J Mater Sci: Mater Med (2007) 18:79–87
DOI 10.1007/s10856-006-0665-x

Lattice energy and mechanical stiffness of hydroxyapatite

Dajun Zhang · Ashok Tamilselvan

Received: 20 October 2005 / Accepted: 28 February 2006

Abstract The lattice energy of the stoichiometric hydroxyapatite is calculated using three methods: the thermochemical method called *Born-Fajans-Haber cycle* (BHFC), the semi-empirical electrostatic method based on the generalized *Kapustinskii equation*, and the Glasser-Jenkins *unit cell volume* method. The three values of the lattice energy of the hydroxyapatite derived by the three methods are within 4% difference to each other (BHFC: 34,191 KJ/mole, generalized Kapustinskii equation: 32,808.9 KJ/mole, unit cell volume: 32,997.4 KJ/mole). The Voigt and Reuss effective elastic moduli of 19 simple ionic crystals, including those of the hydroxyapaptite, are calculated and are found to be linearly dependent on their volumetric lattice energy density (LED).

1 Introduction

The hydroxyapatite is an ionic crystal often used to model mineral in bone and dentine. In nature, the hydroxyapatite always has impurities in it [1], such as the substitution of the phosphate or hydroxyl groups by the carbonate group, etc. The bone mineral is a vacancy-containing, hydroxyl-deficient apatite. Its formula can be written as $Ca_{8.3}\square_{1.7}(PO_4)_{4.3}(CO_3)_1(HPO_4)_{0.7}(OH)_{0.3}\square_{1.7}$ [2]. Here $\square$ represents a vacancy as compared to stoichiometric hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$.

The mechanical properties of bone are largely determined by the molecular-level alliance between bone collagen and bone mineral. The bone collagen is stiff under tension yet compliant under compression, while the bone mineral is stiff under compression yet fragile under tension. The reciprocal property compensation between collagen and mineral enables bone to sustain both tensile and compressive stresses.

The packing of chemical groups in an ionic crystal is largely controlled by the electrostatic interaction as well as the geometric constraints. One way to characterize the integrity of an ionic crystal lattice is through a physical quantity called the *lattice energy*. The lattice energy of an ionic crystal is defined as the amount of energy required to convert 1 mole of the molecular unit into its constituent ions with infinite distances between ions as in the gas phase [3]. The lattice energy of an ionic crystal per lattice unit is dependent on the bond strength and bond density within the lattice unit. A larger lattice energy in magnitude indicates a more stable lattice structure, often represented by a more densely packed lattice. The *lattice energy density* (LED), defined as the lattice energy in a lattice unit divided by the volume of the lattice unit, could be used as a molecular indicator of the overall strength and stiffness of the ionic crystal.

People's fascination with the solid crystal can be dated to 1819, when Dulong and Petit discovered that the heat capacities of solid elements heavier than potassium are about 25 J/(K mol) (3R) at room temperature and above [4, 5]. In 1907, Einstein proposed his quantum theory of the heat capacity of ionic crystals, which is further refined by Debye in 1917 [4, 5]. In 1921, Latimer proposed a simple way to calculate the entropy of solids and gases, drawing a noted relation between the residual entropy and the mass of the element, and under a postulate that the entropy of a compound is the sum of the entropies of the elements in the compound given by the mass law [6]. Latimer's

D. Zhang (✉) · A. Tamilselvan
Bone Mechanics Laboratory, Department of Mechanical and Aerospace Engineering, Rutgers, State University of New Jersey, USA
e-mail: dzhang@jove.rutgers.edu

method, commonly known as Latimer's rules, is often used as a first-line method to estimate the absolute entropy of a solid crystal. This entropy value, coupled with a further knowledge of the lattice enthalpy or lattice energy, can be used to calculate the entropy and the Gibbs' free energy (hence the likelihood) of a chemicophysical process such as dissolution [7].

Naturally occurring hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is a hexagonal crystal with a space group $P6_3/m$ [8, 9]. The lattice energy of this compound, though very important in bone and teeth biology, has not been fully investigated. This quantity cannot be directly determined by experiments since in practice this compound will dissociate into neutral atoms instead of into gaseous ions [10].

Generally, there are three different ways to calculate the lattice energy of a complex compound such as hydroxyapatite. One is to use the *Born-Fajans-Haber cycle* (BHFC) [11, 12], the other is the semi-empirical electrostatic approach based on a generalized *Kapustinskii equation* [13], and the third one is the *unit cell volume* method recently developed by Glasser and Jenkins [10].

Crystal lattice structure of naturally occurring hydroxyapatite from Holly Springs, Georgia, USA, has been obtained by several groups [8, 14–17]. A unit cell of pure hydroxyapatite has a rhombic base with $a = b = 9.4176$ Å, a height $c = 6.8814$ Å [14], and a volume of $V_m = a^2 c \sin(60°) = 528.55$ Å^3.

Similar discussion on the lattice energies of a series of apatites, in the context of chemical reaction and dissolution, has been published in [7]. Our interests on hydroxyapatite, on the other hand, are mainly focused on how to relate the lattice energy densities of both stoichiometric and poorly—crystallized hydroxyapatites to their mechanical properties such as their stiffnesses. During the course of our study, we obtained an updated data on the heat of formation of PO_4^{3-} from the Jenkins group [Jenkins, private communication]. Other than that, our work is independent from theirs, and our results on the lattice energy of hydroxyapatie are comparable to theirs.

2 Lattice energy calculation

2.1 Thermochemical method

Hess's law states that if a reaction is carried out in a series of steps, the change of enthalpy for the reaction is equal to the sum of the enthalpy changes for the individual steps. The *Born-Fajans-Haber cycle* (BHFC) is a multi-stage cycle of chemical and physical processes of substance conversion [11, 12]. It relates the lattice energy precisely to other thermochemical quantities. Considering the following reaction as a part of a BHFC, shown in Fig 1,

$$\begin{aligned}&Ca_{10}(PO_4)_6(OH)_2(cr)\\&\quad\longrightarrow 10Ca^{2+}(g) + 6PO_4^{3-}(g) + 2OH^-(g).\end{aligned}\tag{1}$$

Based on Hess's law, the above cycle provides the thermochemical equation [18] to calculate the *lattice enthalpy* (ΔH_L) of the hydroxyapatite,

$$\begin{aligned}\Delta H_L = {}&10\,\Delta_f H(Ca^{2+}, g) + 6\,\Delta_f H(PO_4^{3-}, g)\\&+ 2\,\Delta_f H(OH^-, g) - \Delta_f H(Ca_{10}(PO_4)_6(OH)_2, cr),\end{aligned}\tag{2}$$

where $\Delta_f H(*)$ is the *heat of formation* of * — the heat consumed to form 1 mole of substance * from its element in its standard, thermodynamically most stable state (under 101.32 kPa and 298.15 K) [18]. The heat of formation of an individual ion is considered to be the energy required for the formation of the ion in gaseous state from its element in standard state. The heat of formation of the hydroxyapatite is that for its crystalline state. These data are [19, 20]: $\Delta_f H(Ca^{2+}, g) =$ 1,925.9 KJ/mole, $\Delta_f H(PO_4^{3-}, g) = 291$ KJ/mole, $\Delta_f H(OH^-, g) = -143.5$ KJ/mole, $\Delta_f H\,(Ca_{10}(PO_4)_6OH_2) = -13{,}477$ KJ/mole at $T = 298.15$ °K.

Substituting the above data for the heat of formation into Eq. (2), we get the lattice enthalpy for the hydroxyapatite, $\Delta H_L = 34{,}195$ KJ/mole.

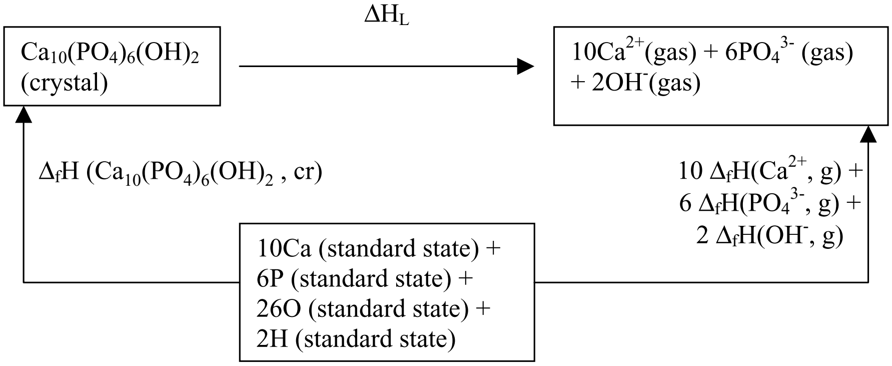


Fig. 1 Born-Fajans-Haber cycle (BHFC) for the hydroxyapatite, with the enthalpy change for each step marked on the process. ΔH_L is the lattice enthalpy of hydroxyapatite, $\Delta_f H(*)$ represents the enthalpy of formation of the entity in the parenthesis (from elements in standard states, and under 101.32 kPa and 298.15° K)

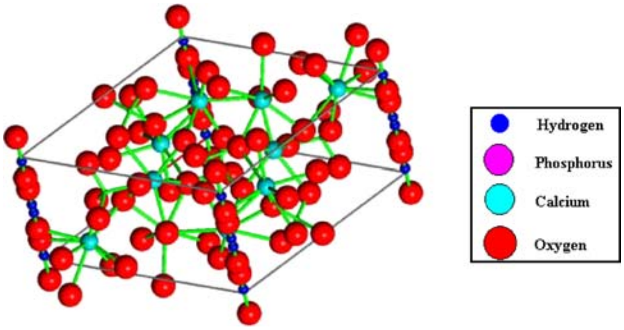


Fig. 2 Crystallographic lattice structure of natural hydroxyapatite crystal (http://www.geo.arizona.edu/AMS/amcsd.php)

ΔH_L, the lattice enthalpy, can be converted to the lattice energy by the following equation [18, 21, 22]:

$$U_{\mathrm{POT}} = \Delta H_{\mathrm{L}} - \left[10\left(\frac{n_M}{2} - 2\right) + 6\left(\frac{n_{NP}}{2} - 2\right) + 2\left(\frac{n_{LP}}{2} - 2\right)\right]\mathrm{RT}. \tag{3}$$

Derivation of this conversion can be found in Jenkins and Glasser [22]. n_{M}, n_{NP}, and n_{LP} are the numbers of degree of freedom of ion particles. For monatomic ions such as Ca^{2+}, there are only 3 translational degrees of freedom, hence $n_{\mathrm{M}} = 3$. For linear, polyatomic ions such as OH^-, $n_{\mathrm{LP}} = 5$ (3 translational, and 2 rotational). For nonlinear, polyatomic ions such as PO_4^{3-}, $n_{\mathrm{NP}} = 6$ (3 translational, and 3 rotational). For one mole of a particle as an ideal gas, the kinetic energy of one degree of freedom is 1/2 RT [5]. R is the *universal gas constant*, $R = 8.3144$ J/(mole · K), $T = 298.15$ K. The purpose of the second term in Eq. (3) is to take account of the phase-change-associated enthalpy change ($\Delta H = \Delta E + P\Delta V$) in the reaction shown in Eq. (1). Namely,

(a) internal energy change (ΔE) due to the non-zero kinetic energies of the gas-phase ions and the ion vibrational (acoustic) energy in a crystal lattice at $T = 298.15$ K (standard state), and
(b) enthalpy change due to volume change ($P\Delta V$).

Certain idealization is used to derive Eq. (3), as discussed in Jenkins and Glasser [22]. Putting all things together, Eq. (3) gives the lattice energy of hydroxyapatite $U_{\mathrm{POT}} = 34{,}190$ KJ/mole.

A recent estimate of the heat of formation of the gaseous phosphate ion PO_4^{3-}, $\Delta_f H(\mathrm{PO}_4^{3-}, \mathrm{g})$, has put its value at 321.8 KJ/mole [7]. If this value is used, the lattice enthalpy ΔH_L will become 34,379.8 KJ/mole. And the lattice energy U_{POT} will become 34,374.8 KJ/mole instead of 34,190 KJ/mole (a 0.5% increase).

2.2 Kapustinskii equation

The lattice energy is dominated by the electrostatic potential energy (attraction energy and repulsion energy), with a minor contribution from the van der Waals interaction (London forces) [5]. Therefore, the lattice energy can also be calculated from the knowledge of its crystal lattice structure, using the concept of the *Madelung constant* [3]. However, since calculating the Madelung constant of a complex lattice such as that of the hydroxyapatite is very cumbersome, a semi-empirical method is generally used. Kapustinskii [23] introduced the concept that for any binary ionic crystal, regardless of its crystal structure, it possesses an equivalent structure of the rock-salt (NaCl) type that has the same lattice energy. Lattice energy of this NaCl-equivalent structure can be calculated using the Madelung constant for NaCl and a set of equivalent ionic radii [12].

Kapustinskii's concept is extended [13] to include multiple, mixed ion systems with more than two types of ions in the crystals. Using this generalized formulation, the lattice energy is found to be,

$$U_{\mathrm{POT}}(\mathrm{kJ/mole}) = \frac{121.4}{<r>}\left(1 - \frac{0.0345}{<r>}\right)\sum n_k z_k^2, \tag{4}$$

where n_{k} = number of an individual ion in a formula unit, z_k = valence of the ion, and $<r>$ = *weighted mean ion radius sum* (in nm). Here $R_{\mathrm{o}} = 1 - 0.0345/<r>$ is the repulsion factor, and $I = (\sum n_k z_k^2)/2$ is often called the *ionic strength*. Eq (4) provides excellent estimates of the lattice energies in conjunction with the *Goldschmidt ionic radii* of the cations and the *thermo-chemical radii* of complex anions, such as the phosphate ion.

The calculation of $<r>$, the mean radius sum, involves all possible cation-anion pairs. For $\mathrm{Ca}_{10}(\mathrm{PO}_4)_6\mathrm{OH}_2$, there are sixty Ca–$\mathrm{PO}_4$ pairs and twenty Ca–OH pairs. Hence,

- Goldschmidt ionic radius [12] of the Ca^{2+}, $r_{\mathrm{Ca}} = 0.106$ nm, and
- the thermo-chemical radii [19] of PO_4^{3-}, $r_{\mathrm{PO4}} = 0.23$ nm and OH^-, $r_{\mathrm{OH}} = 0.152$ nm,
- Number of Ca–PO_4 pairs = 60,
- Number of Ca–OH pairs = 20,
- Total number of cation-anion pairs = 60 + 20 = 80,

$$<r> = \frac{60(r_{\mathrm{Ca}^{2+}} + r_{\mathrm{PO}_4^{3-}}) + 20(r_{\mathrm{Ca}^{2+}} + r_{\mathrm{OH}^-})}{80} = 0.3165\,\mathrm{nm}. \tag{5}$$

Equation (4) gives the lattice energy of hydroxyapatite $U_{\mathrm{POT}} = 32{,}808.9$ KJ/mole.

2.3 Unit cell volume method

Equation (4) can be further simplified. For complex ionic crystals with lattice energies larger than 5,000 KJ/mole, Glasser and Jenkins [10] found that $\langle r \rangle/(V_m/2I)^{1/3}$ is fairly a constant 1.7, and the repulsion factor $R_{\mathrm{o}} = 1 - \rho/\langle r \rangle$ also approaches a constant 0.84. Here V_{m} is the volume of the unit cell of the lattice. I is the ionic strength $I = (\Sigma n_{\mathrm{k}} z_{\mathrm{k}}^2)/2$. Therefore, Eq. (4) can be rewritten as

$$U_{\mathrm{POT}}(\mathrm{KJ/mol}) = AI\left(\frac{2I}{V_m}\right)^{\frac{1}{3}}, \qquad A = 121.39\,\mathrm{KJ} \bullet \mathrm{nm/mole}. \tag{6}$$

The ionic strength I of the hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ is $I = 48$, the unit cell volume V_m is 528.55 Å^3. Substituting these into Eq. (6), we get the third estimate of the lattice energy $U_{\mathrm{POT}} = 32{,}997.4$ KJ/mole.

3 Effective Reuss and Voigt stiffnesses

A single crystal is usually mechanically anisotropic due to the preferred orientation of the lattice. Using the notations adopted in Cowin [24], in order to fully describe the stiffness of a single crystal, a full fourth-rank tensor in three dimensions C_{ijkm} is needed (with 81 components). The stress tensor T_{ij} is related to the strain tensor E_{km} through $T_{ij} = C_{ijkm}\ E_{km}$. Due to the symmetry of the stress tensor (T_{ij}) and the strain tensor (E_{km}) and thermodynamic restraints, the number of independent components reduces to 21. Moreover, it is convenient to write the stress and the strain tensors, each with 6 independent components, as 6-component pseudo-vectors σ_α and ε_β. This way the stress-strain relation $T_{ij} = C_{ijkm}E_{km}$ can be simplified as $\sigma_\alpha = c_{\alpha\beta}\ \varepsilon_\beta$, or alternatively, $\varepsilon_\alpha = k_{\alpha\beta}\ \sigma_\beta$. $c_{\alpha\beta}$ and $k_{\alpha\beta}$ are 6×6 matrices, and $k_{\alpha\beta}.\ c_{\beta\gamma} = \delta_{\alpha\gamma}$, where $\delta_{\alpha\gamma} = 0$ if $\alpha \neq \gamma$ and $\delta_{\alpha\gamma} = 1$ if $\alpha = \gamma$.

A polycrystalline material is composed of randomly oriented single crystal grains. Therefore, a polycrystalline material is mechanically isotropic and its stiffness is related to the stiffness matrix of the corresponding single crystal. As shown in Cowin [24], it can be rigorously proven that the elastic moduli of a polycrystalline solid are bounded by two well-defined bounds: the upper Voigt bound and the lower Reuss bound. These bounds are also called the *Voigt effective isotropic moduli* and the *Reuss effective isotropic moduli*. The Voigt moduli are derived by assuming that the strain field within all the grains is homogeneous, whereas the Reuss moduli are derived by assuming that the stress field in all the grains is homogeneous. The Voigt and Reuss effective moduli can be used as convenient single-value indicators of the overall stiffness of a single crystal, instead of using a full 6×6 stiffness matrix $c_{\alpha\beta}$.

If the constants $c_{\alpha\beta},\ k_{\alpha\beta}, \alpha, \beta = 1, 6$, are known for a single crystal, its Voigt/Reuss bulk and shear moduli K_V, G_V, K_R, and G_R are [24]

$$K_V = \frac{1}{9}tr\mathbf{C}, \quad G_V = \frac{1}{30}(3\,tr\ \mathbf{V} - tr\ \mathbf{C}), \quad K_R = \frac{1}{tr\mathbf{K}}, \quad \text{and} \quad G_R = \frac{15}{2(3tr\ \mathbf{R} - tr\mathbf{K})}, \tag{7}$$

where

$$\begin{aligned} tr\ \mathbf{C} &= c_{11} + c_{22} + c_{33} + 2(c_{12} + c_{13} + c_{23}), \\ tr\ \mathbf{V} &= c_{11} + c_{22} + c_{33} + 2(c_{44} + c_{55} + c_{66}), \\ tr\ \mathbf{K} &= k_{11} + k_{22} + k_{33} + 2(k_{12} + k_{13} + k_{23}), \quad \text{and} \\ tr\ \mathbf{R} &= k_{11} + k_{22} + k_{33} + \frac{1}{2}(k_{44} + k_{55} + k_{66}). \end{aligned} \tag{8}$$

The corresponding Voigt and Reuss Young's moduli, E_V, and E_R, can be obtained from the relation

$$E_{V,R} = \frac{9\ G_{V,R}K_{V,R}}{3\ K_{V,R} + G_{V,R}}\ . \tag{9}$$

The forms of the 6×6 stiffness matrix $c_{\alpha\beta}$ for hexagonal, cubic, and rhombic single crystals can be found in the Appendix of Cowin [24]. Data on $c_{\alpha\beta}$ for 19 ionic single crystal and water ice, belonging to 3 different symmetry groups (cubic, hexagonal, rhombic), can be found in Lide [19]. The data on $k_{\alpha\beta}$ can be calculated as a simple inverse of $c_{\alpha\beta}$. The calculated Voigt and Reuss moduli are listed in Table 1 (in the sequence of increasing lattice energy density, see below).

4 Lattice energy density

The *lattice energy* (KJ/mole) is defined as the energy cost to convert *one mole* of the chemical unit from crystal form into free ions. If we would like to know how much lattice energy is stored in a unit volume, we should use a quantity called the *lattice energy density* (LED) (KJ/cm^3). The volumetric *lattice energy density* LED (KJ/cm^3) of a crystal can be calculated by dividing the lattice energy (KJ/mole) by the molar volume (cm^3/mole) of the formula unit of the crystal. We predict that the volumetric lattice energy density (LED) is correlated with the effective stiffness of a crystal, since both quantities define how strongly atoms bind to each other in a unit volume of a crystal. In this context, the lattice energy density equals to the "*cohesive energy density*" of the crystal as it dissociates into compound ions.

Table 1 Calculated Voigt and Reuss effective stiffnesses as they depend on the lattice energy density (LED). The Voigt and Reuss bulk moduli for cubic crystals are in bold to show their identity with each other. The data for hydroxyapatite are also in bold

Chemical unit	Symmetry	Lattice energy (KJ/mol)	Molar volume (cm^3/mol)	Lattice energy density (KJ/cm^3)	Voigt effective E_V (GPa)	Voigt effective G_v (GPa)	Voigt effective K_v (GPa)	Reuss effective E_R (GPa)	Reuss effective G_R (GPa)	Reuss effective K_R (GPa)
H_2O (Ice)	Hexagonal	57.88	19.56	2.96	9.35	3.52	9.06	9.13	3.43	9.05
CsI	Cubic	600	57.41	10.45	18.44	7.34	**12.56**	17.99	7.13	**12.56**
KI	Cubic	632	53.07	11.91	16.96	6.70	**12.03**	13.16	4.99	**12.03**
CsBr	Cubic	632	47.76	13.23	22.67	9.01	**15.59**	21.92	8.66	**15.59**
KBr	Cubic	671	43.43	15.45	22.22	8.82	**15.43**	17.89	6.85	**15.43**
Cs_2SO_4	Rhombic	1596	84.33	18.93	32.58	12.59	26.34	32.37	12.51	26.14
LiI	Cubic	730	32.95	22.16	27.62	11	**18.83**	25.57	10.04	**18.83**
Rb_2SO_4	Rhombic	1636	73.22	22.34	39.03	15.24	29.63	38.92	15.19	29.61
$Ba(NO_3)_2$	Cubic	2062	80.25	25.69	24.84	9.38	**23.52**	19.46	7.14	**23.52**
K_2SO_4	Rhombic	1700	65.36	26.01	44.32	17.47	31.89	43.85	17.25	31.88
NaCl	Cubic	769	27.02	28.46	37.6	15.04	**25.08**	36.69	14.6	**25.08**
LiBr	Cubic	788	25.01	31.50	38.87	15.58	**25.67**	36.04	14.24	**25.67**
KF	Cubic	808	23.43	34.49	43.99	17.33	**31.77**	39.85	15.43	**31.77**
LiCl	Cubic	834	20.50	40.68	50.03	20.20	**31.82**	46.09	18.31	**31.82**
$BaSO_4$	Rhombic	2469	53.05	46.54	65.29	25.25	52.55	56.45	21.38	52.36
$CaSO_4$	Rhombic	2489	45.98	54.13	88.17	35.43	57.44	60.42	23.11	52.19
BaF_2	Cubic	2341	35.8	65.39	66.75	25.49	**58.38**	66.75	25.49	**58.38**
$CaCO_3$	Rhombic	2804	34.16	82.08	95.07	40.41	48.97	86.38	36.65	44.76
$Ca_{10}(PO_4)_6(OH)_2$	**Hexagonal**	**32809**	**318.3**	**103**	**152.96**	**63.81**	**84.58**	**140.45**	**57.52**	**83.86**
CaF_2	Cubic	2609	24.56	106.23	172.49	74.48	**84.05**	168.94	72.5	**84.05**

In order to test this hypothesis, the effective Voigt and Reuss moduli (bulk, shear, and Young's) are plotted against the lattice energy density for the ionic crystals (plus ice) mentioned above. These 19 crystals are all the simple, ionic crystals we can find with both their lattice energy and anisotropic elastic constants available, and with lattice energy densities close or below that of hydroxyapatite. The data on the lattice energies of these crystals are obtained from Jenkins et al. [21], Lide [19], and Dong et al. [25] (for H_2O ice).

As shown in Figs. 3 to 5, all the Voigt and the Reuss effective stiffnesses, as expected, follow an almost perfect linear dependence on the lattice energy density. The regressed relations are:

$$
\begin{aligned}
&E_V = 1.41\,LED,\ R^2 = 0.98;\\
&E_R = 1.30\,LED,\ R^2 = 0.97;\\
&G_V = 0.59\,LED,\ R^2 = 0.97;\\
&G_R = 0.53\,LED,\ R^2 = 0.96;\\
&K_V = 0.84\,LED,\ R^2 = 0.96;\\
&K_R = 0.83\,LED,\ R^2 = 0.96;
\end{aligned}
\tag{10}
$$

For each crystal, its effective Voigt modulus is always larger than the corresponding Reuss modulus. But the difference is usually not large. For cubic crystals, it can be proven that the Voigt bulk modulus equals to the Reuss bulk modulus [24], a fact represented in the data shown in Table 1.

The above relations in Eq. (10) hold true for a wide range of the lattice energy density (LED) (from 3 to 106 KJ/cm^3), and across different symmetry groups (hexagonal, rhombic, and cubic). Effective moduli of the hydroxyapatite fall nicely along the above regressed lines. This, in a way, validates the reasonableness of our calculation of its lattice energy in this paper. The anisotropic elastic constants of the hydroxyapatite are listed in Lide [19], which is cited in Hearmon [26].

5 Discussion

5.1 Components of a lattice energy

For ionic crystals, the lattice energy of a crystal consists of 3 terms: the Madelung attractive term (this term is positive due to the electrostatic attraction of opposite charges), the electron repulsive term (this term is negative due to the close apposition of electronic orbitals), and the van der Waals term (this term is also positive due to the attractive London forces between charged ions) [5]. The Madelung attractive term is the predominant positive (attractive) term, and the repulsive term is the minor negative (repulsive) term (around 10% of the attractive term [27]). The van der Waals term is also positive (attractive), and its magnitude is usually

Fig. 3 Dependence of the Voigt and Reuss effective Young's moduli, E_V, and E_R, on the volumetric lattice energy density (LED)

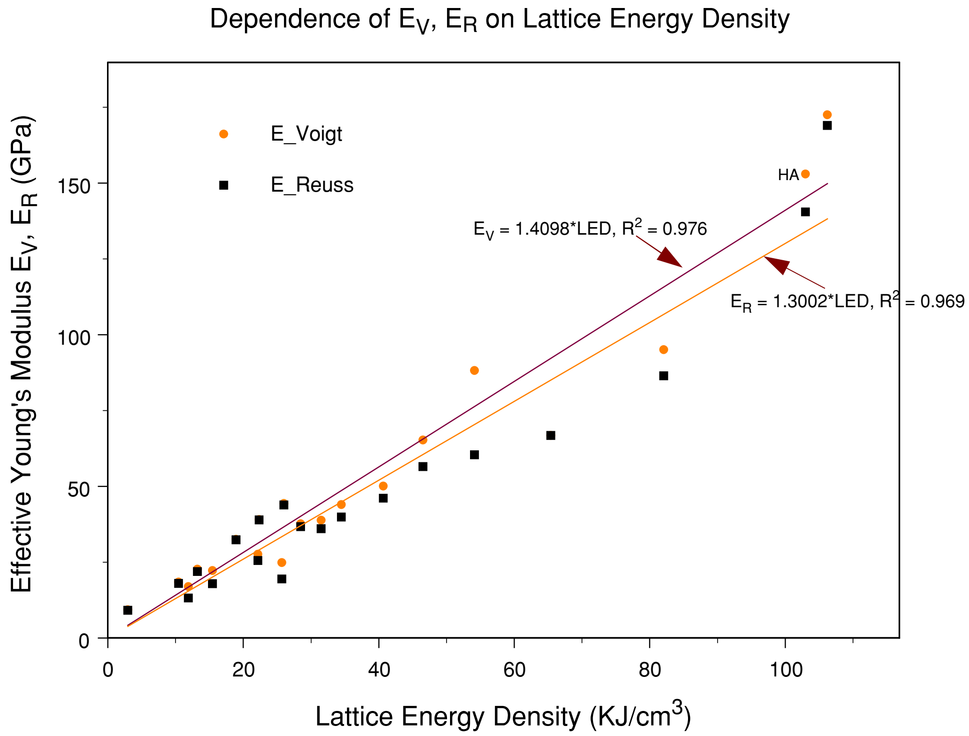
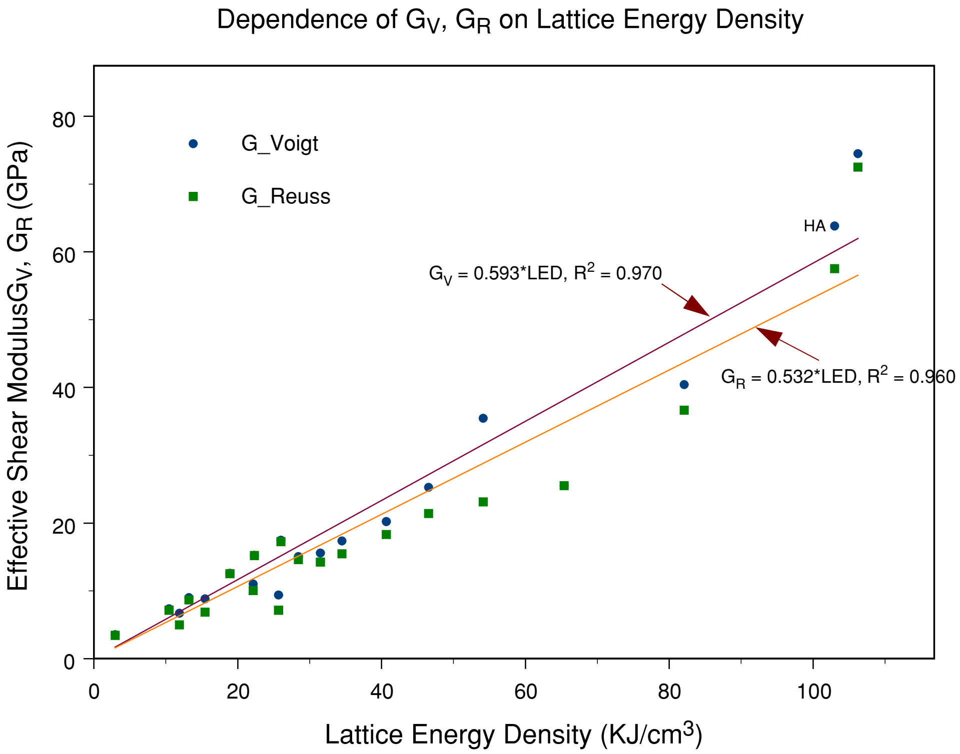


Fig. 4 Dependence of the Voigt and Reuss effective shear moduli, G_v, and G_R, on the volumetric lattice energy density (LED)



smaller than, but often times approaching, the repulsive term.

The most precise method to calculate the lattice energy is to use quantum mechanics (the *ab initio* method). It can evaluate the exact contribution of each of the above three terms. However, this method becomes intractably complicated (and expensive) for large, complicated lattices. The lattice energy of another P6$_3$/m crystal, the pyromorphite $Pb_5(PO_4)_3Cl$, has recently been calculated by *ab initio* methods to be 13,163.82 kJ/mole (or 26,327.64 for $Pb_{10}(PO_4)_6Cl_2$) [29]. The authors

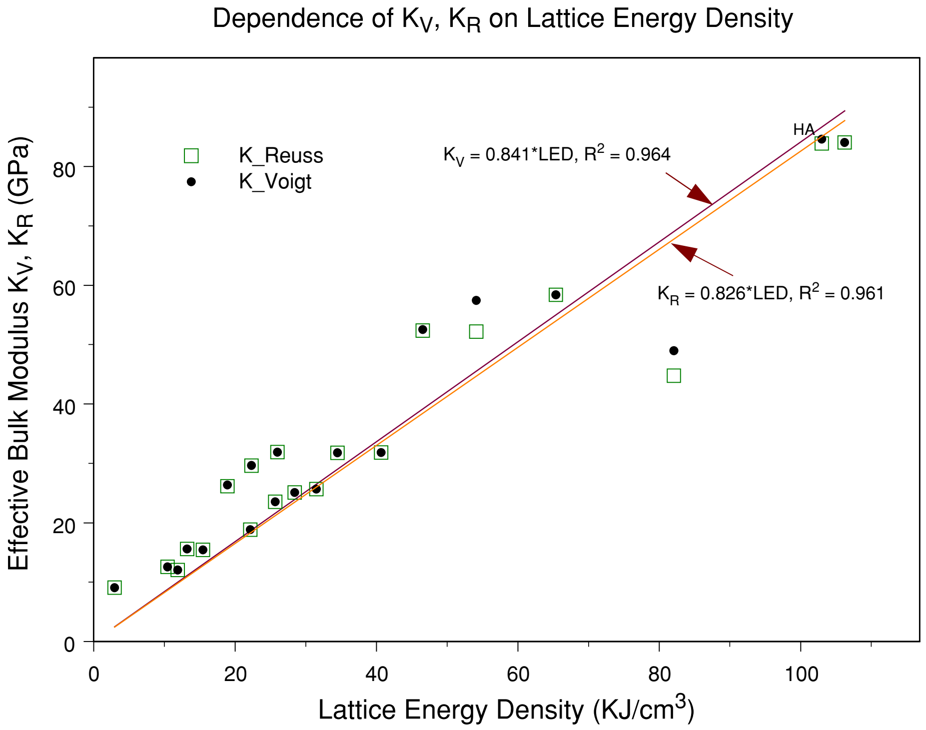


Fig. 5 Dependence of the Voigt and Reuss effective bulk moduli, K_v, and K_R, on the volumetric lattice energy density (LED)

are not aware of any published results on the *ab initio* calculation of the lattice energy of the hydroxyapatite.

5.2 Correlation between lattice energy density and mechanical stiffnesses

Lattice energy values can be used to compare the relative stability of crystal structures in a same space group. For example, the change in stability of an ionic crystal as the cation is progressively substituted by another cation [28]. It can also be used to predict the solubility of a crystal before it is actually fabricated. The lattice energy has to be overcome by the energy of solvation of the ions (and an increase of entropy) in order for the crystal to be dissolved in a solvent [7, 27].

The most interesting application of the lattice energy is the strong correlation between the lattice energy density and the mechanical stiffnesses of the crystals. In this context, the lattice energy equals to the "cohesive energy" of the crystal as it dissociates into compound ions. For hydroxyapatite, the relatively large value of its lattice energy density (103 KJ/cm^3) is the chemical basis for its high stiffness values in polycrystalline form (Young's modulus between $E_R = 140$ GPa and $E_V = 153$ GPa). This large LED is contributed by the closeness of the packing of chemical groups in the hydroxyapatite lattice, as shown in Fig 1. As a result of this, the spatial density of chemical bonds in the hydroxyapatite lattice is very large. Compare to a typical binary salt, NaCl (rock salt). NaCl crystal, which has a cubic structure, has a lattice energy density of only 28.5 KJ/cm^3, and a Young's modulus between $E_R = 36.7$ GPa and $E_V = 37.6$ GPa.

The theoretical basis for the relation between the LED and the elastic stiffnesses may be inferred from the following equation. At extremely low temperature, the bulk modulus K of a perfect ionic crystal is equal to [29]

$$K = V \frac{\partial^2 U_{POT}}{\partial V^2}, \tag{11}$$

where U_{POT} is the lattice energy as a function of the interionic distance, r. V is the volume of the crystal lattice corresponding to U_{POT}. V is also a function of r. At equilibrium, $\partial U_{\mathrm{POT}}/\partial r = 0$, from which the value of K_{Equil} can be evaluated.

5.3 Implications in bone mechanics

Compared to stoichiometric hydroxyapatite, bone apatite is highly imperfect [1]. Typical imperfections include the substitution of PO_4 tetrahedra by smaller CO_3 triangles (B type imperfection), or the substitution of OH by CO_3 (A type imperfection) [30]. As a result, the bone mineral is a vacancy-containing, hydroxyl-deficient apatite, $Ca_{8.3}\square_{1.7}(PO_4)_{4.3}(CO_3)_1(HPO_4)_{0.7}(OH)_{0.3}\square_{1.7}$ [2]. Naturally, the lattice energy of apatite in real bone is expected to be less than, and upper-bounded by, that of the stoichiometric hydroxyapatite. How to calculate the lattice energy of an imperfect bone apatite as a function of the lattice imperfection is a challenging task. The calculation of the lattice energy for a perfect, stoichiometric, hydroxyapatite is the first step in that direction.

The lattice geometry of bone mineral crystal also varies with gender, evolves with age [31], and alters under pathological conditions such as Osteogenesis Imperfecta (OI). For example, the length ratio *c/a* for bone apatite unit cells is significantly higher for females than for males. For males, there is a significant change of *c/a* with age, but this is not observed for females [31].

Subtle mineral lattice indices, such as the bone mineral crystallinity [32], the carbonate to phoshate ratio [33], and the content of poorly crystalline apatite phase [34], vary with age or the maturation stage of bone. Typical diagnostic tools include the infrared spectroscopic method (such as Fourier Transform Infrared Spectroscopy, FTIR) and the nuclear magnetic resonance (NMR) spectroscopy. Osteogenesis Imperfecta (OI), a devastating bone disease associated with disrupted collagen expression, is also accompanied by a measurable decrease in bone mineral size and crystallinity [35]. It is possible that osteoporosis is not just caused by a steady decrease in the bone mineral content, but also by a subtle change in the bone mineral crystal structure. However, there is very little published data on the change of the crystal structure of the bone apatite in osteoporosis.

The lattice energy density could be a useful tool to quantitatively characterize changes in the bone mineral lattice structure in bone pathologies and a way to monitor outcomes of pharmaceutical intervention.

Nomenclature

a	length of hydroxyapatite unit cell in a-axis, $a = 9.4176$ Å
A	constant in Eq. (6), $A = 121.39$ KJ·nm/mole
b	length of hydroxyapatite unit cell in b-axis, $b = a = 9.4176$ Å
c	length of hydroxyapatite unit cell in c-axis, $c = 6.8814$ Å
$c_{\alpha\beta}$	simplified 6 × 6 stiffness matrix relating strain vector ε_β to stress vector σ_α, $\sigma_\alpha = c_{\alpha\beta}\ \varepsilon_\beta$
C_{ijkm}	4th – rank elastic stiffness tensor relating strain tensor E_{km} to stress tensor T_{ij}, $T_{\mathrm{ij}} = C_{\mathrm{ijkm}}\ E_{\mathrm{km}}$
E	internal energy in enthalpy relation, $\Delta H = \Delta E + P \Delta V$
E_R	Reuss effective Young's modulus (GPa)
E_V	Voigt effective Young's modulus (GPa)
E_{km}	strain tensor, where $k, m = 1, 2, 3$
G_R	Reuss effective shear modulus (GPa)
G_V	Voigt effective shear modulus (GPa)
I	ionic strength in Eqs. (4) and (6), $I = (\sum n_k z_k^2)/2$, where n_k is the number of individual ions per formula unit, z_k is the valence of each ion. $I = 48$ for hydroxyapatite
$k_{\alpha\beta}$	simplified 6 × 6 stiffness matrix relating stress vector σ_α to strain vector ε_β, $\varepsilon_\alpha = \mathrm{k}_{\alpha\beta}\ \sigma_\beta$
LED	lattice energy density (KJ/cm^3)
n_k	number of an individual ion in a formula unit, used in Eq. (4)
n_{LP}	number of degrees of freedom for linear, polyatomic ion, $n_{LP} = 5$ (3 translational, 2 rotational)
n_M	number of degrees of freedom for monoatomic ion, $n_M = 3$ (all translational)
n_{NP}	number of degrees of freedom for nonlinear, polyatomic ion, $n_{NP} = 6$ (3 translational, 3 rotational)
P	pressure
< r >	*weighted mean ion radius sum* in Eqs. (4) and (5) (nm)
R	universal gas constant, $R = 8.3144$ J/(mole·K)
R_o	repulsion factor in Eq. (4), $\mathrm{R_o} = 1 - 0.0345/ <r>$
T	absolute temperature (K)
T_{ij}	stress tensor, where $i, j = 1, 2, 3$
U_{POT}	lattice energy, also called total lattice potential energy (KJ/mole)
V	volume
V_m	volume of hydroxyapatite unit cell, $V_m = a^2 c \sin (60^\circ) = 528.55 \mathring{A}^3$
z_k	valence of an ion in a formula unit, used in Eq.(4)
$\delta_{\alpha\gamma}$	unit 6 × 6 matrix, $\delta_{\alpha\gamma} = 0$ if $\alpha \neq \gamma$, and $\delta_{\alpha\gamma} = 1$ if $\alpha = \gamma$. Here $\alpha, \gamma = 1, 6$
ΔH_{L}	lattice enthalpy of hydroxyapatite, enthalpy of formation in reaction Eq. (1) (KJ/mole)
$\Delta_{\mathrm{f}} H(*)$	heat of formation of *, heat consumed to form 1 mole of substance * from its element in its standard, thermodynamically most stable state (under 101.32 kPa and 298.15 K)
ε_β	simplified 6-component strain vector, $\beta = 1, 6$
σ_α	simplified 6-component stress vector, $\alpha = 1, 6$

Acknowledgments This research is supported by the Rutgers University.

References

1. W. T. LEE, M. T. DOVE and E. K. H. SALJE, *J. Phys: Condens. Matter* **22** (2000) 9829.
2. C. REY, J. L. MIQUEL, L. FACCHINI, A. P. LEGRAND and M. J. GLIMCHER, *Bone* **16**(5) (1995) 583.
3. M. DE PODESTA, "Understanding the Properties of Matter," (UCL Press, London, 1996).
4. R. A. ALBERTY and R. J. SILBEY, "Physical Chemistry" 1st edn (John Wiley & Sons, New York, 1992).

5. W. J. MOORE, "Basic Physical Chemistry" (Prentice-Hall, New Jersey, 1983).
6. W. M. LATIMER, *J. Am. Chem. Soc.* **43** (1921) 818.
7. N. J. FLORA, C. H. YODER and H. D. B. JENKINS, *Inorg. Chem.* **43**(7) (2004) 2340.
8. J. M. HUGHES, M. CAMERON and K. D. CROWLEY, *Am. Mineral.* **74** (1989) 870.
9. R. M. WILSON, J. C. ELLIOTT and S. E. P. DOWKER, *Am. Mineral.* **84** (1999) 1406.
10. L. GLASSER and H. D. B. JENKINS, *J. Am. Chem. Soc.* **122** (2000) 632.
11. M. BORN and K. HUANG, "Dynamical Theory of Crystal Lattices," (Clarendon Press, Oxford, England, 1954).
12. W. E. DASENT, "Inorganic Energetics, An Introduction," 2nd edn (Cambridge University Press, Cambridge, England, 1982).
13. L. GLASSER, *Inorg. Chem.* **34** (1995) 4935.
14. J. C. ELLIOT, "Structure and Chemistry of the Apatites and Other Calcium Orthophosphates" (Elsevier, New York, 1994).
15. M. I. KAY, R. A. YOUNG and A. S. POSNER, *Nature* **204** (1964) 1050.
16. A. S. POSNER, A. PERLOFF and A. F. DIORIO, *Acta Cryst.* **11** (1958) 308.
17. K. SUDARSANAN and R. A. YOUNG, *Acta Cryst.* **B25** (1969) 1534.
18. H. D. B. JENKINS and H. K. ROOBOTTOM, "CRC Handbook of Chemistry and Physics (2000/2001)", (Chemical Rubber Company, CRC Press, Boca Raton, Florida, 2000).
19. D. R. LIDE, "CRC Handbook of Chemistry and Physics (2000/2001)", (Chemical Rubber Company, CRC Press, Boca Raton, Florida, 2002/2003).
20. D. D. WAGMAN, W. H. EVANS, V. B. PARKER, R. H. SCHUMM, I. HALOW, S. M. BAILEY, K. L. CHURNEY and R. L. NUTTALL, "The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C1 and C organic subtances in SI units". American Chemical Society and the American Institute of Physics for the National Bureau of Standards, (Washington, D.C, 1982) .
21. H. D. B. JENKINS, H. K. ROOBOTTOM, J. PASSMORE and L. GLASSER, *Inorg. Chem.* **38** (1999) 3609.
22. H. D. B. JENKINS and L. GLASSER, *Inorg. Chem.* **41** (2002) 4378.
23. A. F. KAPUSTINSKII, *Q. Rev., Chem. Soc.* **10** (1956) 283.
24. S. C. COWIN, *Q. J. Mech. Appl. Math.* **42**(2) (1989) 249.
25. S. DONG, Y. WANG and J. LI, *Chem. Phys.* **270** (2001) 309.
26. R. F. S. HEARMON, *Adv. Phys.* **5** (1956) 323.
27. R. C. EVANS, "An Introduction to Crystal Chemistry," 2nd edn (Cambridge University Press, 1964).
28. A. V. SHEVADE, L. ERICKSON, G. PIERZYNSKI and S. JIANG, *J. Hazardous Substance Res.* **3** (2001) 2-1.
29. C. M. SRIVASTAVA and C. SRINIVASAN, "Science of Engineering Materials" (Wiley Eastern Limited, New Delhi, India, 1987).
30. T. I. IVANOVA, O. V. FRANK-KAMENETSKAYA, A. B. KOL'TSOV and V. L. UGOLKOV, *J. Solid State Chem.* **160** (2001) 340.
31. C. B. SMITH and D. A. SMITH, *Calcif. Tissue Res.* **22**(2) (1976) 219.
32. C. REY, V. RENUGOPALAKRISHNAN, B. COLLINS and M. J. GLIMCHER, *Calcified Tissue Int.* **49** (1991) 251.
33. L. M. MILLER, C. S. CARLSON, G. L. CARR and M. R. CHANCE, *Cell. Mol. Biol.* **44**(1) (1998) 117.
34. C. REY, M. SHIMIZU, B. COLLINS and M. J. GLIMCHER, *Calcified Tissue Int.* **46** (1990) 384.
35. U. VETTER, E. D. EANES, J. B. KOPP, J. D. TERMINE and P. G. ROBEY, *Calcif. Tissue Int.* **49** (1991) 248.