}{2} + \frac{x_i}{e^{x_i} - 1} \right) \right]. \quad (43)$$

The equilibrium structure at zero static pressure and related *ab initio* quantities  $V^0$ ,  $E_{\text{coh}}^0$ ,  $B^0$ ,  $K^0$ ,  $\nu_i^0(\Gamma)$ , and  $\sigma^0$  are calculated in the LDA approximation. In addition to that we have carried out a single point energy calculation in the Perdew-Wang<sup>27</sup> generalized gradient approximation (GGA) for the equilibrium structure obtained in the LDA approximation. In the following when stated “GGA-corrected LDA”  $E_{\text{coh}}(V)$  must be understood as

$$E_{\text{coh}}(V) = E_{\text{coh}}(V)(\text{LDA}) - E_{\text{coh}}^0(\text{LDA}) + E_{\text{coh}}^0(\text{GGA}). \quad (44)$$

TABLE IV. Calculated using GGA-corrected LDA and measured structural, elastic parameters, and thermochemical properties of zircon at 298.15 K. See text for the definition of symbols. To compare the experimental and calculated values of the Grüneisen parameter  $\gamma$  we use the expression  $\gamma = B \alpha V / C_v$ . The Debye temperature calculated with Eq. (32) must be multiplied by  $n^{1/3}$  to compare with the literature value (see Ref. 20).

	Experiment	Calculated	Relative error (%)
$V$ ( $\text{\AA}^3/\text{molecule}$ )	65.3 <sup>a</sup>	65.6	0.5
$a$ ( $\text{\AA}$ )	6.607 <sup>a</sup>	6.5139	1.4
$c$ ( $\text{\AA}$ )	5.982 <sup>a</sup>	6.187	3.4
$\gamma_{\text{ac}}$		1.80	
$\gamma_{\text{op}}$		1.46	
$\gamma$	1.08 <sup>b</sup>	1.46	35.0
$\Theta_D$ (K)	724.0 <sup>b</sup>	784.0	8.3
$B$ (GPa)	228.0 <sup>b</sup>	237.0	4.0
$\alpha$ ( $10^{-5}/\text{K}$ )	1.2 <sup>b</sup>	1.6	33.0
$\Delta_f H_{298.15 \text{ K}}^\circ$ (kcal/mol)	-486.0 <sup>c</sup>	-457.0	6.0
$H_{298.15 \text{ K}}^\circ - H_0^\circ$ (kcal/mol)	3.56 <sup>c</sup>	3.95	11.0
$S_{298.15 \text{ K}}^\circ$ (cal/mol K)	20.1 <sup>c</sup>	23.1	15.0
$C_p^\circ$ (cal/mol K)	23.6 <sup>c</sup>	24.6	4.2

<sup>a</sup>Reference 32.

<sup>b</sup>Reference 35.

<sup>c</sup>Reference 4.

TABLE V. Calculated using GGA-corrected LDA and measured structural and elastic parameters and thermochemical properties of coffinite at 298.15 K. See text for definition of symbols. To compare the experimental and calculated values of the Grüneisen parameter  $\gamma$  we use the expression  $\gamma = B \alpha V / C_v$ . The Debye temperature calculated with Eq. (32) must be multiplied by  $n^{1/3}$  to compare with the literature value (see Ref. 20).

	Experiment	Calculated	Relative error (%)
$V$ ( $\text{\AA}^3/\text{molecule}$ )	76.6 <sup>a</sup>	74.8	2.3
$a$ ( $\text{\AA}$ )	6.995 <sup>a</sup>	6.869	1.8
$c$ ( $\text{\AA}$ )	6.263 <sup>a</sup>	6.345	1.3
$\gamma_{\text{ac}}$		1.42	
$\gamma_{\text{op}}$		1.76	
$\gamma$		1.42	
$\Theta_D$ (K)		452.0	
$B$ (GPa)		199.0	
$\alpha$ ( $10^{-5}/\text{K}$ )		1.7	
$\Delta_f H_{298.15 \text{ K}}^\circ$ (kcal/mol)	-476.0 <sup>b</sup>	-483.2	1.5
$H_{298.15 \text{ K}}^\circ - H_0^\circ$ (kcal/mol)		4.6	
$S_{298.15 \text{ K}}^\circ$ (cal/mol K)	28.2 <sup>b</sup>	29.7	5.3
$C_p^\circ$ (cal/mol K)		26.2	

<sup>a</sup>Reference 33.

<sup>b</sup>Reference 9.

This shift of  $E_{\text{coh}}(V)$  does not affect the derivatives of  $E_{\text{coh}}(V)$  with respect to volume. We have observed that gradient corrections lead to a significant improvement in formation or sublimation enthalpy calculations.

Zircon<sup>32</sup> and coffinite<sup>33</sup> are two isomorphic tetragonal structures with the  $I4_1/amd$  space group. The internal parameters are the atomic oxygen position  $v$  and  $w$  in relative coordinates. The theoretical energy-volume relationship is illustrated in Fig. 1 for both compounds. The cohesive energy  $E_{\text{coh}}$  and the unit cell volume  $V$  are given per molecular unit. In Table II, we list zircon and coffinite cohesive energy, volume, and elastic parameters at zero static pressure as deduced from the Vinet *et al.* equation of state, Eq. (37). In addition we give the structural parameters  $a^0$  and  $c^0$  and the internal parameters  $v^0$  and  $w^0$  as well as Poisson's ratio  $\sigma^0$ . From these static parameters and the harmonic vibrational frequencies at the  $\Gamma$  point, which are displayed Fig. 2 in the

TABLE VI. Relative positions of not equivalent atoms in the primitive cell for  $\text{Pb}_{9.85}(\text{VO}_4)_6\text{I}_{1.70}$  (Ref. 14). Positions in parentheses are imposed by the symmetry operations.

	$x$	$y$	$z$
Pb1	0.3333 (1/3)	0.6666 (2/3)	-0.010
Pb2	0.0015	0.2653	0.2779 (1/4)
O1	0.5	0.336	0.25 (1/4)
O2	0.477	0.601	0.25 (1/4)
O3	0.268	0.358	0.069
V	0.3816	0.4100	0.25 (1/4)
I	0.030 (0)	0.024 (0)	-0.023

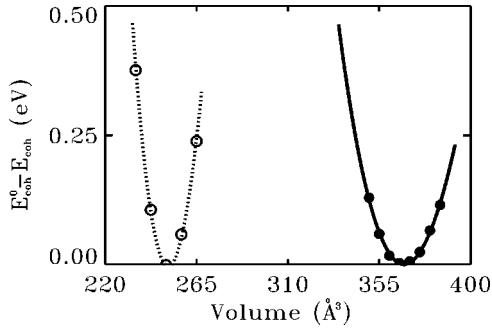


FIG. 5. Theoretical energy-volume relationship based on a fit with the Vinet *et al.* (Ref. 31) integrated equation of state for fluorapatite (dotted line) and iodoapatite (solid line). The open circles for fluorapatite and the closed circles for iodoapatite are results of the DMOL<sup>3</sup> code in DFT/LDA.  $E_{\text{coh}}^0$  is given in Table V.

infrared spectrum shape, we can calculate the thermodynamical functions versus the temperature from 0 K up to the dissociation temperature evaluated at 1973 K for zircon.<sup>34</sup> For coffinite this temperature is unknown to us. The calculated and measured thermochemical functions are shown in Figs. 3 and 4. To fit the theoretical heat capacity at constant pressure it is convenient to use the following regression law:<sup>38</sup>

$$C_p^0 = k_0 + k_1 T^{-0.5} + k_2 T^{-2} + k_3 T^{-3}, \quad (45)$$

where  $k_1$  and  $k_2$  are constrained to be less than or equal to zero. Values of  $k_0$ ,  $k_1$ ,  $k_2$ , and  $k_3$  for coffinite are given in Table III. For the sake of comparison we give in Tables IV and V, for zircon and coffinite, respectively, the calculated and measured values of structural and elastic parameters as well as the main thermochemical properties at 298.15 K. Note that without GGA corrections in the  $E_{\text{coh}}^0$  calculation we would obtain  $\Delta_f H_{298.15 \text{ K}}^0 = -584$  kcal/mol for zircon and  $\Delta_f H_{298.15 \text{ K}}^0 = -605$  kcal/mol for coffinite: GGA corrections lead to a better agreement with experiment.

Fluorapatite<sup>36</sup> has a hexagonal structure with the  $P6_3/m$  space group. Lead vanadoiodoapatite<sup>14</sup> can be also indexed in this hexagonal system. In Table VI we give the relative positions of the atoms in the primitive cell for  $\text{Pb}_{9.85}(\text{VO}_4)_6\text{I}_{1.70}$  and, in parentheses, the relative positions imposed by the symmetry operations. We see that the lead atom Pb2 is out of the plane  $z = 1/4$  and the iodine atom is

TABLE VII. Calculated parameters for fluorapatite and iodoapatite at zero static pressure.

Parameters	Fluorapatite	Iodoapatite
$E_{\text{coh}}^0$ (LDA) (eV/molecule)	139.83	124.90
$E_{\text{coh}}^0$ (GGA) (eV/molecule)	123.46	117.92
$V^0$ (Å <sup>3</sup> /molecule)	251.1	367.2
$\eta$	3.342	2.781
$B^0$ (GPa)	110.7	46.8
$K^0$	3.23	2.85
$a^0$ (Å)	9.2361	10.483
$c^0$ (Å)	6.7971	7.716
$\sigma^0$	0.344	0.368

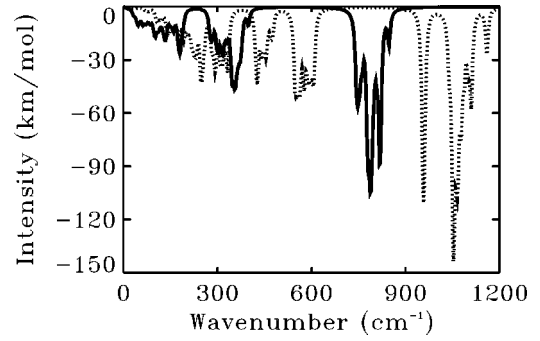


FIG. 6. Theoretical infrared spectrum for fluorapatite (dotted line) and iodoapatite (solid line). The peak shape is Lorentzian. Widths have been arbitrarily set to 10 cm<sup>-1</sup>.

not on the  $z$  axis. This apatite is not stoichiometric and contains some vacancies that can explain this disorder.<sup>14</sup> In order to make *ab initio* calculations tractable we have built an “ideal” lead vanadoiodoapatite in which these shifted atoms are put back into their ideal positions:  $z(\text{Pb2})=0$  and  $x(\text{I})=y(\text{I})=z(\text{I})=0$ . Figure 5 shows the theoretical energy-volume relationship for both compounds. The cohesive energy  $E_{\text{coh}}$  and the unit cell volume  $V$  are given per molecular unit. In Table VII we list for fluorapatite and “ideal” iodoapatite the cohesive energy, the volume, and the elastic parameters at zero static pressure deduced from the Vinet *et al.* equation of state, Eq. (37). In addition we give the structural parameters  $a^0$  and  $c^0$  and the Poisson’s ratio  $\sigma^0$ . From these static parameters and the harmonic vibrational frequencies at the  $\Gamma$  point, which are displayed Fig. 6 in the infrared spectrum shape, we can calculate the thermodynamical functions versus temperature from 0 to 1600 K for fluorapatite and to 800 K (Refs. 14 and 17) for iodoapatite. The calculated and measured thermochemical functions are shown in Figs. 7 and 8.  $C_p$  regression coefficients  $k_0$ ,  $k_1$ ,  $k_2$ , and  $k_3$  for iodoapatite are shown in Table VIII. We give in Tables IX and X, for fluorapatite and iodoapatite, respectively, the theoretical results and the experimental values of structural and elastic parameters as well as the main thermochemical properties at 298.15 K. As for zircon and coffinite the use of gradient corrections in Eq. (44) leads to a much improved agreement between standard enthalpies.

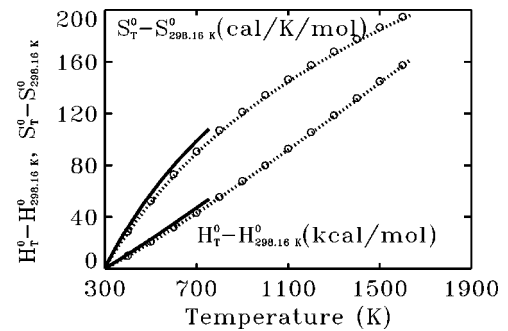


FIG. 7. Theoretical enthalpy and entropy increment vs temperature for fluorapatite (dotted line) and iodoapatite (solid line) calculated using GGA-corrected LDA. The open circles are experimental values for fluorapatite (Ref. 6).

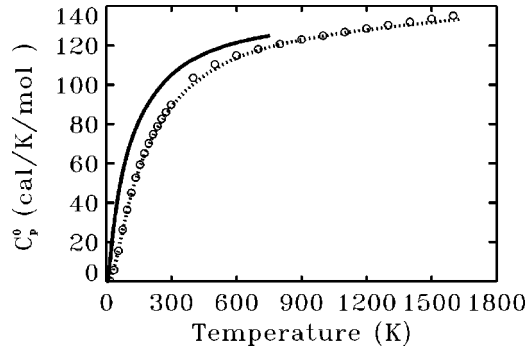


FIG. 8. Theoretical heat capacity at constant pressure vs temperature for fluorapatite (dotted line) and iodoapatite (solid line). The open circles are experimental values for fluorapatite at low temperature (Ref. 5) and high temperature (Ref. 6).

Figures 3 and 4 for zircon and Figs. 7 and 8 for fluorapatite show good agreement between theory and experiment for these two compounds: less than 5% difference at any temperature for enthalpy and entropy increments as well as for heat capacity at constant pressure. This result is quite remarkable, particularly at high temperature where anharmonic effects in the thermodynamical functions are surprisingly well evaluated with this simple treatment. This is likely to give faith in the results obtained for coffinite and iodoapatite. As regards the results at 298.15 K presented in Tables IV and IX the agreement is good for the standard enthalpies of formation (less than 6%) and for the structural parameters (less than 3.5%). These results could be improved by using more  $\vec{k}$  points of the first Brillouin zone to calculate the cohesive energy-volume relationship, but at the expense of extra computation time. The largest discrepancies between theoretical and experimental results are obtained for the thermal expansion coefficient (33%) and to a lesser extent for the bulk modulus. The latter is usually overestimated in DFT LDA.

Equations (22)–(25) show that the thermally activated phonons are responsible for entropy and heat capacity at constant volume and Eqs. (14)–(16) show that anharmonicity taken into account here through Grüneisen parameters is responsible, in part or in full, for total pressure, bulk modulus at constant temperature, the coefficient of thermal expansion, and the heat capacity at constant pressure. However, these thermal and anharmonic contributions only play a minor role in the absolute value of the thermochemical functions as compared with the static contribution. From this point of view we examine in Table XI the standard enthalpy of formation at 298.15 K for the proposed compounds. In the first column we have reported the standard enthalpy of formation

TABLE VIII. Regression coefficients to fit with Eq. (45) the theoretical heat capacity at constant pressure of iodoapatite as shown in Fig. 8.

$k_0$	$k_1$	$k_2$	$k_3$	Relative error (%)
147.887	-570.178	$-1.38998 \times 10^6$	$1.48210 \times 10^8$	0.03 <sup>a</sup>

<sup>a</sup>Maximum absolute percent deviation of theoretical  $C_p^o$ .

TABLE IX. Calculated using GGA-corrected LDA and measured structural, elastic parameters and thermochemical properties of fluorapatite at 298.15 K. See text for definition of symbols. To compare the experimental and calculated values of the Grüneisen parameter  $\gamma$  we use the expression  $\gamma = B\alpha V/C_v$ . The Debye temperature calculated with Eq. (32) must be multiplied by  $n^{1/3}$  to compare with the literature value (see Ref. 20).

	Experiment	Calculated	Relative error (%)
$V$ ( $\text{\AA}^3/\text{molecule}$ )	261.54 <sup>a</sup>	255.0	2.5
$a$ ( $\text{\AA}$ )	9.367 <sup>a</sup>	9.291	0.8
$c$ ( $\text{\AA}$ )	6.884 <sup>a</sup>	6.823	0.9
$\gamma_{ac}$		1.48	
$\gamma_{op}$		1.13	
$\gamma$	1.22	1.15	5.7
$\Theta_D$ (K)		485.0	
$B$ (GPa)	85.6 <sup>b</sup>	106.3	24.0
$\alpha$ ( $10^{-5}/\text{K}$ )	3.4 <sup>c</sup>	2.6	23.0
$\Delta_f H_{298.15 \text{ K}}^o$ (kcal/mol)	-1630.8 <sup>d</sup>	-1587.4	2.7
$H_{298.15 \text{ K}}^o - H_0^o$ (kcal/mol)	15.17 <sup>e</sup>	14.99	1.2
$S_{298.15 \text{ K}}^o$ (cal/mol K)	92.8 <sup>e</sup>	92.96	0.2
$C_p^o$ (cal/mol K)	89.9 <sup>e</sup>	88.5	1.6

<sup>a</sup>Reference 36.

<sup>b</sup>Reference 37.

<sup>c</sup>Reference 13.

<sup>d</sup>Reference 11.

<sup>e</sup>Reference 12.

TABLE X. Calculated using GGA-corrected LDA and measured structural and elastic parameters and thermochemical properties of iodoapatite at 298.15 K. See text for definition of symbols. To compare the experimental and calculated values of the Grüneisen parameter  $\gamma$  we use the expression  $\gamma = B\alpha V/C_v$ . The Debye temperature calculated with Eq. (32) must be multiplied by  $n^{1/3}$  to compare with the literature value, see Ref. 20. Young's modulus is deduced from calculated  $B$  and  $\sigma^0$  using  $E = 3(1 - 2\sigma^0)B$ , see Ref. 21.

	Experiment	Calculated	Relative error (%)
$V$ ( $\text{\AA}^3/\text{molecule}$ )	355.06 <sup>a</sup>	373.76	5.3
$a$ ( $\text{\AA}$ )	10.447 <sup>a</sup>	10.567	1.1
$c$ ( $\text{\AA}$ )	7.513 <sup>a</sup>	7.729	2.9
$\gamma_{ac}$		1.29	
$\gamma_{op}$		0.94	
$\gamma$		0.94	
$\Theta_D$ (K)		178.0	
$B$ (GPa)		44.9	
$E$ (GPa)	26.0 <sup>b</sup>	35.6	37.0
$\alpha$ ( $10^{-5}/\text{K}$ )	1.0 <sup>b</sup>	4.1	
$\Delta_f H_{298.15 \text{ K}}^o$ (kcal/mol)		-1298.5	
$H_{298.15 \text{ K}}^o - H_0^o$ (kcal/mol)		21.48	
$S_{298.15 \text{ K}}^o$ (cal/mol K)		162.36	
$C_p^o$ (cal/mol K)		104.85	

<sup>a</sup>Reference 14.

<sup>b</sup>Reference 17.



TABLE XI. Standard enthalpy of formation (kcal/mol) at 298.15 K calculated using GGA-corrected LDA: without dynamical effects (subscript sta) (i.e., neglecting vibrations), then with dynamical effects but without anharmonicity ( $\gamma_{ac} = \gamma_{op} = 0$ ), next with both contributions. The last column contains the experimental values.

	$\Delta_f H_{sta}^\circ$	$\Delta_f H_{298.15\text{ K}}^\circ (\gamma_{ac} = \gamma_{op} = 0)$	$\Delta_f H_{298.15\text{ K}}^\circ$	$\Delta_f H_{298.15\text{ K}}^\circ (\text{expt.})$
Zircon	-482.1	-456.938	-456.947	-486.0 <sup>a</sup>
Coffinite	-507.5	-483.200	-483.195	-476.0 <sup>b</sup>
Fluorapatite	-1674.9	-1587.374	-1587.390	-1630.8 <sup>c</sup>
Iodoapatite	-1377.3	-1298.607	-1298.471	

<sup>a</sup>Reference 4.

<sup>b</sup>Reference 9.

<sup>c</sup>Reference 11.

(calculated using GGA-corrected LDA) corresponding to the static lattice, i.e., neglecting thermal contributions as well as zero point vibration energy and anharmonicity. If we compare this value to calculated standard enthalpy of formation at 298.15 K, we find that whatever the compound the dynamic contribution accounts for at most 6% of the total. This is comparable to the difference between theory and experiment (less than 6%) and to a lesser extent to the dispersion range of the experimental results as reported for fluorapatite.<sup>11</sup>

In the same way, we can estimate the contribution due to anharmonicity by comparing the enthalpy of formation at 298.15 K calculated without anharmonicity ( $\gamma_{ac} = \gamma_{op} = 0$ ) reported in second column to the calculated standard enthalpy of formation at 298.15 K. For all compounds anharmonicity generates a very small contribution, from 0.001% to 0.01% of the calculated standard enthalpy of formation at 298.15 K. These orders of magnitude justify *a posteriori* the rather crude approximations used in the treatment of anharmonicity. On the other hand, it would not be advisable to neglect anharmonicity altogether since its evaluation is very cheap and it might turn out to be a more important contribution in materials other than those studied here.

The remaining difference between theory and experiment as for standard enthalpies of formation may be equally attributed to both theory (exchange correlation functional and

Brillouin zone coverage) and measurements (quality of the crystals used in the measurement). As far as thermal expansion is concerned, we feel that there is a need to refine the theory if we hope to improve the agreement.

## VI. SUMMARY AND CONCLUSIONS

We have calculated the thermodynamical functions in the quasi-harmonic approximation using *ab initio* calculations for some crystals with large unit cells such as zircon and fluorapatite. To derive these functions we have simplified the thermal contributions using the Debye model for acoustic phonons and the extended Grüneisen method for optical phonons and finally reduced the *ab initio* calculation part to a few static quantities obtained at zero static pressure. These crystals are well known from a thermodynamical point of view, thereby allowing comparison between theoretical and experimental results. Theory and experiment agree to within 6% for standard enthalpies of formation and to within 5% for heat capacities at constant pressure, which shows that the model is very satisfactory for these properties. The limits of the model are reached with the coefficient of thermal expansion, for which the difference is about 33%. This model was used to evaluate the thermodynamical functions of coffinite and lead vanadoiodoapatite, which have not yet or only partially been measured.

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