Elastic properties of olivine Li$_x$FePO$_4$ from first principles

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Using first-principles pseudopotential calculations within the GGA+U framework, we calculate the elastic constants of orthorhombic olivine Li$_x$FePO$_4$ and FePO$_4$. Our results show that olivine Li$_x$FePO$_4$ is anisotropic and that directional bulk moduli change significantly during lithiation. LiFePO$_4$ is predicted to be harder and to exhibit a higher Debye temperature than FePO$_4$.

The olivine series forms an important class of minerals most commonly found in Earth's mantle. Olivines occur as transition-metal silicates or phosphates and have been intensively studied by mineralogists and geophysicists. Recently, olivine phosphates have received much attention after it was shown that lithium can be reversibly extracted from triphylite LiFePO$_4$.[1] As an electrode in rechargeable Li batteries, the material has a theoretical capacity of 170 mAh/g, combined with a lithium intercalation potential of 3.5 V,[2] and exhibits an excellent thermal stability. In addition, it is inexpensive and environmentally benign, making it of interest for large-scale battery applications. Li$_x$FePO$_4$ ($0 < x < 1$) is phase separating at room temperature and undergoes a phase transformation between heterosite FePO$_4$ and triphylite LiFePO$_4$ during the charge and discharge process.[3–5] In order to better control the thermodynamical properties determining its electrochemical performance, a better understanding of its elastic properties is needed. At present, experimental data on mechanical properties such as elastic constants or bulk moduli are not available since Li$_x$FePO$_4$ is usually synthesized as sintered powder and the growth of larger crystals is known to be very difficult. In this study, we focus on the calculation of the elastic constants from first principles and deduce from those estimates of the Debye temperature and other elastic properties.

LiFePO$_4$ has an orthorhombic olivine structure, space group *Pnma*, with experimental lattice parameters of $a = 10.3375$ Å, $b = 6.0112$ Å, and $c = 4.6950$ Å.[6] It consists of a distorted hexagonal close-packed framework containing Fe^{2+} ions which are sixfold coordinated by oxygen atoms forming layers of edge-sharing octahedra. Individual layers are separated by PO$_4$ tetrahedra (see Fig. 1). Although the equilibrium structure of FePO$_4$ is rodolicoite,[7,8] space group $P3_121$, lithium can be electrochemically removed from LiFePO$_4$ without changing the olivine topology. The experimental lattice parameters of such a delithiated FePO$_4$ are $a = 9.7599$ Å, $b = 5.7519$ Å, and $c = 4.7560$ Å.[6]

The computation of elastic constants from first principles is a well-established method which is based on the expansion of the internal energy in powers of the strain tensor. Within this study, we recapture the most essential concepts and refer the reader to the work of Ravindran and co-workers[9] who have reported the formalism for orthorhombic crystals in great detail. For each of the nine independent elastic constants, symmetric distortion matrices have been applied to the equilibrium unit cell containing four formula units of LiFePO$_4$ and FePO$_4$, respectively. The elastic constants are obtained by a polynomial fit of the total energy as a function of the strength of the applied distortion.[9] In order to minimize the effect of higher-order terms on the computed elastic constants very small strains less than ±1.0% have been applied. Although a real material might exhibit plastic deformations already at this level of distortion due to dislocations which are absent in this study, it is observed that the value of the computed elastic constants is independent of the amount of distortion for strains up to 5%.

We follow the notation that *a*, *b*, and *c* correspond to x_1, x_2, and x_3, respectively. The stress tensor σ_{ij} is defined by $dF_i = \Sigma_{j=1}^{3} \sigma_{ij} dA_j$, where dF_i is the force on a small-area element dA_j and the subscripts 1, 2, and 3 refer to the *a*, *b*, and *c* axes, respectively. Correspondingly, the infinitesimal strain matrix is defined as $\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$, where *u* is the displacement vector and *x* is a coordinate. The fourth-rank compliance tensor c_{ijkl} is reduced to the matrix notation c_{ij} according to commonly used conventions.[10]

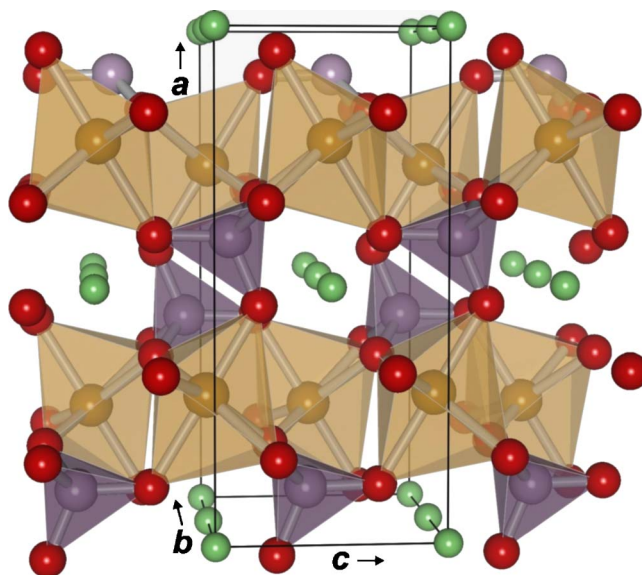Calculations in this work are performed in a plane-wave

FIG. 1. (Color online) LiFePO$_4$ olivine structure. The Fe octahedra shown in light gray (yellow), the P tetrahedra in dark gray (purple), Li atoms in light (green), and O atoms in dark (red).

basis set using the projector augmented-wave (PAW) method[11] in the generalized gradient approximation (GGA).[12] It has been shown that GGA+U is an appropriate method for predicting materials properties of oxides and phosphates containing 3d transition metals. *Ab initio* results obtained with GGA+U on phase stability, thermodynamic properties, and magnetic and electronic structure show significant better agreement with experiment than in the GGA.[5,13–15] The rotationally independent implementation of GGA+U according to Ref. 16 which considers U and J as independent parameters is used for this study. Quantitative results in the GGA+U method are known to be dependent on the value of U. Since the value of U depends on the valence state of the transition-metal ion,[14,17] self-consistently calculated U values for Fe^{2+} and Fe^{3+} ions are different. Specific values of $U=4.7$ eV and $U=5.9$ eV are used for $LiFePO_4$ and $FePO_4$, respectively. The exchange constant $J=1$ eV is used for both material systems. In order to investigate the effect of the U parameter on the elastic constants we also compare the GGA+U results with those obtained using GGA.

For all calculations, the magnetic ground-state structure of high-spin Fe^{2+}/Fe^{3+} in a C-type antiferromagnetic configuration is used.[6,18] A k-point mesh of 96 k points is chosen in order to assure that the total ground-state energy is converged within less than 1 meV per formula unit. Due to a lack of experimental data, we cannot compare the computed elastic constants with experimental values. We estimate the purely numerical error on the elastic constants c_{ii} to be of the order of 5%–10% while the elastic constants c_{12}, c_{13}, and c_{23} are expected to exhibit larger numerical errors since the corresponding polynomial fits also incorporate the calculated values of c_{11}, c_{22}, and c_{33}.[9]

The lattice parameter and elastic constants obtained from GGA and GGA+U calculations are given in Table I. The computed unit-cell dimensions are slightly larger than experimental values. It is interesting to note that a finite U parameter increases the cell volume for $LiFePO_4$ while it is decreased in the case of $FePO_4$. Additionally, the lattice constants a and b increase while c decreases when lithium is inserted into $FePO_4$ which is consistent with experimental findings. The introduction of the Hubbard U correction has only a small effect on the lattice constants.

Although we follow the widely utilized notation a, b, and c for the lattice constants, the elastic constants are given in the commonly used notation c_{ij} with $i,j=1,\ldots,6$. $FePO_4$ is isostructural to $LiFePO_4$ where all lithium crystal sites are unoccupied. Hence it is expected that $FePO_4$ is softer when the crystal is distorted since the PO_4 tetrahedra and the FeO_6 octahedra are able to move towards the empty space. However, the elastic constants c_{11} and c_{66} are larger for $FePO_4$ than for $LiFePO_4$. In order to investigate this anomaly, we have analyzed the relative ionic movement when the distortions are applied. Our results show that under a compression along the a axis, the PO_4 tetrahedra are slightly rotating while moving towards the unoccupied lithium sites. As a consequence, the FeO_6 octahedra which are slightly tilted around the b axis (see Fig. 1) are straightened up along the a axis, increasing the elastic constant c_{11} with respect to that of $LiFePO_4$. A similar argument applies for c_{66}. Furthermore,

TABLE I. Elastic constants (given in GPa) and Debye temperature of Li_xFePO_4.

	$FePO_4$ GGA	$FePO_4$ GGA+U	$LiFePO_4$ GGA	$LiFePO_4$ GGA+U
V [Å^3]	288.06	284.57	297.05	299.54
a [Å]	9.94	9.96	10.39	10.45
b [Å]	5.93	5.88	6.04	6.05
c [Å]	4.88	4.86	4.73	4.74
c_{11}	166.5	175.9	133.0	138.9
c_{22}	127.7	153.6	203.0	198.0
c_{33}	121.3	135.0	172.3	173.0
c_{44}	32.5	38.8	34.9	36.8
c_{55}	43.0	47.5	47.8	50.6
c_{66}	45.6	55.6	42.4	47.6
c_{12}	33.0	29.6	74.3	72.8
c_{13}	57.1	54.0	54.3	52.5
c_{23}	9.2	19.6	55.2	45.8
ϱ [g/cm^3]	3.47	3.51	3.52	3.49
T_D [K]	473	511	509	533

the constants c_{11} (c_{22}) of $FePO_4$ ($LiFePO_4$) are significantly larger than other elastic constants, resulting in a pronounced elastic anisotropy which will be discussed later in more detail.

The Debye temperature T_D is a fundamental attribute of a solid connecting elastic properties with thermodynamic properties such as specific heat, melting temperature, or vibrational entropy. It can be calculated from the average sound velocity obtained by integrating the elastic-wave velocities over several crystal directions using the elastic constants and using the following equation[19]:

$$T_D = \frac{h}{k_B}\left(\frac{9N}{4\pi V}\right)^{1/3}\varrho^{-1/2}a_0^{-1/3},$$

where h is Planck's constant, k_B is Boltzmann's constant, N is the number of atoms in the unit cell, V is the volume of the unit cell, ϱ is the density, and a_0 is a function of the elastic constants. The explicit expression of a_0 for a model incorporating ten different directions is given in Ref. 19. The computed values of the Debye temperatures are listed in Table I. Our results predict that T_D is higher for $LiFePO_4$ than for $FePO_4$, suggesting that $FePO_4$ is softer than $LiFePO_4$. GGA+U values are slightly larger than those obtained with the GGA.

As mentioned before, large single crystals of Li_xFePO_4 are currently unavailable and measurement of the individual elastic constants is not possible. However, measurement of the bulk modulus B and shear modulus G may be determined on polycrystalline samples. On the basis of the approximations by Voigt[20] and Reuss[21] and Hill's empirical average,[22] we have calculated the corresponding bulk and shear moduli

TABLE II. Polycrystalline shear and bulk moduli, Young modulus (in GPa), and Poisson ratio.

	FePO$_4$ GGA	FePO$_4$ GGA+U	LiFePO$_4$ GGA	LiFePO$_4$ GGA+U
G_R	42.9	50.3	44.3	47.2
G_V	45.3	52.5	46.7	49.6
G_H	44.1	51.4	45.5	48.4
B_R	63.5	72.7	94.3	93.0
B_V	68.2	74.5	97.3	94.7
B_H	65.9	73.6	95.8	93.9
E_H	108.2	125.0	117.8	123.9
ν_H	0.23	0.22	0.30	0.28

which are listed in Table II. Additionally the Young modulus E_H and Poisson ratio ν_H have been calculated using Hill's empirical average and the equations:

$$E_H = 9B_H G_H/(3B_H + G_H)$$

and

$$\nu_H = (3B_H - 2G_H)/(6B_H + 2G_H).$$

As a result, Li$_x$FePO$_4$ exhibits a smaller values for bulk, shear, and Young moduli than most transition-metal oxides.[23,24] Furthermore, our results show that LiFePO$_4$ is a harder material than FePO$_4$ which is consistent with the prediction that lithium transport is expected to be faster in FePO$_4$ than in LiFePO$_4$.[25,26]

It is speculated that the cracking of crystallites is one of the factors leading to capacity fading of Li$_x$FePO$_4$ when it is used as a cathode material in rechargeable Li batteries and Li is cycled in and out of it.[27] The formation of such cracks and dislocations can be induced by elastic anisotropy.[28,29] For orthorhombic materials anisotropy arises from shear anisotropy as well as from the anisotropy of the linear bulk modulus. The shear anisotropic factors are

$$A_1 = 4c_{44}/(c_{11} + c_{33} - 2c_{13})$$

for the {100} shear planes in ⟨010⟩ and ⟨011⟩ directions,

$$A_2 = 4c_{55}/(c_{22} + c_{33} - 2c_{23})$$

for the {010} shear planes in ⟨001⟩ and ⟨101⟩ directions, and

$$A_3 = 4c_{66}/(c_{11} + c_{22} - 2c_{12})$$

for the {001} shear planes in ⟨010⟩ and ⟨110⟩ directions.[9] The deviation of the anisotropic factors from unity is a measure for the elastic anisotropy.

In order to investigate the anisotropy arising from the linear bulk moduli, it is useful to calculate the bulk moduli along the crystal axes, defined as[9] $B_a = a\frac{dP}{da}$, $B_b = b\frac{dP}{db}$, and $B_c = c\frac{dP}{dc}$. The anisotropy of the bulk modulus along the a axis with respect to the b and c axes can then be written as

$A_{B_b} = B_a/B_b$ and $A_{B_c} = B_a/B_c$. Note that a value of unity for these two fractions represents elastic isotropy and any deviation from 1 provides a measure of the degree of anisotropy. Alternatively, Chung and Buessem introduced[30,31] a more practical measure of elastic anisotropy for polycrystalline materials where the percentage anisotropy in compressibility and shear is defined as

$$A_B = (B_V - B_R)/(B_V + B_R)$$

and

$$A_G = (G_V - G_R)/(G_V + G_R),$$

respectively, where B and G are the bulk and shear moduli and the subscripts V and R correspond to the Voigt and Reuss limits. For these expressions, a value of zero identifies elastic isotropy and a value of 100% is the largest possible anisotropy. The calculated values of the anisotropic factors and directional bulk moduli are given in Table III.

Compared to the large number of anisotropic crystals investigated in Ref. 30, Li$_x$FePO$_4$ is moderately anisotropic. However, two observations are noteworthy: First, the shear and bulk modulus anisotropy is higher for GGA than for GGA+U calculations. Second, the anisotropy changes significantly during lithium insertion, i.e., the transformation from FePO$_4$ to LiFePO$_4$. It is most pronounced when the bulk moduli along the a axis are compared to those along the b and c axes. It can be expected that A_{B_b} and A_{B_c} differ from unity since the a axis is perpendicular while the b and c axes are parallel to the transition-metal and lithium layers. However, the change in the anisotropy factors is remarkable and is also suggesting that Li$_x$FePO$_4$ is susceptible to crack propagation during battery cycling as it has been observed by Wang and co-workers.[27] Using very small LiFePO$_4$ particles would be a way of minimizing phase transformation cracking.

TABLE III. Anisotropic factors and directional bulk moduli (in GPa).

	FePO$_4$ GGA	FePO$_4$ GGA+U	LiFePO$_4$ GGA	LiFePO$_4$ GGA+U
A_1	0.749	0.766	0.709	0.712
A_2	0.746	0.761	0.722	0.724
A_3	0.800	0.822	0.906	0.995
A_{B_b}	2.794	1.654	0.450	0.573
A_{B_c}	2.737	1.709	0.739	0.846
A_G [%]	2.76	2.11	2.56	2.44
A_B [%]	3.57	1.26	1.56	0.87
B_a	415	317	207	255
B_b	148	192	459	393
B_c	152	186	279	266
B	64	73	94	93

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