Equation of State and Raman Frequency of Diamond from Quantum Monte Carlo Simulations

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We report variational and diffusion quantum Monte Carlo (VMC and DMC) calculations of the equation of state and Raman frequency of diamond. The pressure derivative of the bulk modulus, which has not been accurately determined experimentally, is calculated to be 3.8 (VMC) and 3.7 (DMC). The values of the Raman frequency calculated at the experimental volume are 1373 cm^{-1} (VMC) and 1359 cm^{-1} (DMC), in good agreement with the experimental value of 1333 cm^{-1}.

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Diamond anvil cells are used to study condensed matter over a wide range of pressures and temperatures. The range of static pressures attainable today extends at least as far as the conditions prevailing in the center of the Earth ($\sim$ 360 GPa). A thorough understanding of the physical properties of diamond at high pressure is of great importance in the design and operation of such cells, but although there have been many experimental studies of this material some properties, including the equation of state, remain imperfectly characterized.

The equation of state (EOS) of a substance is the equilibrium relationship between its pressure, volume, and temperature. At fixed temperature, the EOS can be described over a wide range of pressures in terms of the zero-pressure values of the volume V_0, the isothermal bulk modulus B_0, and its pressure derivative B_0'. The values of V_0 and B_0 for diamond are well established over a wide range of temperatures, but there is considerable uncertainty about B_0'. A recent study [1] gave $B_0' = 3.0 \pm 0.1$ at room temperature, although it has been argued that the pressure calibration should be revised [2]. The most commonly cited experimental value [3] is $B_0' = 4.0 \pm 0.5$, but the large error bar leads to considerable uncertainty in the EOS at high pressures.

Diamond is highly transparent to electromagnetic radiation over a large range of wavelengths, and the sample within a diamond anvil cell may be examined *in situ* under elevated pressure by x-ray diffraction techniques and by Raman, Brillouin, and infrared spectroscopies. The Raman technique, in particular, has been used extensively to study the zone-center optical phonon mode of diamond under pressure. It has been suggested [1,4] that the volume dependence of the Raman frequency could be used as a pressure gauge in diamond anvil cell experiments, and more information about the Raman frequency under high compression would help in the calibration process.

The EOS and Raman frequency of diamond have been extensively studied using density functional theory (DFT) [5]. These calculations, performed using the standard local density approximation (LDA) and Perdew-Burke-Ernzerhof [6] generalized gradient approximation (PBE-GGA) exchange-correlation functionals, gave values of B_0' intermediate between the two experimental values mentioned above. Fahy *et al.* [7] have studied the EOS with the variational quantum Monte Carlo (VMC) method [8], but the statistical accuracy was insufficient to obtain a value of B_0'.

In view of the unsatisfactory knowledge of the EOS of diamond and the importance of the material, we believe that a study using highly accurate continuum quantum Monte Carlo (QMC) techniques [8] would be useful. We have therefore calculated the EOS up to a pressure of about 500 GPa and the Raman frequency of diamond up to about 320 GPa using both the VMC and diffusion quantum Monte Carlo (DMC) techniques [8].

VMC and DMC techniques are stochastic methods for evaluating expectation values of many-body wave functions which have the desirable properties of extremely high accuracy and a favorable (cubic or better) scaling with system size. In VMC, expectation values are evaluated using an approximate trial wave function and Monte Carlo integration. In the more accurate DMC method, the imaginary-time Schrödinger equation is used to evolve an ensemble of electronic configurations towards the ground state. The fermionic symmetry is maintained by the fixed-node approximation where the nodal surface of the wave function is constrained to equal that of a trial wave function.

The QMC calculations were performed with the CASINO [9] code using Slater-Jastrow trial wave functions, $\Psi_T = D^{\uparrow} D^{\downarrow} \exp[J]$, where $D^{\uparrow}$ and $D^{\downarrow}$ are Slater determinants of up- and down-spin orbitals and $\exp[J]$ is a Jastrow correlation factor. The orbitals were obtained from the CASTEP [10] code, using the PBE-GGA functional, Dirac-Fock-based pseudopotentials representing the C^{4+} ionic cores [11], and a plane wave cutoff energy of 100 a.u. The orbitals were reexpanded in a B-spline or "blip" basis for greater efficiency in the QMC calculations [12]. We used Jastrow factors of the form described in Ref. [13] containing both long-ranged electron-electron terms and short-ranged electron-nucleus terms. The free parameters in the Jastrow factors were optimized using a variance minimization technique [14]. A target population of 640 configurations and a time step of 0.01 a.u. were used in the DMC calculations, corresponding to acceptance ratios of 99.6%. We expect the size of the time-step error to be similar at all volumes.

For the EOS calculations we used simulation cells subject to periodic boundary conditions containing 128 and 250 atoms, made up of $4 \times 4 \times 4$ and $5 \times 5 \times 5$ arrays of two-atom primitive unit cells. The orbitals were calculated at the L wave vector of the simulation-cell Brillouin zone, which corresponds to an efficient special k-points integration scheme [15]. It is important to check that errors arising from the use of finite-sized simulation cells are small, and to correct for the remaining errors. The finite size errors can be divided into kinetic energy errors arising from using a single k-point in the Brillouin zone, and long range exchange-correlation effects. The errors in the DFT kinetic energies were very small and no correction for the single k-point was required. The long range exchange-correlation errors were accounted for by extrapolating the 128 and 250-atom energies to infinite simulation-cell size using the formula $E_\infty(V) = E_N(V) + b(V)/N$, where V is the volume per atom, N is the number of atoms in the simulation cell, E_N is a calculated energy, and E_∞ and b are parameters.

We fitted the calculated energies to the Vinet EOS [16], which has been demonstrated to work well over large pressure ranges [17]. The parameters in the Vinet EOS are V_0, B_0, B_0', and an energy constant C.

We carefully selected the volumes at which the QMC calculations were performed. If the range is too small, the statistical errors in the QMC energies lead to large statistical errors in the EOS parameters. If the range is too large, the estimates of the EOS parameters are biased. After some experimentation we chose to perform the QMC calculations at seven volumes with a target error bar in the energies of 0.0001 a.u. per atom. We then used the PBE-GGA energies with an additional noise of root-mean-square amplitude 0.0001 a.u. per atom to model the QMC data. We took seven volumes within a range around the experimental equilibrium volume, $V_0^{\mathrm{exp}} = 38.284$ a.u. per atom, and fitted the model data to the Vinet EOS, averaging over the noise to obtain statistical error bars. Figure 1 shows both the bias and statistical error bars associated with a particular choice of volume range. This led us to use a volume range of 28.5 a.u. per atom, which results in acceptably small statistical error bars and biases in the EOS parameters.

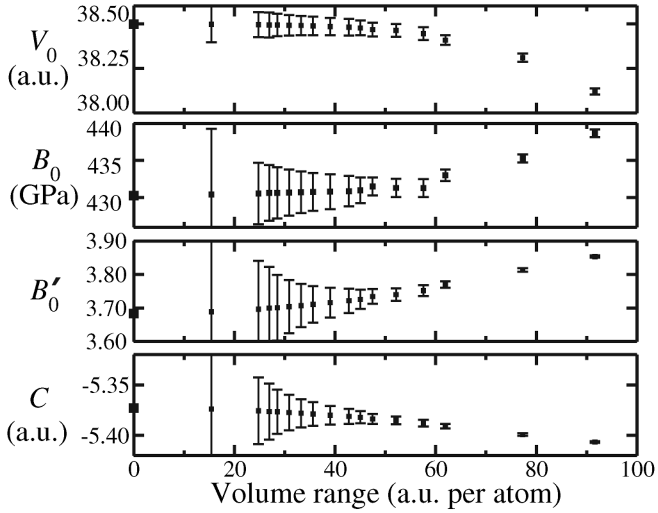

FIG. 1. Values of the EOS parameters with statistical error bars corresponding to a noise added to the PBE-GGA energies of root-mean-square amplitude 0.0001 a.u. per atom. The values obtained from a very small volume range without noise are shown as black squares at zero volume range.

The calculated VMC and DMC energies are shown in Fig. 2, together with the values extrapolated to infinite system size. The finite size corrections are very small. Note that the VMC curves are smooth, indicating that the quality of the trial wave function varies smoothly with volume, even though separate stochastic optimizations were performed at each volume. Having obtained the EOS parameters, we calculated QMC energies at three smaller volumes. Figure 2 shows that the Vinet fits obtained from the seven higher-volume points describe the behavior at the more compressed volumes very well.

To compare with measured p-V relations we have added corrections for the zero-point motion and finite tempera-

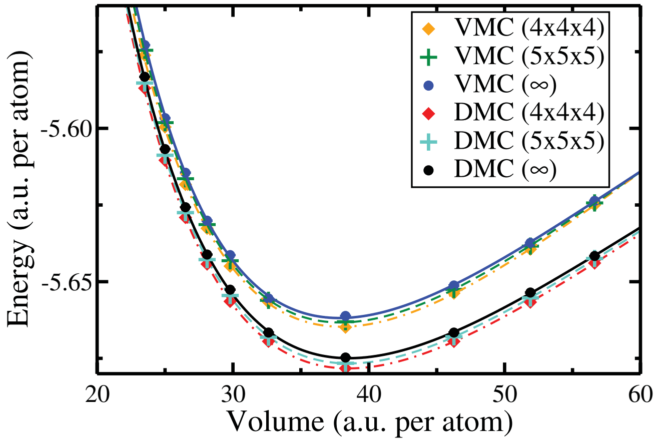

FIG. 2 (color). QMC energies per atom as a function of volume. The lines are Vinet fits to the data points. The statistical error bars are not visible on this scale.

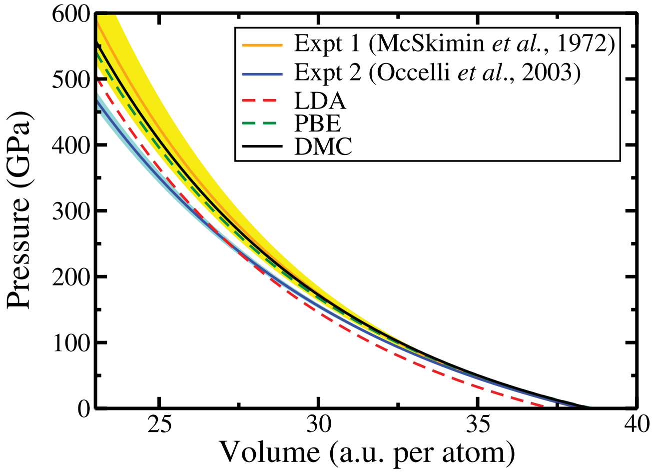

FIG. 3 (color). p-V relation for diamond. The width of the blue region indicates the uncertainty in the measured EOS according to the authors of Ref. [1], and the yellow region that in the measured EOS of Ref. [3].

ture vibrational effects at 300 K, calculated at the DFT level within the quasiharmonic approximation. These corrections are very similar for the LDA and PBE-GGA functionals and amount to changes of only about +0.37 a.u. per atom in V_0, -11 GPa in B_0, and +0.03 in B_0'. The resulting p-V relations are plotted in Fig. 3, and the EOS parameters are given in Table I. (The VMC data are not plotted as they are indistinguishable from the DMC curve on this scale.)

The experimental EOS data of Refs. [1,3] differ markedly at low volumes. The VMC, DMC, and PBE-GGA EOS curves fall within the region of uncertainty of the measured EOS of Ref. [3], but the pressure from the LDA EOS is significantly lower, and falls between the regions of uncertainty of the experimental curves. The DMC values of V_0 and B_0 are the closest to experiment. The value of B_0' from the different theoretical methods fall between 3.65 and 3.8(1), with the lowest value coming from the LDA and the highest from VMC. The LDA EOS seems the least satisfactory and, rejecting this result, the theoretical values of B_0' range only from 3.72 to 3.8(1). Given the level of agreement between the various theoretical methods it seems that the experimental value [1] of $B_0' = 3.0 \pm 0.1$ cannot be sustained. Our QMC results are thus consistent with the ideas of Holzapfel [2] regarding the refinement of the ruby luminescence pressure scale used in analyzing diamond anvil data.

TABLE I. Vinet EOS parameters. ZPE and temperature effects at 300 K have been included in the theoretical data.

	LDA	PBE	VMC	DMC	Experiment (300 K)
V_0 (a.u.)	37.31	38.61	37.82(6)	38.54(6)	38.284 [18]
B_0 (GPa)	454	422	472(4)	437(3)	442(4) [3]
B_0'	3.65	3.72	3.8(1)	3.7(1)	4.0(5) [3], 3.0(1) [1]

We computed the frequency of the first-order Raman mode of diamond at four volumes corresponding to a pressure range of approximately 0–320 GPa using the "frozen phonon" method. In the Raman mode, two nearest-neighbor atoms are displaced in opposite directions along their mutual bond by a distance u from their equilibrium positions, with the pattern of displacements being repeated in each primitive unit cell.

The observed frequency is renormalized from that corresponding to the harmonic potential by anharmonic effects. This renormalization has been deduced from experiment to be about $-20\ \mathrm{cm}^{-1}$ at zero pressure [19], in good agreement with the theoretical estimate of $-17.4\ \mathrm{cm}^{-1}$ obtained in Ref. [20]. We performed a thorough study of the Raman mode within DFT, including the effects of anharmonicity, calculating the renormalization of the Raman frequency as a function of volume using Eq. (16) of Vanderbilt *et al.* [20]. The renormalization is dominated by the cubic anharmonicity, although the contribution from the quartic terms is not negligible. The renormalization of the Raman frequency varies weakly with volume, at V_0^{exp} we obtained $-18.0\ \mathrm{cm}^{-1}$ (LDA) and $-15.6\ \mathrm{cm}^{-1}$ (PBE-GGA), while at the smallest volume studied of $V = 26.5$ a.u. per atom we obtained $-19.4\ \mathrm{cm}^{-1}$ (LDA) and $-19.5\ \mathrm{cm}^{-1}$ (PBE-GGA).

The QMC calculations were performed using the larger $5 \times 5 \times 5$ simulation cells. The statistical errors in the frequencies are reduced by taking u to be large, in a similar way to the EOS calculations, but the results are then affected by anharmonicity. We calculated QMC energies for the undistorted crystal and for Raman mode displacements of magnitude u_1 and u_2, which allows us to extract the cubic anharmonicity in the potential. Suitable values of u_1 and u_2 were selected assuming the PBE-GGA energy to be a reasonable model for the QMC energy, and choosing values which resulted in errors of only a few cm^{-1} in the harmonic frequencies due to "contamination" with quartic and higher order terms in the potential. The results are not very sensitive to the values of u_1 and u_2, and we selected values in the range 0.17–0.35 a.u.

We added finite size corrections to the QMC frequencies, obtained from PBE-GGA calculations, of $+11.9\ \mathrm{cm}^{-1}$ at V_0^{exp}, and $+7.4\ \mathrm{cm}^{-1}$ at $V = 26.5$ a.u. per atom, resulting in the harmonic frequencies shown in Table II. The cubic anharmonic terms calculated within VMC and DMC are very similar and are about 20% larger than the DFT ones at V_0^{exp} and 10% larger at $V = 26.5$ a.u. per atom. To obtain the frequencies including anharmonic effects given in Table II and Fig. 4, we added a correction

TABLE II. The harmonic and renormalized Raman frequencies at the experimental equilibrium volume in cm^{-1}.

	LDA	PBE	VMC	DMC	Experiment
ω (harmonic)	1281	1292	1389(3)	1375(4)	⋯
ω (renorm.)	1263	1277	1373(4)	1359(4)	1333 [1]

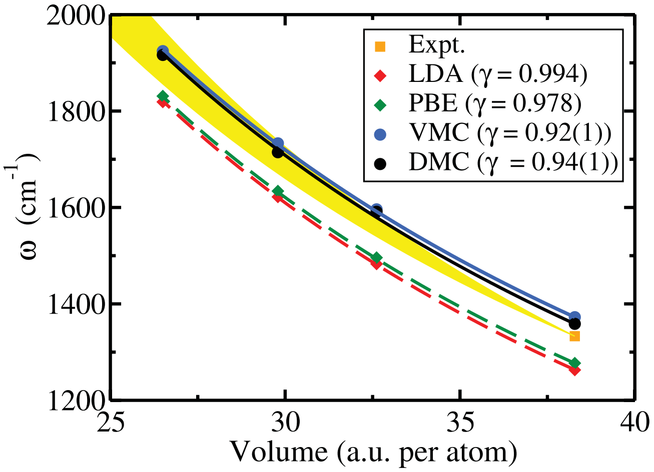

FIG. 4 (color). The Raman frequency as a function of volume. The shaded yellow region shows the range of values obtained by using Gruneisen parameters in the range $\gamma = 0.9$–1.06.

calculated using Eq. (16) of Vanderbilt *et al.* [20]. As the small quartic terms were not evaluated within QMC we used PBE-GGA values instead.

The Raman frequency has been measured at atmospheric pressure and room temperature by many researchers, with a high level of consistency, and the value of 1333 cm^{-1} is accurate to better than 1 cm^{-1}. The calculated and experimental data at V_0^{exp} are compared in Table II. The LDA and PBE-GGA Raman frequencies are significantly lower than the experimental value, while the VMC and DMC values are higher. The DMC result is closest to the experimental one.

We have chosen to plot the Raman frequencies against volume rather than pressure, because this allows a comparison of frequencies calculated with identical structures; see Fig. 4. Although the value of the Raman frequency is well established at V_0^{exp}, its behavior under high compressions is less certain. Experimental frequencies are often quoted in terms of the expression $\omega(V) = \omega(V_0^{\mathrm{exp}}) \times (V/V_0^{\mathrm{exp}})^{-\gamma}$, where γ is the Gruneisen parameter. The range of reported experimental behavior is illustrated by the yellow shaded region in Fig. 4, which corresponds to $\gamma = 0.9$–1.06 [5].

Figure 4 shows that the LDA and PBE-GGA frequencies are very close to each other and are lower than the experimental range at all volumes, while the VMC and DMC data are also very close to each other and are a little higher than experiment at large volumes and within the experimental range at lower volumes. The renormalized DMC phonon frequencies are 1375(4), 1592(4), 1715(3), and 1916(3) cm^{-1} at volumes of 38.284, 32.615, 29.791, and 26.500 a.u. per atom, respectively. The calculated data were fitted to obtain Gruneisen parameters of 0.994 (LDA), 0.978 (PBE-GGA), 0.92(1) (VMC), and 0.94(1) (DMC).

In summary, we have studied the equation of state and Raman frequency of diamond using quantum Monte Carlo methods. The VMC and DMC equations of state are in good agreement with the experimental data of Ref. [3], and with PBE-GGA results, but disagree with those of Ref. [1]. The DFT and QMC results support a value of the pressure derivative of the bulk modulus, B_0', of a little below 4. We have also shown that accurate Raman frequencies can be obtained in diamond by combining QMC with frozen phonon techniques.

The calculations were performed on the Hitachi SR11000 computers at the National Institute for Materials Science, at the High Performance Computing System of Hokkaido University, and at the Information Technology Center of the University of Tokyo. We acknowledge financial support from the EPSRC, and from a Grant-in-Aid for Scientific Research in Priority Areas "Development of New Quantum Simulators and Quantum Design" (No. 17064016) of The Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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