First-Principles Determination of the Soft Mode in Cubic ZrO_2

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A direct approach to calculate the phonon dispersion using an *ab initio* force constant method is introduced. The phonon dispersion and structural instability of cubic ZrO_2 are found using a supercell method in the local-density approximation. The force constants are determined from the Hellmann-Feynman forces induced by the displacement of an atom in the $2 \times 2 \times 2$ fcc supercell. This size of the supercell gives "exact" phonon frequencies at Γ, X, L, W Brillouin zone points. The phonon dispersion curves show a pronounced soft mode at the X point, in agreement with the experimentally observed cubic to tetragonal phase transition. [S0031-9007(97)03230-4]

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The calculation of phonon frequencies of the crystalline structure is one of the fundamental subjects when considering the phase stability, phase transitions, and thermodynamics of crystalline materials. The approaches of *ab initio* calculations fall into two classes: the *linear response method* [1] and the *direct method*. In the first approach, the dynamical matrix is expressed in terms of the inverse dielectric matrix describing the response of the valence electron density to a periodic lattice perturbation [1] (for a review, see Ref. [2]). For a number of systems the linear-response approach is difficult, since the dielectric matrix must be calculated in terms of the electronic eigenfunctions and eigenvalues of the perfect crystal.

There are two variants of the direct method. In the frozen-phonon method [3], the phonon energy is calculated as a function of the displacement amplitude in terms of the difference in the energies of the distorted and ideal lattices. This approach is restricted to phonons whose wavelength is compatible with the periodic boundary conditions applied to the supercell used in the calculations. Another approach of the direct method uses the forces calculated via the Hellmann-Feynman theorem in the total energy calculations, derives from them the values of the force constant matrices assuming a finite range of interaction, and hence the dynamical matrix and phonon dispersion curves [4]. This method has been applied to alkali metals [4]. Similar calculations, using the ultrasoft pseudopotentials have been carried out successfully for diamond and graphite [5], and for perovskite $PbTiO_3$ [6]. The linear response method has been applied to ideal cubic perovskite structure as well. For $KNbO_3$ [7] the linearized augmented plane-wave method calculations confirmed that a soft mode at the Γ point is responsible for the cubic to tetragonal phase transition.

The *ab initio* force constant approach is based on the supercell with periodic boundary conditions [4,5]. In such a supercell, a displacement $\mathbf{u}(0,\nu)$ of a single atom induces forces $\mathbf{F}(\mathbf{n},\mu)$ acting on all other atoms,

$$\mathbf{F}(\mathbf{n},\mu) = -\sum_{\mathbf{L}} \mathbf{B}(\mathbf{n},\mu;\mathbf{L},\nu) \cdot \mathbf{u}(0,\nu)\,, \qquad (1)$$

where $\mathbf{B}(\mathbf{n},\mu;\mathbf{L},\nu)$ are the (3×3) harmonic force constant matrices relating atoms $(\mathbf{n},\mu)$ and $(\mathbf{L},\nu)$. Here $\mathbf{n}$ is the index of the primitive unit cell. We denote by $\mathbf{L}$ indices of the lattice constants of the supercell. The μ and ν are indices of atoms in the primitive unit cell. Because of the periodic boundary conditions, on each atom of the supercell acts a force coming from the atom displaced inside the supercell, and from the equivalent atoms displaced in all images of the supercell. The summation over supercells $\mathbf{L}$ in Eq. (1) takes care of this fact. It is straightforward to introduce the cumulant force constant matrix

$$\mathbf{B}_{\Sigma}(\mathbf{n},\mu;0,\nu) = \sum_{\mathbf{L}} \mathbf{B}(\mathbf{n},\mu;\mathbf{L},\nu) \qquad (2)$$

which has the same symmetry as $\mathbf{B}(\mathbf{n},\mu;0,\nu)$ [8]. The (3×3) $\mathbf{B}_{\Sigma}$ matrix can be equally well represented as a (9×1) column matrix $\mathcal{B}_{\Sigma}$, so that $(\mathcal{B}_{\Sigma})_k = (B_{\Sigma})_{i,j}$ and $k = 3(i-1) + j$. It is useful to decouple $\mathcal{B}_{\Sigma}$ to part $\mathcal{A}$ of dimensions $(9 \times p)$ and part $\mathcal{P}_{\Sigma}$ of dimensions $(p \times 1)$

$$\mathcal{B}_{\Sigma}(\mathbf{n},\mu;0,\nu) = \mathcal{A}(\mathbf{n},\mu;0,\nu) \cdot \mathcal{P}_{\Sigma}(\mathbf{n},\mu;0,\nu)\,. \qquad (3)$$

The matrix $\mathcal{A}$ is determined by symmetry considerations only, and is independent of the potential strength, contrary to $\mathcal{P}_{\Sigma}$ which is characterized by the potential. Inserting Eq. (3) into Eq. (1), one finds

$$\mathbf{F}(\mathbf{n},\mu) = -\mathcal{U}(0,\nu) \cdot \mathcal{A}(\mathbf{n},\mu;0,\nu) \cdot \mathcal{P}_{\Sigma}(\mathbf{n},\mu;0,\nu)\,, \qquad (4)$$

where the displacement vector $\mathbf{u}(0,\nu)$ has been converted into the (3×9) matrix $\mathcal{U}(0,\nu)$, with elements of $\mathbf{u}(0,\nu)$ such that the multiplication rules $\mathbf{B} \cdot \mathbf{u}$ in Eq. (1) are fulfilled. Denoting $\mathcal{C}(\mathbf{n},\mu;0,\nu) = -\mathcal{U}(0,\nu) \cdot \mathcal{A}(\mathbf{n},\mu;0,\nu)$, Eq. (4) is simplified to

$$\mathbf{F}(\mathbf{n},\mu) = \mathcal{C}(\mathbf{n},\mu;0,\nu) \cdot \mathcal{P}_{\Sigma}(\mathbf{n},\mu;0,\nu)\,. \qquad (5)$$

This equation can be written in the global matrix form

$$\underline{\mathcal{F}} = \underline{\mathcal{C}} \cdot \underline{\mathcal{P}}_{\Sigma}\,, \qquad (6)$$

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where $\underline{\mathcal{F}}$, $\underline{\mathcal{C}}$, and $\underline{\mathcal{P}}_\Sigma$ are $(3ns \times 1)$, $(3ns \times p)$, and $(p \times 1)$ dimensional matrices, respectively. Here, n is the number of atoms in the supercell; s is the number of force fields. A force field is a set of $3n$ Hellmann-Feynman forces obtained for a run with a single displaced atom. Usually, a single input force field is not sufficient for finding all parameters. The minimum number of force fields is equal to the number of nonequivalent atoms in the crystal primitive unit cell multiplied by a number of independent x, y, z coordinates in the site symmetry of a given atom.

As a rule, the number of force field data is considerably greater than the number of parameters, i.e., $3ns \gg p$, and the system, Eq. (6), is overdetermined. To solve it we apply the single value decomposition method [9] to the matrix $\underline{\mathcal{C}}$, and express the parameters in terms of forces $\underline{\mathcal{P}}_\Sigma = \underline{\mathcal{C}}^{-1} \cdot \underline{\mathcal{F}}$. This method produces a solution, which is the best approximation in the least-squares sense, and is able to treat problems with the singular matrix $\underline{\mathcal{C}}$.

The aim of the referred direct method is to describe the dynamical matrix $\mathbf{D}(\mathbf{k})$ of the crystal, which is defined as

$$\mathbf{D}(\mathbf{k};\mu\nu) = \frac{1}{\sqrt{M_\mu M_\nu}} \sum_{\mathbf{m}} \mathbf{B}(0,\mu;\mathbf{m},\nu) \times \exp\{-2\pi i \mathbf{k} \cdot [\mathbf{R}(0,\mu) - \mathbf{R}(\mathbf{m},\nu)]\}. \quad (7)$$

Here the summation $\mathbf{m}$ runs over all atoms, M_μ, M_ν and $\mathbf{R}(0,\mu), \mathbf{R}(\mathbf{m},\nu)$ are masses and positions of atoms, respectively. Using the cumulant force constants, Eq. (2), one may define an approximate dynamical matrix as

$$\mathcal{D}(\mathbf{k};\mu\nu) = \frac{1}{\sqrt{M_\mu M_\nu}} \sum_{\mathbf{M}} w_{\mathbf{M}} \mathcal{B}_\Sigma(0,\mu;\mathbf{M},\nu) \times \exp\{-2\pi i \mathbf{k} \cdot [\mathbf{R}(0,\mu) - \mathbf{R}(\mathbf{M},\nu)]\}. \quad (8)$$

The atom $(0,\mu)$ is always placed in the center of the supercell. One defines an "extended" supercell, which has the same volume as the original one, but which includes atoms on all its surfaces, and restores the local symmetry around a given atom $(0,\mu)$. Of course, the extended supercell contains more atoms than the conventional one. To guarantee the Hermitian property of $\mathcal{D}(\mathbf{k})$, Eq. (8), the summation $\mathbf{M}$ must run over all neighbors inside the extended supercell. The summation over images of supercells $\mathbf{L}$ is already included in the definition of cumulant force constant $\mathbf{B}_\Sigma(\mathbf{n},\mu;0,\nu)$ in Eq. (2). It could happen, however, that atoms located at the surfaces of the extended supercell are separated by $\mathbf{L}$. These are the equivalent displaced atoms, because of periodic boundary conditions. They influence the central atom with a similar strength. Therefore, in the definition of the approximate dynamical matrix, the $\mathcal{B}_\Sigma(0,\mu;\mathbf{M},\nu)$ must be taken with fractional weight $w_{\mathbf{M}}$, so that at the wave vector $\mathbf{k}_{\mathbf{L}}$ fulfilling the condition

$$\exp(2\pi i \mathbf{k}_{\mathbf{L}} \cdot \mathbf{L}) = 1 \quad (9)$$

the approximate and conventional dynamical matrices are equal, $\mathcal{D}(\mathbf{k}_{\mathbf{L}}) = \mathbf{D}(\mathbf{k}_{\mathbf{L}})$. Hence, the phonon dispersion curves calculated by the new direct method are exact at discrete wave vectors $\mathbf{k}_{\mathbf{L}}$, given by Eq. (9). Usually, the $\mathbf{k}_{\mathbf{L}}$ wave vectors correspond to high-symmetry points of the Brillouin zone. However, increasing the size of the supercell, one increases the density of the wave vector grid $\mathbf{k}_{\mathbf{L}}$; in this way better accuracy of the phonon dispersion curves is achieved. The advantage of the introduced direct method is that it does not impose any limit to the range of interaction. An interaction with the range far beyond the supercell will also give exact solutions at the wave vectors $\mathbf{k}_{\mathbf{L}}$. The method interpolates the dispersion curves between exact points; however, if the force constants outside the supercell are so small that they could be neglected, then the dispersion curves are exact for all the wave vectors. Thus, for $\mathbf{k} \neq \mathbf{k}_{\mathbf{L}}$ the deviation from correct solution might increase with an increasing range of interaction. The referred method combines the frozen phonon [3] and the direct approach with a finite range of interaction [4]. Knowledge of the $A(\mathbf{n},\mu;0,\nu)$ matrices allows us to use crystal symmetry in order to reduce the statistical errors of Hellmann-Feynman forces. This technique can be applied to crystals of any complexity, provided sufficient memory and computer time are avaliable to solve Eq. (6).

In this Letter we apply the *ab inito* force constant approach to calculate phonons in cubic ZrO_2 (zirconia). In the highest temperature phase, the cubic ZrO_2 has a simple fluorite structure ($Fm\bar{3}m$, $Z = 1$). At about 2600 K with decreasing temperature, it undergoes a cubic to tetragonal ($P4_2/nmc$, $Z = 2$) phase transition, driven by the irreducible representation X_2^- [10] from the X point at the boundary of the fcc Brillouin zone. The total energy calculation for cubic ZrO_2, using the full-potential linear augmented plane wave method have been performed already in Ref. [11]. The linear combination of atomic orbitals method has been used to study the band structure and density of states [12]. The potential induced breathing model has been applied to calculate the equation of state and elasticity of ZrO_2 [13]. A simple model with pair-wise force constants and only four free parameters [14] has been used to calculate the phonon dispersion curves along the Γ-X line in the cubic phase. The free parameters have been fitted to the elastic constants and to the longwave T_{2g} Raman-active vibrational frequency [15]. One phonon branch underwent a drop to the low frequency at the boundary X, but it did not become soft.

Our calculations of the Hellmann-Feynman forces for cubic ZrO_2 have been performed using the CASTEP *ab initio* program [16], and the results have been obtained within the local-density-functional approximation using a pseudopotential approach and $(2 \times 2 \times 2)$ fcc supercell with 96 atoms. The electronic wave functions were represented as plane waves with cut-off energy at 700 eV. To describe the ion-electron interaction the optimized norm-conserving pseudopotentials according to the kinetic-energy-optimization scheme [17,18] have been used to describe the ion-electron interaction. The atomic configurations $4d^25s^2$ for Zr, and $2s^23p^4$ for O atoms were used to generate the pseudopotentials in the Kleinman-Bylander form [19]. The exchange-correlation potential due to Ceperley and Alder as parametrized by Perdew and Zunger [20] was employed. Brillouin zone integrations have been carried out using only the Γ point. Checking calculations with the $(2, 2, 2)$ mesh of k points [21] were also performed and they did not show a significant difference from the result obtained with the Γ point only.

With the $2 \times 2 \times 2$ supecell, the phonons calculated from Hellmann-Feynman forces are exact at Γ, X, L, W, and two other wave vector points, namely, at the midpoint between Γ and X along $\langle 1, 0, 0\rangle$ and $\langle 1, 1, 0\rangle$ directions. The positions of $\mathrm{Zr} = (0, 0, 0)$, $\mathrm{O}(1) = (1/4, 1/4, 1/4)$, and $\mathrm{O}(2) = (3/4, 3/4, 3/4)$ are fixed by symmetry. The only free parameter to be found in the optimization is the lattice constant a_0. Figure 1 shows the calculated total energy as a function of the lattice constant. The minimum occurs at $a_0 = 5.13$ Å. This may be compared with the experimental value $a_0 = 5.256$ Å at a temperature of 2600 K [22].

In the direct method the amplitude of the atomic displacements has been limited to $u_0 = \pm 0.010 a_0$. Four independent runs of Hellmann-Feynman force fields have been carried out: two for Zr and two for O atoms, all displaced along z. This gives 1152 force field data. The symmetry analysis of force constants within the supercell leads to 68 independent parameters. Solving Eq. (6), one finds 59 independent parameters to be nonzero. The remaining nine parameters vanish due to additional symmetry imposed by the choice of a $2 \times 2 \times 2$ supercell. Each parameter is a result of averaging over 8 to 32 force field data. The nearest neighbor force constants between Zr and O atoms are strongly negative, supporting the tendency to displace Zr and O. The same behavior is found for two nearest neighbor O atoms. A pair of oxygen atoms diminish the energy when they are simultaneously displaced along the $\langle 1, 0, 0\rangle$ direction. Different force constants are found between oxygen atoms at $a_0\sqrt{3}/2$ distance, depending on the presence of an intermediate Zr atom. Namely, the O-Zr-O force constants are by one order of magnitude greater than these of the direct O-O bond. We checked the translational invariance condition which has been satisfied within 0.25%.

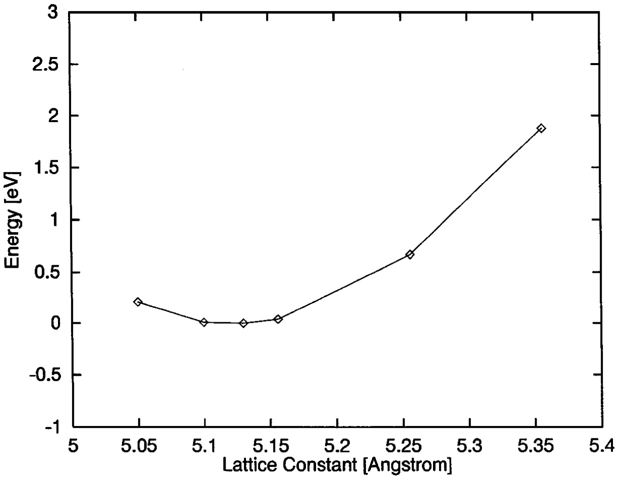

FIG. 1. Ground state total energy of cubic $\mathrm{ZrO_2}$ per $1 \times 1 \times 1$ supercell, as a function of the lattice constant a_0. The minimum has been set to zero energy.

The phonon frequencies have been calculated using Eq. (8) and are plotted along high-symmetry directions in Fig. 2. The Γ-X, X-W, and L-Γ lines are along $\langle 1, 0, 0\rangle$, $\langle 1, 2, 0\rangle$, and $\langle 1, 1, 1\rangle$ directions, respectively. At the Γ point the Raman active optical mode of T_{2g} symmetry occurs at 16.49 THz (550.2 cm^{-1}) being lower than the experimental value (640 cm^{-1}) [15,23] by 14%. Unfortunately, the phonon dispersion curves, as given in Fig. 2, cannot be compared directly with experiment, because such data, to the best of our knowledge, do not exist.

In Fig. 2 imaginary phonon frequencies of unstable modes are represented as negative values. A nondegenerate mode has been found at the X point. Its value reads $i5.86$ THz. It stiffens up rapidly away from the X point. Examination of the soft mode polarization vector reveals that it is polarized along the $\langle 1, 0, 0\rangle$ direction. It indicates that neighboring chains of oxygen atoms displace in opposite directions, towards the structure stabilized in the tetragonal phase.

In summary, we have shown that the direct method allows for efficient *ab initio* calculations of the complete phonon dispersions, including the specification of the soft mode.

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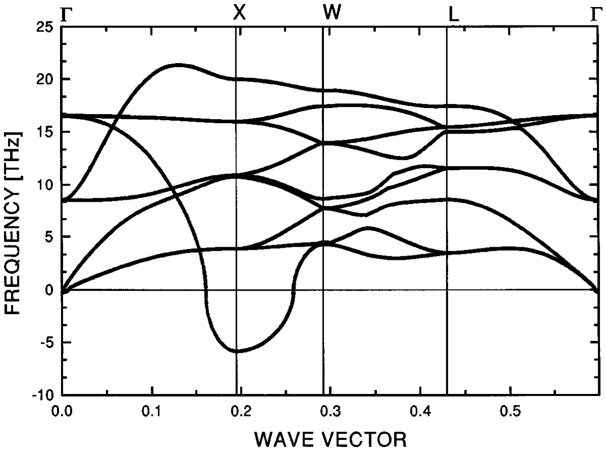

FIG. 2. Calculated phonon dispersions of $\mathrm{ZrO_2}$ in the cubic structure at the extremum lattice constant $a_0 = 5.13$ Å.

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