

Full *ab initio* geometry optimization of all known crystalline phases of Si_3N_4

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The crystal structures of the four experimentally observed phases of Si_3N_4 with space groups $P6_3/m$, $P6_3$, $P3_1/c$, and Fd_3/m are fully optimized by means of first-principles total-energy calculations. The relaxation of all internal parameters is achieved by using a simple finite difference method. For β - Si_3N_4 , the structure $P6_3$ without the mirror symmetry has a lower energy than the $P6_3/m$ with mirror symmetry by 0.238 eV per formula unit. The calculated ground-state properties are found to be in good agreement with experimental values.

Silicon nitride continues to attract many researchers because of the important role it plays as a structural ceramic and as a dielectric insulator. The electronic structure of Si_3N_4 has been studied by several groups since the early 1980s.^{1–7} More recently, attention has been focused on the structural aspects and on the ground-state properties.^{8–11} There are two well-known phases of Si_3N_4 α - and β - Si_3N_4 . Both have a hexagonal lattice with different stacking sequences of the layered atoms perpendicular to the c axis. There is still controversy as to the exact structure of the β phase. Early measurements on β - Si_3N_4 gave it a space group of $P6_3/m$ with a mirror symmetry in the plane perpendicular to the c axis.^{12,13} In 1979, Grün¹⁴ showed that the space group for β - Si_3N_4 should be $P6_3$, with no mirror symmetry. Since then, there were conflicting reports in support of both structures. Goodman and O’Keeffe¹⁵ studied a powdered sample of pure β - Si_3N_4 using converging beam electron diffraction, and concluded its space group to be $P6_3/m$. Using the same technique, Bando concluded that the $P6_3/m$ structure is compatible only with the data for a thin crystal. For a thick crystal, the space group $P6_3$ may be more appropriate.¹⁶ On the other hand, neutron-diffraction data appear to favor the $P6_3/m$ structure.¹⁷ The structure for the α phase is less controversial as it has an unambiguous space group of $P3_1/c$.^{18,19} Experimentally, it was found that the α to β transformation takes place at high temperature, but not the reverse.²⁰ It is generally believed that β - Si_3N_4 is a more stable phase. Very recently, it was reported that stoichiometric Si_3N_4 could also exist in the cubic spinel phase under high pressure and temperature.²¹ This exciting discovery has opened a new dimension to the elucidation of the structure and bonding in silicon nitrides and the microscopic understanding of the interaction that is responsible.^{21,22}

In recent years, *ab initio* total-energy (TE) calculations based on density-functional theory (DFT)²³ have been successful in predicting crystal structures and properties of materials with no experimental input other than an initial starting structure for the desired local minimum. For crystals with high symmetry, such predictions have become a routine exercise, assuming one can garner sufficient computational power to carry out the demanding task. However, for a rela-

tively complex crystal with many internal parameters such as Si_3N_4 , it is still a reasonably time-consuming task to optimize its geometry. Past investigations on Si_3N_4 were limited to equilibrium lattice constants and volumes without optimizing the internal parameters.^{4–5,8–10} When comparing the calculated results with the measured ones for the β phase, no distinction was made for the structure with or without the mirror symmetry. This has caused a lot of confusion, but also casts some doubt on the often-claimed good agreements. Studies on the α phase are almost nonexistent because the unit cell is twice as large as in the β phase. Empirical or semiempirical calculations based on classical pair potentials have been rather popular for studies on Si_3N_4 .^{10,23–26} The accuracy of such studies is usually much lower than that which can be obtained by *ab initio* methods, but they can be very effective in the simulations of large structures such as those involving interfaces,²⁶ disordered-amorphous systems, or for systems approaching the continuum limit.²⁵

In this paper, we report the results of full geometry optimization of the four experimentally reported crystalline phases of Si_3N_4 , β - Si_3N_4 ($P6_3/m$), and β - Si_3N_4 ($P6_3$), α - Si_3N_4 ($P3_1/c$), and the cubic spinel phase c - Si_3N_4 (Fd_3/m). We have developed a computational strategy based on *ab initio* TE calculations using the orthogonalized linear combination of atomic orbitals (OLCAO) method.²⁷ The basis set and the exchange-correlation potential used are the same as in the previous studies.^{6,10} All internal parameters are optimized and the relative stability at zero temperature compared. From the TE data as a function of crystal volume with internal parameters relaxed at each volume, much more reliable values of bulk modulus B_0 are obtained.

The OLCAO method of electronic structure calculation has been established as an accurate and efficient *ab initio* method especially for complex systems.²⁷ In fact, the first band structures of β - Si_3N_4 and α - Si_3N_4 were calculated using this method.¹ Over the years, the method has been steadily refined and the scope of the investigation significantly enlarged to include calculations on TE and bulk modulus,^{4,10} optical properties,⁶ solid solutions of SiAlON ,²⁸ and other spectroscopic properties such as electron-energy-loss near-edge spectra, etc.²⁹ Recently, we have also derived

TABLE I. The experimentally reported phases of Si_3N_4 . N_A , N_P , N_k are the number of atoms per unit cell, the number of independent geometric parameters, and the number of k points in the BZ used, respectively.

| Crystal | Space group | N_A | N_P | N_k |
|------------------------------------|-------------|-------|-------|-------|
| β - Si_3N_4 | $P6_3/m$ | 14 | 6 | 32 |
| β - Si_3N_4 | $P6_3$ | 14 | 8 | 32 |
| α - Si_3N_4 | $P3_1/c$ | 28 | 16 | 16 |
| c - Si_3N_4 | Fd_3/m | 14 | 2 | 84 |

effective pair potentials for β - Si_3N_4 and α - Si_3N_4 based on the *ab initio* TE data, and used them for lattice dynamic studies in Si_3N_4 crystals.¹⁰ One drawback of the OLCAO method is the difficulty of obtaining the forces on each atom directly, in comparison to plane-wave techniques, and therefore this makes it difficult to optimize all the internal parameters of a crystal as the basis functions in the OLCAO method are nuclear-position dependent. There is a significant Pulay correction³⁰ to the Hellmann-Feynman forces, which is difficult to obtain with the local orbital methods. Accurate forces can still be obtained if careful corrections of sufficient accuracy are accounted for, as has been demonstrated by Jackson and Pederson³¹ on small molecules. A general scheme based on the current OLCAO method applicable to complex crystals will be very difficult because the programming and coding will be onerous. The complication arises from the need for multicenter integrals of higher order when the basis functions are differentiated with respect to the nuclear position. On the other hand, methods based on plane-wave expansion can calculate forces very easily,³² but a large number of plane waves is usually required for a well-converged result. To circumvent the difficulty of direct force calculation in the OLCAO method, we introduce a simple scheme of evaluating the force by the finite difference of the TE. Let $E_T(a,b,c,\alpha,\beta,\gamma;x_1,x_2,x_3\dots)$ be the TE of a general crystal with lattice parameters specified by $a,b,c,\alpha,\beta,\gamma$; and internal parameters by $x_1,x_2,x_3\dots$, etc. The energy gradient for each parameter P_i is obtained by the finite difference approach according to

$$\frac{\partial E_T}{\partial P_i} \approx \frac{E_T(P_i + \Delta P_i) - E_T(P_i - \Delta P_i)}{2 \times \Delta P_i}. \quad (1)$$

We then use the first-order-gradients-only algorithms such as the conjugate gradient or steepest descent, etc to minimize the TE in the entire parameter space. In the present case, we have integrated the OLCAO method with the General Lattice

TABLE II. Optimized geometry of β - Si_3N_4 ($P6_3/m$).

| Parameter | Experiment ^a | This work | Difference |
|---------------------|-------------------------|-----------|------------|
| c (Å) | 7.607 | 7.6220 | 0.0150 |
| a (Å) | 2.911 | 2.9102 | -0.0008 |
| $x_{\text{Si}(6h)}$ | 0.174 | 0.1723 | -0.0017 |
| $y_{\text{Si}(6h)}$ | 0.766 | 0.7645 | -0.0015 |
| $x_{\text{N}(6h)}$ | 0.321 | 0.3341 | 0.0131 |
| $y_{\text{N}(6h)}$ | 0.025 | 0.0250 | 0.0000 |

^aReference 13.

TABLE III. Optimized geometry of β - Si_3N_4 ($P6_3$).

| Parameter | Experiment ^a | This work | Difference |
|---------------------|-------------------------|-----------|------------|
| c (Å) | 7.5950 | 7.6226 | 0.0276 |
| a (Å) | 2.9023 | 2.9014 | -0.0009 |
| $x_{\text{Si}(6h)}$ | 0.1744 | 0.1737 | -0.0007 |
| $y_{\text{Si}(6h)}$ | 0.7686 | 0.7663 | -0.0023 |
| $x_{\text{N}(6h)}$ | 0.3294 | 0.3337 | 0.0043 |
| $y_{\text{N}(6h)}$ | 0.0298 | 0.0271 | -0.0027 |
| $z_{\text{N}(6h)}$ | 0.2628 | 0.2726 | 0.0098 |
| $z_{\text{N}2(6h)}$ | 0.2392 | 0.2353 | -0.0039 |

^aReference 14.

Utility Program (GULP) to achieve the geometry optimization of crystal.³³ The GULP program fully utilizes crystal symmetry to reduce the parameter space thereby greatly reducing the number of derivatives to be determined by finite differences.

The key element of the above simple scheme is that the TE calculation must be sufficiently fast and efficient. For each energy gradient, a minimum of two full self-consistent field (SCF) calculations for the ground state are needed, in addition to the original SCF calculation for the geometry whose derivatives are to be found. Fortunately, the OLCAO method is very efficient and fast, thus making this scheme practical. Convergence in SCF iterations is efficient since the input potential for the new configuration is not much different from that of the previous configuration for small difference intervals. The whole optimization process takes about 10 cycles for the geometry to converge to the desirable limit, which is loosely defined as no change in the fourth decimal point of the lattice constants or the internal parameters. Another important decision is the choice of ΔP_i in Eq. (1). We find in general, a ΔP of 0.0005 (0.05%) of the parameter value produces the most satisfactory results. The estimated accuracy in the present calculation is at least 0.001 eV per atom in the final relaxed total energy.

TABLE IV. Optimized geometry of α - Si_3N_4 ($P3_1/c$).

| Parameter | Experiment ^a | This work | Difference |
|----------------------|-------------------------|-----------|------------|
| c (Å) | 7.766 | 7.7917 | 0.0713 |
| a (Å) | 5.615 | 5.6141 | -0.0009 |
| $x_{\text{Si}1(6c)}$ | 0.5130 | 0.5111 | -0.0019 |
| $y_{\text{Si}1(6c)}$ | 0.4305 | 0.4283 | -0.0022 |
| $z_{\text{Si}1(6c)}$ | 0.6580 | 0.6542 | -0.0038 |
| $x_{\text{Si}2(6c)}$ | 0.1680 | 0.1634 | -0.0046 |
| $y_{\text{Si}2(6c)}$ | 0.9150 | 0.9123 | -0.0027 |
| $z_{\text{Si}2(6c)}$ | 0.4504 | 0.4513 | 0.0009 |
| $x_{\text{N}(6c)}$ | 0.6124 | 0.6149 | 0.0025 |
| $y_{\text{N}(6c)}$ | 0.9592 | 0.9621 | 0.0029 |
| $z_{\text{N}(6c)}$ | 0.4343 | 0.4387 | 0.0044 |
| $x_{\text{N}2(6c)}$ | 0.3199 | 0.3264 | 0.0065 |
| $y_{\text{N}2(6c)}$ | 0.0046 | 0.0262 | 0.0216 |
| $z_{\text{N}2(6c)}$ | 0.7045 | 0.6903 | -0.0142 |
| $z_{\text{N}3(2b)}$ | 0.4520 | 0.4312 | -0.0208 |
| $z_{\text{N}4(2b)}$ | 0.1015 | 0.1398 | 0.0383 |

^aReference 19.

TABLE V. Calculated and measured crystal parameters of Si_3N_4 phases. B_0 is the bulk modulus, E_0 is the total energy per formula unit (excluding core electrons). The number in parentheses for B_0 is from the previous calculation (Ref. 10) with no relaxation for internal parameters.

| | Present calculation | Experiments | Other calculations | | |
|---|---------------------|--|---------------------|--------|---------|
| $\beta\text{-Si}_3\text{N}_4 [P6_3/m]$ | | | Ref. 5 | Ref. 8 | Ref. 11 |
| a (Å) | 7.622 | 7.607 ^a | 7.61, | 7.61, | 7.562 |
| c (Å) | 2.910 | 2.911 ^a | | 2.91, | 2.893 |
| c/a | 0.382 | 0.383 | | | |
| B_0 (Gpa) | 274 (270) | 256, ^e 258, ^f 273 ^g | 265, | 297, | 263 |
| E_0 (eV) | -1415.088 | | | | |
| $\beta\text{-Si}_3\text{N}_4 [P6_3]$ | | | | | |
| a (Å) | 7.623 | 7.595 ^b | | | |
| c (Å) | 2.901 | 2.902 ^b | | | |
| c/a | 0.381 | 0.382 | | | |
| B_0 (Gpa) | 278 | 256, ^e 258, ^f 273 ^g | | | |
| E_0 (eV) | -1415.326 | | | | |
| $\alpha\text{-Si}_3\text{N}_4 [P3_1/c]$ | | | | | |
| a (Å) | 7.792 | 7.766 ^c | | | |
| c (Å) | 5.614 | 5.615 ^c | | | |
| c/a | 0.720 | 0.723 | | | |
| B_0 (Gpa) | 257 (260) | 228, ^h 248, ⁱ 282 ^e | | | |
| E_0 (eV) | -1414.871 | | | | |
| $c\text{-Si}_3\text{N}_4 [Fd_3/m]$ | | | | | |
| a (Å) | 7.837 | 7.80 ± 0.08 ^d | 7.76 ^d | | |
| x | 0.3844 | 0.3875 ^d | 0.3824 ^d | | |
| B_0 (Gpa) | 280 | | 300 | | |
| E_0 (eV) | -1411.795 | | | | |

^aReference 13. ^dReference 21. ^gReference 37.
^bReference 14. ^eReference 40. ^hReference 36.
^cReference 19. ^fReference 39. ⁱReference 38.

Table I lists the four Si_3N_4 crystals whose geometries were optimized, the total parameters relaxed, and the number of \mathbf{k} points in the irreducible portion of the Brillouin zone (IBZ) used. The number of k points used in the calculation was carefully tested to ensure full convergence. We feel that the number of k points used in some existing calculations may not be sufficient. The relaxed parameters for the four crystals are listed in Tables II–V. Also listed are the differences from the experimentally measured values. As can be seen, the agreements between the calculated and the measured values are excellent. The average deviations on the lattice constants are less than 0.5%. Generally speaking, the current level of accuracy in other local-density-approximation–DFT based calculations is in the range of 1–1.5% in the lattice constant. The differences in the internal parameters are also satisfactory. In general, the agreement is better for the Si parameters than for the N parameters. There are a few cases where the relative difference appears to be large, and these are usually associated with the cases where the parameters themselves are quite small. Such differences cannot perhaps be totally attributed to deficiencies in the calculated values since the experimental parameters were obtained by a constrained fit to the measured diffraction spectra and their accuracy depends on the final R factor.

The TE at the equilibrium geometry for the four crystals

are listed in Table V. (The TE values are for valence electrons only, since core states were eliminated by the orthogonalization process). The bulk modulus B_0 of each crystal is obtained by fitting the E - V data to three types of equation-of-state EOS, the Murnaghan,³⁴ the Birch-Murnaghan,³⁵ and the fourth-order polynomial expansion. The results are quite close and the ones obtained by the Murnaghan EOS are listed in Table V. In each calculation with a specific volume expansion or contraction, the c/a ratio is fixed at the equilibrium value, while all internal parameters are relaxed. Also listed in Table V are the measured values of B_0 (Refs. 36–40) and those from other calculations. $\alpha\text{-Si}_3\text{N}_4$ ($c\text{-Si}_3\text{N}_4$) has the lowest (highest) B_0 and those of the two β phases are very close. We believe the present calculations provide the most accurate and consistent B_0 values for the Si_3N_4 phases since they were obtained by using a single method with all parameters relaxed and with sufficient k -space convergence. We also note that there are considerable differences among various experimental measurements.^{36–34} This could be partly due to the lack of availability of high-quality single crystals of Si_3N_4 .

The E - V data for the four crystals as a function of molecular volume are shown in Fig. 1. As can be seen from Table V, the $\beta\text{-Si}_3\text{N}_4$ ($P6_3$) is lower in energy than the $\beta\text{-Si}_3\text{N}_4$ ($P6_3/m$) by 0.238 eV per formula unit. On the

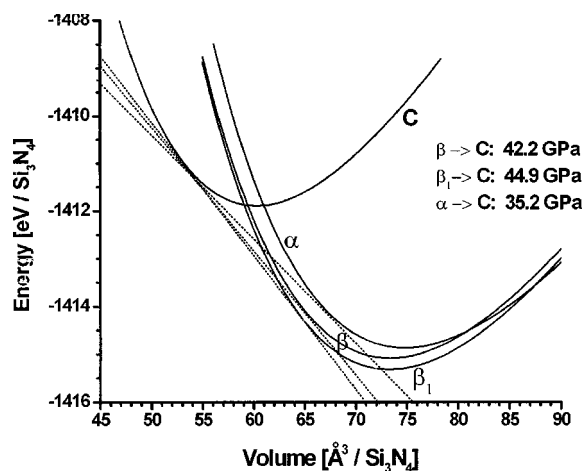


FIG. 1. Total energy in eV per Si_3N_4 formula unit vs crystal volume. The slopes of the dashed lines give the transition pressures. β , β_1 , α , c stands for the four Si_3N_4 crystals with space groups of $P6_3/m$, $P6_3$, $P3_1/c$, and Fd_3/m , respectively.

other hand, the α - Si_3N_4 ($p3_1$) is higher than β - Si_3N_4 ($p6_3$) by 0.455 eV per formula unit. This is a much smaller difference than the value (1.65 eV/molecule) reported before with no optimizations for the internal parameters.⁶ Recently, Liang *et al.* measured the enthalpy of formation of α - Si_3N_4 to be -850.9 ± 22.4 KJ mol, and that of β - Si_3N_4 to be -852.0 ± 8.7 KJ mol⁻¹,⁴¹ showing the β phase to be more stable than the α phase but the difference should be small. The equilibrium volumes of the α and β phases are quite

close to each other. This is not surprising since the structure and bonding in α and β phases are very similar. On the other hand, the spinel c - Si_3N_4 is at a much higher energy and a smaller equilibrium volume, consistent with the fact that it is formed at high pressure.²¹ From the slopes of the common tangents shown in Fig. 1, we deduce the transition pressures from the two β - Si_3N_4 phases to c - Si_3N_4 to be 42.2 and 44.9 GPa, and that from α - Si_3N_4 to be 35.2 GPa.

In summary, we have demonstrated that full geometry optimization based on finite difference in total energy without direct force calculation is feasible, and can be effectively applied to complex ceramic crystals. Results for β - Si_3N_4 confirm that the Grün structure without the mirror symmetry has a slightly lower energy and therefore represents the true minimum. The higher symmetry form is likely to have an imaginary mode that removes the mirror symmetry, rather than being metastable. Both structures of β - Si_3N_4 have lower energy per molecule than α - Si_3N_4 . The calculated bulk moduli for β - Si_3N_4 and α - Si_3N_4 are within the experimental uncertainties. We have successfully used the same technique to optimize the geometry of several complex ceramic oxides including Al_2O_3 , Y_2O_3 , MgAl_2O_4 , and $\text{Y}_3\text{Al}_5\text{O}_{12}$, with equally impressive results.⁴² The present method has a great potential in the structural relaxation of defects, impurities, surfaces, and interfaces. Such studies are currently in progress and will be reported at a later time.

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¹S. Y. Ren and W. Y. Ching, Phys. Rev. B **23**, 5454 (1981).
²R. J. Sokel, J. Phys. Chem. Solids **41**, 899 (1980); J. Robertson, Philos. Mag. A **44**, 215 (1981).
³Y.-N. Xu and W. Y. Ching, Physica B **150**, 32 (1988).
⁴Y.-N. Xu, and W. Y. Ching, in *Silicon Dioxide and Its Interface*, edited by S. T. Pantelides and G. Lucovsky (MRS, Pittsburgh, 1988), p. 181.
⁵A. Y. Liu and M. L. Cohen, Phys. Rev. B **41**, 10 727 (1990).
⁶Y.-N. Xu and W. Y. Ching, Phys. Rev. B **51**, 17 379 (1991).
⁷G. L. Zhao and M. E. Bachlechner, Phys. Rev. B **58**, 1887 (1998).
⁸A. R. Serrato, D. Galvan, and I. L. Garzon, Phys. Rev. B **52**, 6293 (1995).
⁹A. Y. Liu and R. M. Wentzcovitch, Phys. Rev. B **50**, 10 362 (1994).
¹⁰W. Y. Ching, Y. N. Xu, J. D. Gale, and M. Rühle, J. Am. Ceram. Soc. **81**, 3189 (1998).
¹¹R. Belkada, M. Kohyama, T. Shibayanagi, and M. Naka (unpublished).
¹²S. Wild, P. Grieson, and K. H. Jack, in *Special Ceramics 5*, edited by P. Popper (British Ceramic Research Association, Stoke-on-Trent, 1972), p. 385.
¹³O. Borgen and H. M. Seip, Acta Chem. Scand. **15**, 1789 (1961).
¹⁴R. Grün, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **35**, 800 (1979).
¹⁵P. Goodman and M. O'Keeffe, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **36**, 2891 (1980).
¹⁶Y. Bando, Acta Crystallogr., Sect. B: Struct. Sci. **39**, 185 (1983).

¹⁷M. Billy, J.-C. Labbe, A. Selvaraj, and G. Roult, Mater. Res. Bull. **18**, 921 (1983).
¹⁸I. Kohastu and J. W. McCauley, Mater. Res. Bull. **9**, 917 (1974).
¹⁹H. F. Priest, F. C. Burns, G. L. Priest, and E. C. Skaar, J. Am. Ceram. Soc. **56**, 395 (1973).
²⁰D. S. Thompson and P. L. Pratt, *Science of Ceramics* (Academic, New York, 1967), Vol. 3, p. 33; J. L. Browen, R. J. Weston, T. G. Carruthers, and R. J. Brook, J. Mater. Sci. **13**, 341 (1978).
²¹A. Zerr, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fuess, P. Kroll, and R. Boehler, Nature (London) **400**, 340 (1999).
²²S.-D. Mo, L. Ouyang, W. Y. Ching, I. Tanaka, Y. Koyama, and R. Riedel, Phys. Rev. Lett. **83**, 504 (1999).
²³P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).
²⁴J. A. Wendal and W. A. Goddard III, J. Chem. Phys. **97**, 5048 (1992).
²⁵R. K. Kalia, A. Nakano, K. Tsuruta, and P. Vashishta, Phys. Rev. Lett. **78**, 689 (1997); R. K. Kalia, A. Nakano, A. Omeltechnko, K. Tsuruta, and P. Vashishta, *ibid.* **78**, 2144 (1997); C. K. Loong, P. Vashishta, R. K. Kalia, and I. Ebbsjö, Europhys. Lett. **31**, 201 (1995).
²⁶M. Yoshiya, I. Tanaka, and H. Adachi (unpublished).
²⁷W. Y. Ching, J. Am. Chem. Soc. **73**, 3135 (1990).
²⁸W. Y. Ching, M.-Z. Huang, and S.-D. Mo, J. Am. Chem. Soc. (to be published).
²⁹S.-D. Mo and W. Y. Ching (unpublished).

- ³⁰P. Pulay, *Mol. Phys.* **17**, 197 (1969).
- ³¹K. Jackson and M. Pederson, *Phys. Rev. B* **42**, 3276 (1990).
- ³²M. C. Payne, M. P. Tetter, D. C. Allen, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).
- ³³J. D. Gale, *J. Chem. Soc., Faraday Trans.* **93**, 629 (1997).
- ³⁴F. D. Murnaghan, *Proc. Natl. Acad. Sci. USA* **30**, 244 (1944).
- ³⁵F. Birch, *J. Geophys. Res.* **83**, 1257 (1978).
- ³⁶M. B. Kruger, J. H. Nguyen, Y. M. Li, W. A. Caldwell, M. H. Manghnani, and R. Jeanloz, *Phys. Rev. B* **55**, 3456 (1997).
- ³⁷Y. M. Li, M. B. Kruger, J. H. Nguyen, W. A. Caldwell, and Raymond Jeanloz, *Solid State Commun.* **103**, 107 (1997).
- ³⁸O. Yeheskel and Y. Gefen, *Mater. Sci. Eng.* **71**, 95 (1985).
- ³⁹L. Cartz and J. D. Jorgensen, *J. Appl. Phys.* **52**, 236 (1981).
- ⁴⁰S. R. Srinivasa, L. Cartz, J. D. Jorgensen, T. G. Worlton, R. Beyerlein, and M. Billy, *J. Appl. Crystallogr.* **10**, 167 (1977); also, S. R. Srinivasa, Ph.D thesis, Marquette University, 1977.
- ⁴¹J. Liang, L. Topor, A. Navrotsky, and M. Mitomo, *J. Mater. Res.* **14**, 1959 (1999).
- ⁴²L. Ouyang and W. Y. Ching (unpublished).