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Ab Initio Equation of State of an Organic Molecular Crystal: 1,1-Diamino-2,2-dinitroethylene

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A complete equation of state for the molecular crystal 1,1-diamino-2,2-dinitroethylene has been calculated from first principles for temperatures between 0 and 400 K, and for specific volumes from 61 to 83 cm^3/mol, corresponding to relative volumes from 0.78 to 1.06. The calculated 300 K isotherm agrees very well with the experimentally measured pressure−volume relation reported by Peiris et al. (Peiris, S. M.; Wong, C. P.; Zerilli, F. J. *J. Chem. Phys.* **2004**, *120*, 8060). The volumetric thermal expansion coefficient is calculated to be 140 ppm/K at 300 K and atmospheric pressure and varies considerably with specific volume as well as temperature. The Grüneisen parameter varies significantly with temperature, but its variation with specific volume is small. The calculated specific heat (160 J/mol/K at 300 K and atmospheric pressure) has only a very small dependence on specific volume.

1. Introduction

The theoretical prediction of equations of state is important in many fundamental and practical problems, in fields as far ranging as planetary science and military applications, where experimental data may be difficult, expensive, or, in some cases, impossible to obtain. In this regard, there is great interest in computing the equation of state for a class of organic molecular crystals that are the ingredients of materials often referred to as energetic materials because of their propensity for rapid explosive decomposition under shock conditions. While fits of experimental data to analytic equations of state have achieved some success, ab initio calculations hold the promise for calculating the equation of state as well as a number of other chemical and physical properties of these materials in cases in which experimental data is not available and not easy to obtain.

In this article, we describe the ab initio calculation of the complete equation of state for an organic molecular crystal,1,1-diamino-2,2-dinitroethylene ($C_2H_4N_4O_4$), over a pressure range from 0 to 4 GPa and a temperature range of 0−400 K. The temperature-independent mechanical compression was obtained with numerical solutions of the many-body Schrödinger equation using the Hartree−Fock method with a computational scheme utilizing a basis set consisting of linear combinations of atomic orbitals as implemented in the computer program CRYSTAL.[1,2] A complete description of the 0 K isotherm calculations has been reported in previous publications.[3] The $T > 0$ vibrational contributions to the Helmholtz free energy were obtained in the quasi-harmonic approximation from solutions of the Schrödinger equation using density functional theory methods as implemented in the computer program ABINIT, a plane wave pseudopotential code developed by Gonze, et al.[4]

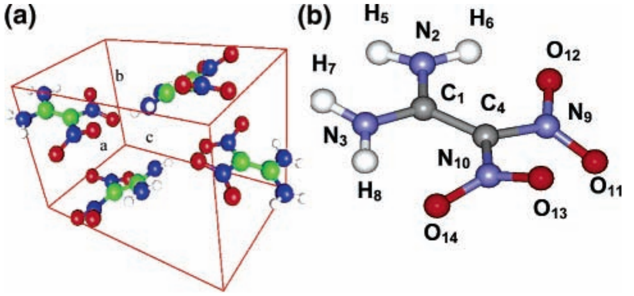

Figure 1. FOX-7 unit cell (a) and molecular unit (b). The entire molecule comprises the irreducible asymmetric unit.

Bemm and Östmark[5] determined the crystal structure of 1,1-diamino-2,2-dinitroethylene, which they named FOX-7, to be monoclinic with space group $P2_1/n$ and four molecules per unit cell. They reported the values of the lattice parameters $a = 6.9410$, $b = 6.5690$, $c = 11.315$ Å, $\beta = 90.55°$. Gilardi[6] has also studied the structure of FOX-7 and found the values $a = 6.9396$, $b = 6.6374$, $c = 11.3406$ Å, and $\beta = 90.611°$. The unit cell and molecular conformation are depicted in Figure 1. The irreducible asymmetric unit of the unit cell consists of one complete molecule. The crystal has a layered structure with strong hydrogen bonding within the layers due to the proximity of NH_2 groups from one molecule with NO_2 groups from an adjacent molecule. Only a relatively weak van der Waals binding exists between layers. Later, Bemm and Eriksson[7] reported four phases of FOX-7, and Kempa and Herrmann[8] have observed three phases at atmospheric pressure using temperature-resolved X-ray powder diffraction, designated α, β, and γ. The α phase is the $P2_1/n$ monoclinic structure; the β phase is an orthorhombic $P2_12_12_1$ structure. The structure of the γ phase was not determined. The transition from α to β occurs at about 386 K, and β to γ occurs at 448 K. In the temperature and pressure range studied here, FOX-7 very likely remains in the α phase

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because the specific volume of the β phase is slightly larger than that of the α phase. There is some experimental evidence of loss of crystal structure at pressures exceeding 4 GPa, which may indicate change to an amorphous structure or the beginnings of decomposition.[9]

In the next section we will review the details of the calculations, and in section 3 we present the results of the computations.

2. Details of the Calculations

The thermodynamic properties of the system are obtained by calculating the Helmholtz free energy, which may be written

$$F(V,T) = U_0(V) + F_{\mathrm{vib}}(V,T) + F_{\mathrm{elect}}(V,T) \qquad (1)$$

where $U_0(V)$ is the temperature-independent energy of mechanical compression, F_{vib} is the vibrational contribution to the free energy, written in the harmonic approximation as

$$F_{\mathrm{vib}}(V,T) = \frac{1}{2}\sum_{i=1}^{N}\sum_{\vec{q}} \hbar\omega(i,\vec{q}) + kT\sum_{i=1}^{N}\sum_{\vec{q}} \ln(1 - e^{-\hbar\omega(i,\vec{q})/kT}) \qquad (2)$$

and F_{elec} is the electronic contribution. In the quasi-harmonic approximation used in this work, $\omega(i, \vec{q})$, the frequency of the i'th vibrational mode at a point $\vec{q}$ in the Brillouin zone, is a function of the geometry, and hence the specific volume, of the crystal. For the temperature range considered here, the electronic contribution is negligible and we need only consider the vibrational contribution.

2.a. Mechanical Compression. The calculation of the mechanical compression energy $U_0(V)$ was reported previously,[3] and a brief summary is given here. The basic quantum calculations for a periodic structure were performed with the CRYSTAL98[1] computer program, using the Hartree−Fock method and a linear combination of atomic orbitals basis set (6-21G in Pople's notation). Scaling factors were applied to the outer valence orbitals, reducing their range, to adapt what would normally be a basis set optimized for isolated clusters of atoms for use in a periodic structure computation. Optimizations of the atomic coordinates and lattice parameters were done separately and iteratively. The atomic coordinates were first optimized using Zicovich-Wilson's LoptCG script,[10] which calls CRYSTAL98 to calculate the energy for each configuration. The lattice parameters then were optimized under a fixed volume constraint for a set of volumes representing a number of hydrodstatic compressions using an in-house written program based on the downhill simplex method of Nelder and Mead.[11,12] This was repeated until satisfactory convergence was achieved. All optimizations preserved the space group of the crystal.

In recent work,[13] we have calculated the mechanical compression curve for solid nitromethane with the 2003 version of CRYSTAL using both Hartree−Fock and density functional theory (DFT) methods. In addition, calculations with both 6-21G and 6-31G** basis sets were performed, and the effect of basis set superposition error (bsse) was estimated using the counterpoise method.[14] The 6-31G** basis set was optimized by scaling the outer valence and polarization orbitals. It was found that Hartree−Fock calculations with a 6-21G basis set, uncorrected for basis set superposition error, gave the best agreement with experiment. The DFT methods (Perdew−Wang generalized gradient approximation[15]) calculations gave nearly the same results. As one moves toward higher compressions away from the zero pressure equilibrium state, the 6-21G and 6-31G** basis sets gave comparable results, whether corrected for bsse or not.

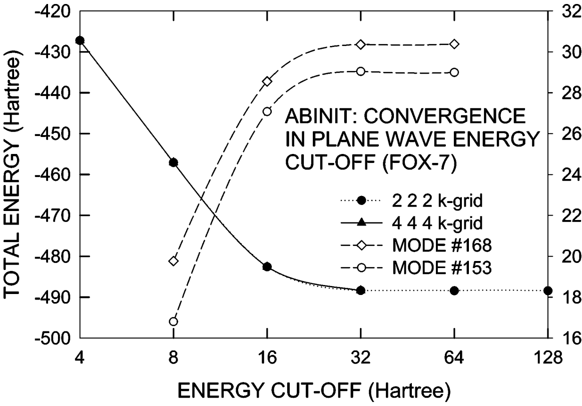

Figure 2. Total energy calculated by ABINIT as a function of the maximum energy of plane waves included in the basis set. Energies were calculated with a 4 × 4 × 4 Monkhorst−Pack reciprocal space grid as well as a 2 × 2 × 2 grid. Also shown are the frequencies of the highest and 16th highest frequency zero wave vector modes (points connected with the dashed curves, scale at right).

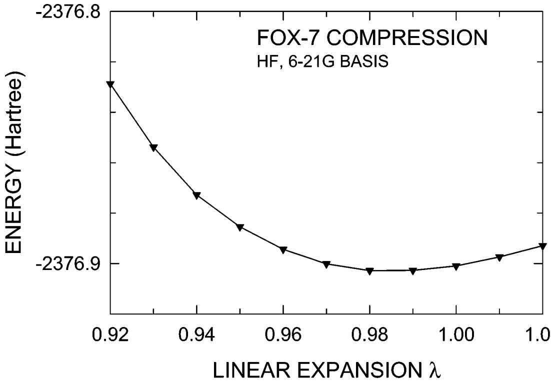

Figure 3. Energy along the temperature-independent mechanical compression curve for FOX-7 as a function of effective linear expansion $\lambda = (V/V_0)^{1/3}$.

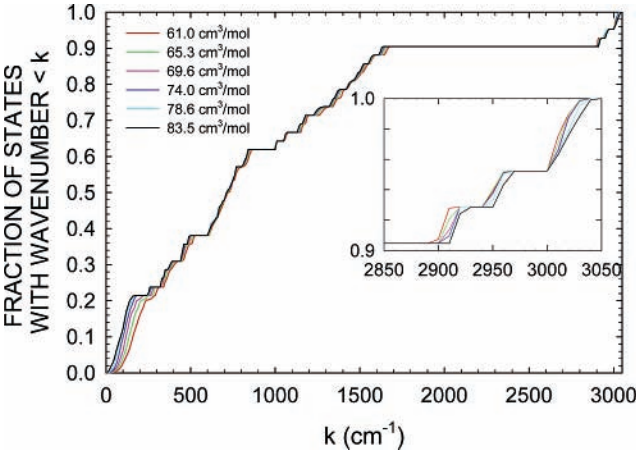

Figure 4. Phonon density of states for FOX-7 for various specific volumes from 61 to 83 cm^3/mol. The inset shows a detail of the region from 2850 to 3050 wave numbers.

Because it gives a result most closely corresponding to experiment, we choose here to rely on the results of the Hartree−Fock calculation with a 6-21G basis set, uncorrected for basis set superposition error, for the mechanical compression curve of FOX-7. The calculations were, however, repeated, using CRYSTAL 2003 with much higher precision (3 orders of magnitude) in the calculation of the bielectronic overlap

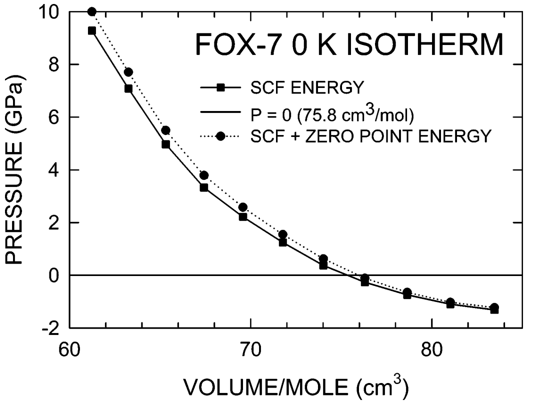

Figure 5. Pressure−volume relation for FOX-7 on a 0 K isotherm calculated with Hartree−Fock self-consistent field energy with vibrational mode zero-point energy included.

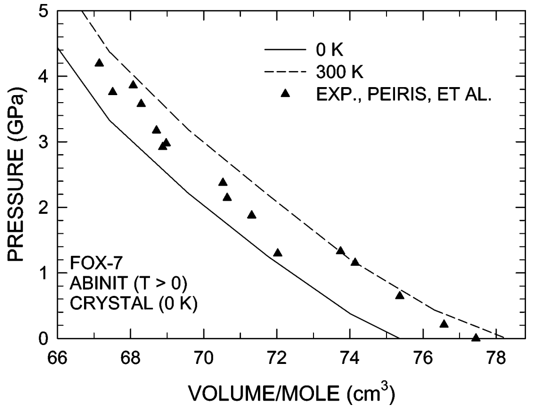

Figure 6. Calculated 300 K isotherm of FOX-7 compared to experimental data of Peiris et al. (ref 21).

integrals, which resulted in much smoother curves for the bulk modulus as a function of specific volume.

2.b. Vibrational Contribution. The dynamical matrix was calculated with the code ABINIT, which utilizes a plane wave basis set with pseudopotentials to describe the core electron configuration. In this work, the local density approximation (LDA) was used together with pseudopotentials built by Allan and Khein,[16] generated with the Troullier−Martins technique.[17] Several convergence studies were performed with respect to both energy and zero wave vector phonon frequencies, and it was determined that a plane wave energy cutoff of 32 Hartree (871 eV) with a 2 × 2 × 2 Monkhorst−Pack[18] grid in reciprocal space would give sufficiently precise results. In particular, the energy for a typical self-consistent field calculation was 0.05 H (1.4 eV) lower (0.01%) with a cutoff of 64 H as opposed to 32 H, and the highest frequency zero wave vector mode was calculated to be 3036 cm^{-1} at 32 H and 3038 cm^{-1} at 64 H. The results of the convergence studies are summarized in Figure 2. Also shown are calculations with a 4 × 4 × 4 Monkhorst−Pack grid compared to a 2 × 2 × 2 grid in reciprocal space. There is no discernible difference between the calculated energies indicating that the 2 × 2 × 2 grid is quite sufficient to obtain precise results.

The method used in ABINIT to compute the responses to atomic displacements and homogeneous electric fields is described by Gonze,[19] and the subsequent computation of dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants are described by Gonze and Lee.[20]

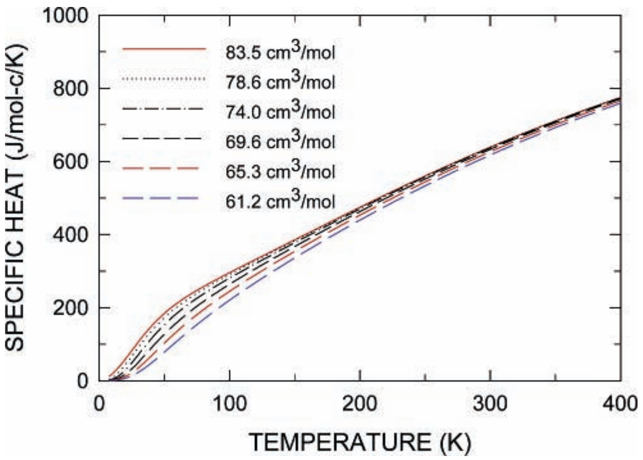

Figure 7. Calculated specific heat of FOX-7 as a function of temperature for a number of specific volumes from 61 to 83 cm^3/mol. The values are for a cell-mole. Divide by 4 to obtain values per mole.

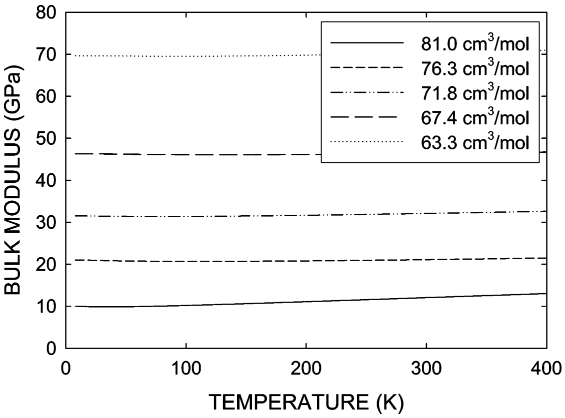

Figure 8. Calculated bulk modulus of FOX-7 as a function of temperature for a number of specific volumes from 61 to 83 cm^3/mol.

The optimized lattice parameters and atomic positions obtained as a result of the calculations for the mechanical compression were used as a starting point for the phonon spectrum calculations. These results were again optimized at fixed volume with ABINIT in the local density approximation, and the dynamical matrices for the eight wave vectors (0 0 0), ($^1/_2$ 0 0), (0 $^1/_2$ 0), (0 0 $^1/_2$), (0 $^1/_2$ $^1/_2$), ($^1/_2$ 0 $^1/_2$), ($^1/_2$ $^1/_2$ 0), and ($^1/_2$ $^1/_2$ $^1/_2$) were then obtained from calculations using the newly optimized structures. Thermodynamic properties and the phonon density of states are calculated on a fine grid in the dual space by Fourier transforming the dynamical matrices on this regular eight-point grid to obtain interatomic force constants and then using the interatomic force constants to obtain the dynamical matrix at an arbitrary point in the dual space.

3. Results

The mechanical compression curve for FOX-7 is shown in Figure 3. Both atomic coordinates and lattice parameters were optimized under a fixed volume constraint for each value of specific volume. CRYSTAL03 was used to calculate the Hartree−Fock self-consistent field energy for each configuration. The energy in Figure 3 is shown as a function of effective linear expansion λ defined as $(V/V_0)^{1/3}$, where the reference volume V_0 corresponds to the unit cell volume experimentally determined by Gilardi,[6] 522 Å.[3] The energy is shown for a range of λ from 0.92 to 1.02, which corresponds to a range of relative volumes from 0.78 to 1.06 and a range of specific volumes from 61 to 83 cm^3/mol.

The phonon density of states obtained by sampling the Brillouin zone is shown in Figure 4. The cumulative distribution

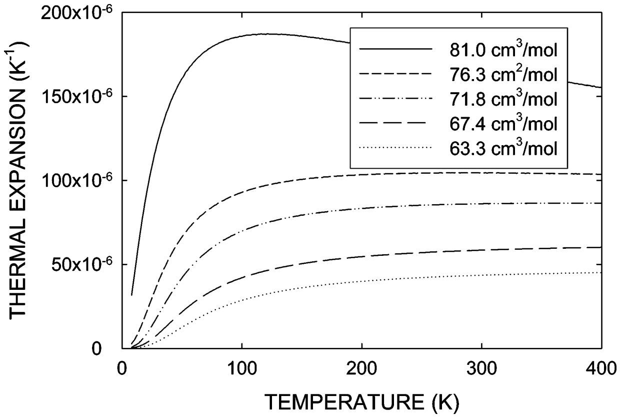

Figure 9. Calculated thermal expansion of FOX-7 as a function of temperature for a number of specific volumes from 63 to 81 cm^3/mol.

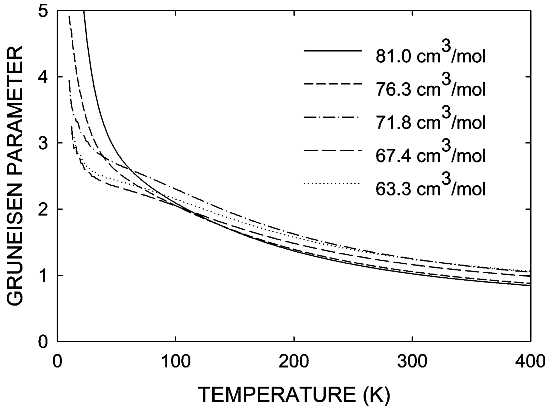

Figure 10. Calculated Gruneisen parameter of FOX-7 as a function of temperature for a number of specific volumes from 63 to 81 cm^3/mol.

is shown for each compression in the range from 61 to 83 cm^3/mol as a histogram with a bin width of 10 cm^{-1}. The most significant changes in the distribution occur for the low-frequency modes, which move higher in frequency with compression. A much smaller change occurs in the 16 highest frequency modes, which decrease in frequency with compression. The 16 highest frequency modes are separated from the lower frequency modes by a gap in the density of states extending from approximately 1650 up to about 2900 cm^{-1}. From this density of states we may determine the effect of the zero-point energy on the 0 K pressure−volume relation, displayed in Figure 5.

Experimental measurements of the 300 K isotherm using X-ray crystallography of the material compressed in a diamond anvil cell have been reported by Peiris et al.,[21] and we compare the ab initio calculated 300 K isotherm with the experimental measurements in Figure 6. We note very good agreement between the calculated and the measured isotherm. The calculated unit cell volume at 300 K is 519 Å^3 as compared with the experimentally determined value of 522 Å^3. Figures 7−10 summarize the calculated thermodynamic properties (bulk modulus, thermal expansion coefficient, Gruneisen parameter, and specific heat) of FOX-7 over the temperature range from 0 to 400 K and a number of specific volumes between 61 and 83 cm^3/mol.

The specific heat is calculated to be 160 J/mol/K at 300 K and atmospheric pressure with only a very small variation with respect to specific volume (see Figure 7).

The bulk modulus is relatively insensitive to variation in temperature (see Figure 8) and is calculated to be 15 GPa at 300 K and atmospheric pressure. Peiris, et al.[21] experimentally determined the bulk modulus to be 17.6 ± 0.4 GPa at normal temperature and pressure.

The volumetric thermal expansion coefficient is calculated to be 140 ppm/K at 300 K and atmospheric pressure and varies considerably with specific volume as well as temperature, falling to less than 80 ppm/K at 300 K and 70 cm^3/mol, corresponding to a pressure of the order of 4 GPa (Figure 9). Kempa and Herrmann[8] reported the volumetric thermal expansion coefficient to be 195 ppm/K at 293 K and atmospheric pressure.

The Grüneisen parameter γ varies from 1.09 at 300 K and atmospheric pressure to about 2.5 at 75 K. At temperatures greater than about 75 K, its variation with specific volume is small. At 300 K it ranges from 1.02 at 81 cm^3/mol to 1.24 at 63 cm^3/mol. At temperatures less than about 50 K, γ/V is approximately constant, the more so with decreasing temperature (Figure 10).

4. Conclusions

An equation of state was calculated from first principles for an organic molecular crystal using separate methods for the temperature-independent mechanical compression and the thermal vibrational contributions to the free energy. The mechanical compression was obtained by means of solutions of the Schrödinger equation utilizing the Hartree−Fock method as implemented in the computer program CRYSTAL. The vibrational contributions to the free energy were obtained from the phonon frequency spectrum as calculated with the computer program ABINIT utilizing a density functional theory method with the local density approximation. From comparison with limited experimental data, it appears that the calculation is reasonably accurate. The equation of state was obtained for a temperature range of 0−400 K, and a range of specific volumes from 61 to 83 cm^3/mol, corresponding to a range of densities from 1.8 to 2.4 g/cm^3.

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References and Notes

(1) Dovesi, R.; Saunders, V. R.; Roetti, C.; Causà, M.; Harrison, N. M.; Orlando, R.; Zicovich-Wilson, C. M. *CRYSTAL 98 User's Manual*; University of Torino: Torino, 1998.

(2) Saunders, V. R.; Dovesi, R.; Roetti, C.; Orlando, R.; Zicovich-Wilson, C. M.; Harrison, N. M.; Doll, K.; Civalleri, B.; Bush, I. J.; D'Arco, Ph.; Llunell, M. *CRYSTAL: A Computational Tool for Solid State Chemistry and Physics* [online]; Theoretical Chemistry Group, University of Torino, and Computational Materials Science Group, CCLRC Daresbury Laboratory, 2003. Available from http://www.crystal.unito.it/ [accessed June 2, 2005].

(3) (a) Zerilli, F. J.; Kuklja, M. M. *J. Phys. Chem. A* **2006**, *110*, 5173−5179. (b) Kuklja, M. M.; Zerilli, F. J.; Peiris, S. M. *J. Chem. Phys.* **2003**, *118*, 11073. (c) Zerilli, F. J.; Kuklja, M. M. Ab-initio 0 K Isotherm for Organic Molecular Crystals. In *Shock Compression of Condensed Matter—2003*, AIP Conference Proceeding 706, American Institute of Physics; Furnish, M. D., Gupta, Y. M., Forbes, J. W., Eds.; Melville, NY, 2004; p 123.

(4) Gonze, X.; Beuken, J.-M.; Caracas, R.; Detraux, F.; Fuchs, M.; Rignanese, G.-M.; Sindic, L.; Verstraete, M.; Zerah, G.; Jollet, F.; Torrent,

M.; Roy, A.; Mikami, M.; Ghosez, Ph.; Raty, J.-Y.; Allan, D. C. *Comput. Mater. Sci.* **2002**, *25*, 478−492.

(5) Bemm, U.; Östmark, H. *Acta Crystallogr., Sect. C* **1998**, *54*, 1997−1999.

(6) Gilardi, R. Naval Research Laboratory. Private communications, 2001.

(7) Bemm, U.; Eriksson, L. *Proc. IM&EM Techn. Symp.* **2001**.

(8) Kempa, P. B.; Herrman, M. *Part. Part. Syst. Charact.* **2005**, *22*, 418−422.

(9) Piermarini, G. National Institute of Standards and Technology. Private communication, 2002.

(10) Zicovich-Wilson, C. M. *LoptCG—Script for Numerical Gradient Optimization* [online], 1998. Available from http://www.crystal.unito.it/LoptCG/LoptCG.html [accessed May 10, 2005].

(11) Nelder, J. A.; Mead, R. *Comput. J.* **1965**, *7*, 308.

(12) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes*; Cambridge University Press: New York, 1989.

(13) Zerilli, F. J.; Hooper, J. P.; Kuklja, M. M. *J. Chem. Phys.*, to be published.

(14) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(15) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(16) Khein, A.; Allan, D. C. *Troullier-Martins Pseudopotentials* [online], 1995. Available from http://www.abinit.org/Psps [accessed May 11, 2005].

(17) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993.

(18) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188.

(19) Gonze, X. *Phys. Rev. B* **1996**, *55*, 10337.

(20) Gonze, X.; Lee, C. *Phys. Rev. B* **1996**, *55*, 10355.

(21) Peiris, S. M.; Wong, C. P.; Zerilli, F. J. *J. Chem. Phys.* **2004**, *120*, 8060.