Equation of state for diamond in wide ranges of pressure and temperature

John S. Tse\textsuperscript{1,a)} and Wilfried B. Holzapfel\textsuperscript{2,b)}

\textsuperscript{1}Department of Physics and Engineering Physics, University of Saskatchewan Saskatoon, S7N 5E2, Canada
\textsuperscript{2}Department-Physik, Universität Paderborn, D-33095 Paderborn, Germany

(Received 24 March 2008; accepted 19 June 2008; published online 28 August 2008)

Theoretical total energy and phonon calculations for diamond under strong compressions up to 3 TPa are analyzed with different analytical forms for the representation of $p$-$V$ isotherms. A simple model with only two characteristic (volume dependent) phonon parameters—an acoustic Debye temperature and an additional Einstein temperature of the optical phonons—provides a complete modeling of all the thermophysical properties of diamond in this extended range of pressure up to the melting curve. The comparison with thermophysical data at ambient pressure provides additional information on weak intrinsic anharmonic contributions and gives the frame for the complete modeling up to 3 TPa in pressure and temperatures up to the melting curve. © 2008 American Institute of Physics. [DOI: 10.1063/1.2969909]

I. INTRODUCTION

Diamond is a very unique material with the highest incompressibility of all the elements at ambient pressure. In addition its high melting temperature, high Debye temperature, small intrinsic anharmonicity, and chemical inertness qualify diamond as a special reference material for the realization of an “International Practical Pressure Scale” (IPPS).\textsuperscript{1–4} The realization of this IPPS depends on the knowledge of pressure-volume relations for a variety of materials with widely different incompressibilities, or in other words, on accurate values for the (isothermal) bulk modulus $K_0$, at ambient conditions, and additional information on $K'_0$, the (isothermal) pressure derivative of the bulk modulus at ambient condition. More generally, one is interested not only in the $p$-$V$ relation for ambient temperature, but in a robust complete $p$-$V$-$T$ relation for wide ranges in pressure and temperature, which is just the complete equation of state (EOS). For diamond very accurate values for $K_0$ are available from ultrasonic and Brillouin scattering measurements,$^5$–$^9$ but large uncertainties are still noticed in the experimental values for $K'_0$ (Refs. 2, 6, and 10) in comparison with the narrow range of recent theoretical data.$^{11–13}$ Since the uncertainty in the experimental data for $K'_0$ can be traced back to the uncertainty in the “practical pressure scale,” or more specifically to the curvature of the ruby line shift, the best estimate of this uncertainty may be obtained by a comparison with more reliable theoretical data.

Due to its simple and highly symmetric structure diamond remains a special candidate for the testing of various theoretical approaches concerning structural stability and thermophysical properties. The high accuracy obtained in recent years in the calculations of ground state properties and quasiharmonic phonon contributions$^{11–13}$ allows for a detailed comparison with experimental data and offers a new approach for a significant improvement in the realization of a robust EOS for diamond in a wide range of pressures up to 2 TPa and temperatures up to melting around 5000 K, especially, when reasonable estimates for contributions from intrinsic anharmonicities of the lattice vibrations are also taken into account.$^{14}$ The most accurate first-principles calculation on the EOS of diamond is the use of the diffusion quantum Monte Carlo method where many electron correlation effects were considered explicitly.$^{15}$ The results obtained at 300 K are consistent with other electronic structure calculations. The new theoretical data obtained here are used to find the most appropriate analytical form for the representation of the $p$-$V$ relation for the static lattice of diamond in wide ranges of compression. In the second step, theoretical data for the quasiharmonic lattice dynamics are analyzed in such a way that simple analytic forms can be used to represent the quasiharmonic phonon contributions to the EOS. Finally, estimates for the intrinsic anharmonic contributions are derived from experimental data for the heat capacity at ambient pressure and theoretical relations used to estimate pressure dependence of these terms.

II. THE STATIC LATTICE

One of the motivations for the present study relates to the question, which “parametric” EOS form may be most suitable for the representation of EOS data covering wide ranges in compression.$^{15–20}$ Most commonly, the Birch equation of order $L$ (BEL) (Ref. 16),

$$p_{\text{BEL}} = \frac{3}{2}K_0 \frac{1-x^2}{x^3} \left(1 + \sum_{k=2}^{L} c_k (x^2 - 1)^{k-1}\right),$$

is used in its second order form BE2, where $x=(V/V_0)^{1/3}$, $c_2=(3/2)(K'_0-4)$, and all the higher order terms are neglected. With a finite value for $c_3$ one obtains the third order form BE3, which allows in addition for the adjustment of $K'_0$.

More recently$^{17}$ an “effective” (second order) Rydberg form ER2,

\textsuperscript{a)}Electronic mail: john.tse@usask.ca.
\textsuperscript{b)}Electronic mail: holzapfel@physik.upb.de.
\[ p_{\text{ER2}} = 3K_0 \frac{1-x}{x^2} e^{\epsilon_{\text{ER2}}(1-\epsilon)}, \]

has been introduced with \( \epsilon_{\text{ER2}} = (3/2)(K_0^* - 1) \). Since this form does not approach the correct asymptotic behavior under very strong compression, an adapted polynomial expansion was later introduced as a more convenient form,\(^{18-21}\)

\[ p_{\text{APL}} = 3K_0 \frac{1-x}{x^5} e^{\epsilon_{\text{APL}}(1-\epsilon)} \left( 1 + \sum_{L=2}^{L} c_L (1-x)^{L-1} \right). \]

The parameter \( \epsilon_0 = -\ln(3K_0/p_{\text{FG}}) \) with \( p_{\text{FG}} = a_{\text{FG}}(Z/V_0)^{5/3} \) for the pressure of a Fermi gas with the total electron number \( Z \) in the (atomic) volume \( V_0 \) and the Fermi-gas parameter \( a_{\text{FG}} = 0.023 \) 37 GPa nm\(^5\) takes care of the correct high pressure limit. The second order parameter \( c_2 = (3/2)(K_0^* - 3) - c_0 \) is usually already very small for regular solid. One may also notice that this form can be integrated still analytically to obtain the corresponding energy-volume relation even when higher order contributions are present.\(^{20,21}\)

To compare the different behaviors of these EOS forms under strong compression, the total energy calculations for diamond are extended here up to the 2 TPa region, where the diamond structure may be metastable.\(^{22-27}\) Theoretical studies show that above about 1 TPa a (body-centered) BC8 structure should be stable. However, nothing is known about the metastabilities at low temperature in this high pressure regime.\(^{26,27}\)

\textit{Ab initio} calculations of the EOS (\( E-V \)) for diamond were performed with the pseudopotential plane wave method within the gradient corrected density functional theory (Perdew–Wang 91) implemented in the electronic code \textsc{vasp}.\(^{28}\) A hard projector augmented wave potential\(^{29}\) with plane wave energy cutoff of 700 eV was used. A Monkhorst–Pack \( k \)-mesh of \( 12 \times 12 \times 12 \) was used in the electronic calculations. The convergence in the energy was set at \( 10^{-7} \). A very tight convergence criterion was needed for the accurate evaluation of the Hellman–Feynman forces for the calculations of the phonon band structure and the vibrational density of states (DOS) using the supercell method.\(^{30}\) Supercells ranging from \( 16 \) (\( 2 \times 2 \times 2 \)) to \( 54 \) (\( 3 \times 3 \times 3 \)) atoms were used to ensure the accuracy of the calculated vibrational properties. At selective pressures, results from the supercell calculations are check against those obtained from linear response method. The results reported here were obtained with the large 54 atoms supercell.

The (theoretical) value for the volume at zero pressure, \( V_{0\text{th}} = 5.7013(100\text{ pm})^3 \), was determined by least square fitting of a BE2-related energy form to a symmetrically restricted number of data points around the minimum. \( V_{0\text{th}} \) is slightly larger than the experimental value for ambient temperature;\(^{31}\) \( V_{0\text{exp}} = 5.6738(13)(100\text{ pm})^3 \). This difference can be taken into account most reasonably, when the theoretical (static lattice) \( p-V \) relation is compared later with an experimental isotherm at elevated temperatures giving the corresponding thermal expansion at ambient pressure to match the theoretical \( V_{0\text{th}} \). In other words, the theoretical \( p-V \) relation is used primarily to determine the value for \( K_0^* \), which depends only very slightly on this (“thermal”) shift in volume. With this fixed \( V_{0\text{th}} \), the three parameters \( E_0, K_0, \) and \( K_0^* \) are fitted to the theoretical data using the second order \( E-V \) relations, which correspond to the EOS forms BE2, ER2, and AP2, respectively. In addition third order parameters are included in the fits with the third order forms BE3 and AP3. The deviations of the fitted curves from the theoretical data are illustrated in Fig. 1, which shows that the deviations for the second order forms BE2, ER2, and AP2 are an order of magnitude larger than for the third order forms BE3 and AP3. The deviations are largest for ER2 and smallest for AP3. The form BE3 shows small deviations from the theoretical data (and from AP3) only around ambient pressure and in the very high pressure range. The corresponding differences in pressure with respect to the form AP3 are illustrated in Fig. 2, which shows more clearly the small differences between AP3 and BE3 on the one hand, and the large differences with respect to the second order forms. Where again AP2 gives the best fit of these second order forms. All these differences decrease strongly for fits over smaller ranges in compression, usually applied in previous comparisons of EOS forms.

The numerical values of these fits are given in Table I.
TABLE I. EOS parameters from total energy fits with different EOS forms discussed in the text for the full range of data from −98 GPa to 2.9 TPa. The values for $K_0''$ are obtained in fits with constrained $K_0=438$ GPa and the standard deviations in the last column refer to the unconstrained fits.

<table>
<thead>
<tr>
<th>$K_0$ (GPa)</th>
<th>$K_0'$</th>
<th>$K_0''$</th>
<th>Dev. (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP3</td>
<td>432.9</td>
<td>3.69</td>
<td>3.64</td>
</tr>
<tr>
<td>BE3</td>
<td>438.9</td>
<td>3.56</td>
<td>3.59</td>
</tr>
<tr>
<td>AP2</td>
<td>442.5</td>
<td>3.50</td>
<td>3.56</td>
</tr>
<tr>
<td>BE2</td>
<td>432.4</td>
<td>3.64</td>
<td>3.76</td>
</tr>
<tr>
<td>ER2</td>
<td>419.3</td>
<td>3.92</td>
<td>3.81</td>
</tr>
</tbody>
</table>

which shows in the last column that the standard deviation increases from 0.3 meV for AP3 to 6.7 meV for ER2 in these fits of the energies. Large differences in the values for $K_0$ and $K_0''$ for the different forms are seen in Table I. If one restricts the fits to data in the range from $-9 < p/\text{GPa} < 600$ these differences are reduced significantly, as shown in Table II. In fact, one may notice that the third order forms do not improve the fits significantly in this restricted range of pressure, but ER2 shows still the largest deviations. One may notice that the extended range of theoretical data up to 2 TPa gives good physical constraints on the EOS forms, which can be modeled accurately only by the third order forms AP3 and BE3. These constraints are physically realistic and only very slightly affected by the density functional theory approximation.

A strong anticorrelation in values for $K_0$ and $K_0''$ can be noticed most clearly in Table I as a result of the different constraints applied by the different EOS forms. With the reduced constraint in the restricted range of compression applied in the fit of Table II the values of $K_0$ show much smaller differences and one can select as best value. When this fixed value is used in additional fits of the data, one gets more stable values for $K_0''$ as indicated in both tables under $K_0''$. The value $K_0''=3.60(5)$ represents the most reasonable average for the better fits and agrees very well with the value 3.65(5) from another recent calculation 12 and also with the value required for the self-consistent revision of the ruby pressure scale. 14,32 If one wants to compare the theoretical value $K_{0\text{th}}=438(1)$ GPa with the experimental value $K_{0\text{exp}}=444.4$ GPa from literature, 9,10 one has to correct for the different values of the theoretical and experimental $V_{0\text{th}}=5.704(8)(100 \text{ pm})^3$ and $V_{0\text{exp}}=5.674(5)(100 \text{ pm})^3$, respectively. From the theoretical volume dependence of $K(V)$ one can estimate a second theoretical value for zero pressure, if one uses just the experimental value for $V_0$. This corrected value $K_{0\text{th-corr.}}=446$ GPa would be even much closer to the experimental value and confirms that no further corrections on $K_0''$ due to correlation are needed.

Some features of the different EOS forms are most easily inspected by the use of a special “linearization scheme,” 21,35 which compares all EOS forms with the Fermi-gas behavior at very high pressures. Since one can expect that the ratio of the pressure with respect to the Fermi-gas pressure at the same compression approaches 1 at very high pressure, the logarithm of this ratio should approach 0. This approach should be almost linear on a logarithmic scale with respect to the scaled linear compression $x=\sqrt[5]{V/V_0}$. The divergence in this logarithmic scaling at zero pressure can be removed by the subtraction of a $\ln(1-x)$ term. When one uses for the Fermi-gas pressure $P_{FG}(x)=\alpha_{FG}(Z/V_0)^{1/3}x^{-5}$, with the Fermi-gas parameter $\alpha_{FG}=0.0237$ GPa nm$^5$ and the usual meaning of $Z$ for the atomic number and $V_0$ for the atomic volume, one obtains for this doubly scaled logarithmic ratio $\ln R(x)=\ln[p(x)]-\ln[p_{FG}(x)]-\ln(1-x)$. In $R(x)$ gives an almost linear scaling over very wide ranges in compression for many regular solids 18,19,21 with a predictable slope at very strong compression. The situation for diamond is illustrated in Fig. 3. The theoretical $p-V$ data are represented by the chain of solid dots in the range up to 3 TPa. The dashed line with diamonds represents the EOS of ideal solids with less dilation in the range from 0 to 3 TPa representative of the theoretical data. The thick solid line closest to these dots corresponds to the form AP3; the thin line corresponds to AP2. The dotted line represents a linear interpolation corresponding to a first order AP1 form. The dashed line with diamonds represents the line for ideal solids discussed in the text. The solid and thin dashed line with crosses represent the BE3 and BE2 forms, respectively. The thick line with diagonal crosses corresponds to ER2. The deviations between AP2 and AP3 at 30 TPa correspond to an uncertainty in pressure of 4% only.

FIG. 3. (Color online) Reduced linearized representation of the different EOS forms discussed in the text with constraint to the best values for $V_{0\text{th}}=5.704(100 \text{ pm})^3$ and $K_0=438$ GPa from the fits in the restricted range of pressure from $-9$ to 575 GPa corresponding to the data given in Table II. The coordinate $x=\sqrt[5]{V/V_0}$ represents the linear compression. The solid dots in the range from 0 to 3 TPa represent the theoretical data. The thick solid line closest to these dots corresponds to the form AP3; the thin line corresponds to AP2. The dotted line represents a linear interpolation corresponding to a first order AP1 form. The dashed line with diamonds represents the line for ideal solids discussed in the text. The solid and thin dashed line with crosses represent the BE3 and BE2 forms, respectively. The thick line with diagonal crosses corresponds to ER2. The deviations between AP2 and AP3 at 30 TPa correspond to an uncertainty in pressure of 4% only.

TABLE II. EOS parameters from total energy fits with different EOS forms discussed in the text for a range of data from $-9$ to 575 GPa. The values for $K_0''$ are obtained in fits with constrained $K_0=438$ GPa and the standard deviations in the last column refer to the unconstrained fits.

<table>
<thead>
<tr>
<th>$K_0$ (GPa)</th>
<th>$K_0'$</th>
<th>$K_0''$</th>
<th>Dev. (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP3</td>
<td>438.2</td>
<td>3.57</td>
<td>3.57</td>
</tr>
<tr>
<td>BE3</td>
<td>437.0</td>
<td>3.60</td>
<td>3.57</td>
</tr>
<tr>
<td>AP2</td>
<td>438.2</td>
<td>3.57</td>
<td>3.57</td>
</tr>
<tr>
<td>BE2</td>
<td>437.0</td>
<td>3.60</td>
<td>3.73</td>
</tr>
<tr>
<td>ER2</td>
<td>432.3</td>
<td>3.77</td>
<td>3.69</td>
</tr>
</tbody>
</table>
constraints on the electron arrangement, a typical behavior for the covalent elements. The common starting point at \( x = 1 \) for all the other curves results from same \( K_{\text{0th}} = 438 \) GPa used here in all the different EOS forms for diamond. The almost equal slopes at \( x = 1 \) correspond to the very narrow range of values for \( K_{\text{0th}} \) obtained in these fits. The slightly S-shaped solid interpolation between zero and ultimate compression represents the best fitting AP3 form. The thin convex interpolating line comes from AP2. The straight dotted interpolation shows the first order form AP1 with its constrained \( K_{\text{0AP1}} = 3.45 \), which can be regarded as a lower bound at moderate compression. The three remaining EOS forms are represented by the curves with crosses. The solid line with diagonal crosses results from ER2. Due to the finite value of the Rydberg potential at very strong compression this form diverges always with respect to the well established limiting Fermi-gas behavior. This constraint affects already seriously the quality of the fit at moderate compression. This form is useful therefore only at very moderate compression and even then its wrong constraint will always bias the related fits. The solid line with regular crosses represents the best fitting third order Birch form BE3 with only minor deviations within the range of theoretical data. However, its extrapolation diverges most rapidly and in the opposite direction with respect to the second order Birch form BE2 represented by the dashed curve with crosses. This comparison of the flexibility and constraints in the different commonly used EOS forms illustrates here very clearly the kind of errors introduce by the use of inadequate EOS forms.

**III. THE THERMAL PRESSURE**

On the basis of these theoretical EOS data for diamond, one can now construct the complete set of \( p-V \) isotherms (or the complete EOS) by the use of all the thermophysical data from ambient pressure together with the best starting values \( K_{\text{0exp}} = 444.4 \) GPa, \( K'_{\text{0}} = 3.67 \), and \( c_3 = -0.67 \) for an AP3 isotherm at ambient temperature. For the calculation of any other isotherm the thermal pressure (at the given volume) must be known, which means, that the contributions from all the different thermal excitations have to be understood. In an insulatorlike diamond (at moderate temperatures) the dominant contribution results from quasiharmonic phonon excitations. The corresponding thermal contribution of the quasiharmonic phonon pressure can be calculated from the phonon DOS, when the corresponding phonon “mode” Grüneisen parameters are also known. Additional contributions from intrinsic anharmonicity and defects have to be taken into account in the high temperature regime, when the temperature becomes comparable or larger than the Debye temperature. For the calculation of the quasiharmonic phonon pressure an earlier calculation of the phonon DOS for diamond is extended here to much higher pressures. These theoretical data are used at first for a calculation of the specific heat capacity at constant volume, which is then fitted by an optimized pseudo-Debye–Einstein (opDE) model with the following three characteristic temperature parameters \( TD, TE1 \), and \( TE2 \): a low temperature Debye temperature parameter for the zone center phonon contribution \( TD \), one

\[
c_{\text{quh}}(T, TD, TE1, TE2) = g \left( \frac{T}{TD} \right)^3 \left[ 4a_0g + \left( \frac{T}{TD} \right)^3 \right] + \frac{1 - g}{2} c_1 + \frac{T}{2T} c_2 \left( \frac{T}{TE1} \right),
\]

with

\[
a_0 = 0.0434, \quad g = 0.040, \quad \text{and}
\]

\[
c_1(T, TE) = \left( \frac{TE}{2T} \right)^2 \sinh \left( \frac{TE}{2T} \right).
\]

are used in the fit of the theoretical \( c_{\text{quh}} \) data near ambient pressure illustrated in Fig. 4, where the deviations between the calculated data and the fitted curve are represented by a string of circles on a 100 times expanded scale to illustrate the very small systematic deviations at very low temperatures. Since these deviations are much below the 1% level and restricted to the low temperature regime, where the thermal pressure is very small anyhow, these deviations are very small with respect to all the uncertainties in the experimental data and do not effect the present evaluations anywhere. The stability of this fitting is much enhanced, if a correlation between \( TD \) and \( TE1 \) is introduced by a fixed correlation parameter \( fTE1 = 0.91 \) in the relation \( TE1 = fTE1(3/4)TD \). This
means that only two parameters—the average $T_{Da} = TD[1 + (1/g)E1]$ for the acoustic modes and the average $T_{Do} = (4/3)TE2$ for the optic modes—are finally determined in the fits of the theoretical $c_V$ data at elevated pressures. The very smooth variations in $T_{Da}$, $T_{Do}$, and of the corresponding average $T_{ Dh}$ are shown in Fig. 5. In fact, $T_{ Dh}$ gives thereby also the high temperature limit of the (quasiharmonic) Debye temperature.

The variation in $T_{ Da}$ shows clearly an approach toward a maximum somewhere above 1 Pa, where $T_{ Do}$ and $T_{ Dh}$ are still increasing. Cubic polynomials $T_{ Di}(a) = T_{ Di}0(1 - a/ar) + C_i(1 - a/ar)^2 + C_i(1 - a/ar)^3$ with respect to the normalized lattice parameter $a/ar = 356.7$ pm are fitted to the theoretical results for $T_{ Do}$, $T_{ Dh}$, and $T_{ Da}$, as shown in Fig. 5. The numerical results of these fits are given in Table III for practical applications. The variation in the standard deviations of these fits is given in Fig. 6, and shows that the present model with only two different phonon parameters $T_{ Da}$ and $T_{ Do}$ for the acoustic and the optic modes, respectively, gives very good fits up to about 500 GPa. The systematic increase in the standard deviations at higher pressures indicates some limitations of the present model. In this extended range of pressure an additional “free” parameter for the zone center acoustic phonons could improve these fits significantly. However, for the present range of interest one does not need these more extended fits. The quality of these fits is illustrated also Fig. 7 by the three fitted curves with the theoretical data points.

The strong dispersion of the variation in the corresponding mode Grüneisen parameters $\gamma_{ Do}$, $\gamma_{ Dh}$, and $\gamma_{ Da}$ is shown in Fig. 8. One may not expect that a simple Mie–Grüneisen model with only one average Grüneisen parameter $\gamma_{ Dh}$ for all the modes would be a very good choice for diamond under high pressure; however, it is interesting to see that the procedure for the calculation of an average Grüneisen parameter from data for one $p-V$ isotherm developed by Barton and Stacey on the basis of a classical free volume approach results in the $\gamma_{ BS}$ in Fig. 8, which shows indeed a very similar pressure dependence as the average $\gamma_{ Dh}$ obtained from the theoretical data for the average (or high temperature) $T_{ Dh}$. This observation lends further confidence to the Barton–Stacey approximation and to the recent calculation of anharmonic contributions within the same free volume approach.

At this point it is interesting to analyze the present modified Mie–Grüneisen approach with its two different mode Grüneisen parameters in more detail. First of all, the dispersion of the mode Grüneisen parameters results in a significant temperature dependence of both the “thermobaric” and the thermal Grüneisen parameters related to the calculation of the thermal pressure from the internal phonon energy and to the calculation of the thermal expansion coefficient from the specific heat capacity, respectively. Figure 9 illustrates this variation by the additional curves for the thermobaric $\gamma b$ at three different temperatures. One can notice that the curve for 300 K coincides almost with acoustic $\gamma_{ Da}$, and the curve for 5000 K comes close to the average or high temperature $\gamma_{ Dh}$ at ambient temperature, but decreases much more strongly. For practical applications, the intermediate $\gamma b$ curve for 1000 K is most interesting because it shows an especially strong decrease at elevated pressures.

### IV. COMPARISON WITH EXPERIMENTAL DATA

Fits of the experimental $c_V$ data need a correction for anharmonic contributions with an additional anharmonicity

---

**Table III.** Parameters for the polynomial fits of the volume depended theoretical values for the effective Debye temperatures of the optic and acoustic phonons, $T_{ Do}$ and $T_{ Dh}$, and for the average or high temperature limit of the Debye temperature, $T_{ Da}$, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$T_{ Do}$</th>
<th>$C_{ I1}$</th>
<th>$C_{ I2}$</th>
<th>$C_{ I3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{ Do}$</td>
<td>2287</td>
<td>-3.48</td>
<td>4.91</td>
<td>-24.0</td>
</tr>
<tr>
<td>$T_{ Dh}$</td>
<td>1915</td>
<td>-2.94</td>
<td>2.82</td>
<td>-8.5</td>
</tr>
<tr>
<td>$T_{ Da}$</td>
<td>1540</td>
<td>-2.11</td>
<td>0.02</td>
<td>15.2</td>
</tr>
</tbody>
</table>

---

**Fig. 5.** (Color online) Effect of pressure on the calculated effective Debye temperatures for the optic, average, and acoustic phonons, respectively, given by the dots with lines for the best fitting polynomials.

**Fig. 6.** (Color online) Variation in the standard deviation with pressure for the restricted opDE2 fits discussed in the text.

**Fig. 7.** (Color online) Effect of pressure in the calculated and fitted reduced specific heat data.
A in the corresponding form for the heat capacity. When the same constraints as in the fits of the theoretical data are used also here, one obtains as experimental values for ambient pressure \(TDop=2252\text{ K}, TDh=1937\text{ K}, \) and \(TDac=1616\text{ K},\) which are reasonably close to the theoretical values given in the corresponding column of Table III. Furthermore, this fit gives also a reasonably small value for the anharmonicity parameter \(A=0.006.\) The best fit and the deviations of the experimental data from the fitted curve are illustrated in Fig. 10. These deviations are also here much smaller than 1% of the high temperature value. The systematic trend of these deviations looks slightly different than the trend seen in the plot of the theoretical data in Fig. 4. Most likely these deviations are partly related to a special smoothing of the experimental data and represent therefore also some of the typical uncertainties in the experimental data. The fact that these deviations are so small illustrates that limitations of the present model are significant only at the extremely high pressures in the theoretical calculations extending far beyond the present range of static high pressure techniques; however, for some of the dynamic techniques extending into the terapascal range one may need in\- \(\text{p} pressure techniques; however, for some of the dynamic techniques extending far beyond the present range of static high pressure and room temperature, the isothermal bulk modulus and its isothermal pressure derivative \(K'_\text{th}\) (usually also at zero pressure and room temperature), and an average anharmonicity parameter \(A\) (for ambient conditions). Effects from electronic excitations and defects are neglected in the present case. On the basis of this modeling, a software package had been developed for the refinements of the Debye temperatures, the related Grüneisen parameters, the first order anharmonicity parameter \(A\) and two additional higher order anharmonicity parameters \(f4\) and \(f6\) using experimental data for the thermal expansion at ambient pressure, \(V_\text{0}(T),\) the thermal volume expansion coefficient \(\alpha_\text{v}(T),\) and the specific heat capacity \(c_\text{v}(T)\) for constant volume at (ambient) pressure. A comparison of these model calculations with the experimental data for the temperature dependence of the bulk modulus at ambient pressure gives always a sensitive test for the accuracy of the model and of the experimental data as we will see also in the present case in Sec. IV.

The representation of the thermal expansion at ambient pressure results in deviations, which remain always smaller than 500 ppm. Since the \(\gamma\)-dispersion is not yet very strong at ambient pressure, the quality of the fits is almost the same, when only one average \(\gamma\) is used in this fit. However, the effect of \(\gamma\)-dispersion becomes much more significant at higher pressures, as illustrated in Fig. 11, which presents the difference in thermal pressure calculated with and without \(\gamma\) dispersion. The line with circles for ambient pressure shows indeed only a very marginal effect; however, at 500 GPa this effect is already quite remarkable and increases further at higher pressures. The weak dashed line near zero pressure represents the total phonon pressure with phonon dispersion

\[ 
\begin{align*}
\text{FIG. 8. (Color online) Effect of pressure in the calculated optic, average (high temperature limit), and acoustic Grüneisen parameters, } \gamma_\text{op}, \gamma_\text{oh}, \text{ and } \gamma_\text{ac}, \text{ respectively. The dotted line and the line with crosses represent the calculated variation for the Barton–Stacey (Ref. 34) approximation and for the less constrained fit of a purely volume dependent free Grüneisen parameters discussed later in the text.}
\end{align*}
\]

\[ 
\begin{align*}
\text{FIG. 9. (Color online) Effect of pressure on the optic, average (high temperature limit), and acoustic Grüneisen parameters (thick solid lines), } \gamma_\text{op}, \gamma_\text{oh}, \text{ and } \gamma_\text{ac}, \text{ respectively, and three isotherms for the thermobaric Grüneisen parameter, } \gamma_\text{tb}, \text{ used in the calculation of the thermal pressure.}
\end{align*}
\]

\[ 
\begin{align*}
\text{FIG. 10. (Color online) Reduced molar heat capacity for constant volume with data points from literature (Ref. 31) and a best fitted curve from the opDE2 model discussed in the text. The pseudo-Debye–Einstein contribution for acoustic phonons and the Einstein contribution for the optic phonons are shown by thin and thick dashed curves, respectively. The circles repre-
\end{align*}
\]
at 2 TPa, which indicates that an average Grüneisen parameter gives much to strong phonon pressures in this pressure range.

An interesting feature of the $\gamma$-dispersion is also illustrated in Fig. 12, which shows the data points\textsuperscript{31} for the thermal volume expansion coefficient at ambient pressure together with the calculated (solid) curve and calculations for elevated pressure. The strong decrease in the acoustic $\gamma_{ac}$ with negative values above 2 TPa results here also in small negative values for $\alpha_v(T,p)$ at moderate temperatures, similar to the situation in Si (Ref. 35) and Ge (Ref. 36) at ambient pressure and low temperature.

Figure 13 illustrates, that the use of the Barton–Stacey\textsuperscript{34} approximation with its fixed relation for the volume dependence of the average Grüneisen parameter leads to problems in the calculation of the temperature dependence for the (adiabatic) bulk modulus of diamond at ambient pressure. The experimental data from literature\textsuperscript{6–9} are represented by the solid dots. The calculated data are scaled from isothermal to adiabatic values with the use of the experimental values for $\alpha_v(T)$, $K_0(T)$, and $c_p(T)$ from the respective literature.\textsuperscript{6–9,31} The upper curve with crosses and estimated boundaries for the uncertainty represents the variation, when the present best estimate for the pressure derivative of the isothermal bulk modulus at ambient condition $K_0' = 3.67(10)$ is used together with phonon contributions calculated in the Barton–Stacey\textsuperscript{34} approximation. With this approximation, only a completely unreasonable value $K_0' = 5.6$ could fit the data in contrast to recent observation\textsuperscript{37,38} with Cu, Ag, and Au, where the Barton–Stacey\textsuperscript{34} approximation worked very well with the given values of $K_0'$. When we use the $\gamma$-dispersion of the present calculation, we obtain almost the same variation with no good fit either. However, if one follows a common procedure and uses a more flexible form for the average $\gamma_{ac}$, one can adjust the volume dependence $\Gamma_{ac} = \partial \ln \gamma_{ac}/\partial \ln V$ at ambient conditions to fit the $K_{0}(T)$ data, as shown by the dotted curve in Fig. 14. In detail, this fit uses the form attributed to Al’tshuler\textsuperscript{39} and Oganov and Dorogokupets\textsuperscript{40} with the limiting $\gamma_{ac} = 2/3$ and the additional parameter $\Gamma_{ac} = 2.3$, which is quite large in comparison to the small Barton–Stacey\textsuperscript{34} value $\Gamma_{BS} = 0.6$ for diamond. This fit of a free $\gamma(V)$ gives a hint to solve the problems encountered with the calculated $\gamma$-data. A larger curvature for the $TD_a$-curve near ambient pressure could solve the problem!
A good solution for this problem with the same initial values for $TDac_0$ and $TDop_0$ but with different initial slopes and curvatures is illustrated in Fig. 14. The corresponding variation in $K_{30}(T)$ is shown in Fig. 13 by the solid line, which fits almost as good as the dotted curve for the case with free $\gamma(V)$. The small deviations in the solid modified $TD$-curves in Fig. 14 with respect to the dashed initial curves seem to be well compatible with the original data, especially if one considers that this evaluation is not very accurate at moderate pressures, where the splitting between the two temperature parameters is small. This means that strong changes in variations of the corresponding Grüneisen parameters at moderate pressures are not in conflict with the theoretical data. Figure 15 shows at moderate pressures indeed a steep decrease in $\gamma_{ac}$, a steep increase in $\gamma_{op}$ with a crossover, and a steep decrease also in $\gamma_{dh}$ similar to the decrease in fitted $\gamma_{free}$. It may be interesting to note that the effect of temperature on the different Grüneisen parameters at ambient pressure due to thermal expansion results in very similar variations for $\gamma_{free} 0(T)$ and the modified $\gamma_{dh0}(T)$, as shown in Fig. 16. The thermobaric $\gamma_{tb0}(T)$ with its intrinsic temperature dependence, however, starts at low temperatures close to the curve for the acoustic $\gamma_{ac0}$ and approaches the curve for $\gamma_{free} 0(T)$ only at high temperatures.

This opDE2 model with the modified phonon dispersion fits now all the data at ambient pressure as indicated also by the quality of the fits for thermal expansion in Fig. 17, which shows that the deviations of the present model (solid dots) remain also in the range of 500 ppm typical for the experimental data with systematics similar to the results from free $\gamma(V)$ fits. Although the fits of $K_{30}(T)$ for both the models with free $\gamma(V)$ and the modified phonon dispersion look very similar, the results for the calculated temperature dependence of $K'_{30}(T)$ show significant differences in Fig. 18, which includes a dashed line for the pure volume dependence of $K'_{30}(T)$ without other phonon contributions. The crosses reproduce effective values for a representation of the isotherm in the range up to 300 GPa by an AP2 form with adjusted $K'_{30}(T)$ values and the line with circles shows the values of a best fitting AP3 form with adjusted $K'_{30}(T)$ and $c3(T)$ values.

For practical applications one may not always want to repeat the present full EOS calculations indeed. Therefore Table IV presents a set of parameters to be used in effective AP2 forms for selected isotherms. The column under $K'_{30}$ shows in this table the best thermodynamic values of the present model. The column under $K'_{0}$ gives effective values to be used with the AP2 form as best adaptation for the range from 0 to 300 GPa. Deviations in this effective representa-
tion with respect to the detailed thermodynamic calculation are forced to be 0 at 200 GPa and remain smaller the 1% in pressure anywhere in the range up to 300 GPa, as shown in Fig. 18, for the isotherms at 3000 K. One may notice also that these data are based on a refined zero temperature theoretical isotherm with \(K_{0}^{th}/H_{20849}/H_{20850}=3.68\), which takes into account, that the zero pressure volume of the initial theoretical static lattice case corresponds to an isotherm at 922 K. What can be noticed in this Table IV is the somewhat weaker temperature dependence in the \(K_{o}^{eff}/H_{20849}/H_{20850}\) and a significant increase in the third order coefficient in the last column, which corresponds to a fit of the thermodynamic isotherm with an AP3 form with the thermodynamic \(K_{0}^{th}/H_{20849}/H_{20850}\) and for a best mix.

TABLE IV. Temperature dependence of the EOS parameters from the full thermodynamic model, for the adapted parametric AP2 form with \(K_{o}^{eff}\) replacing the correct thermodynamic \(K_{0}^{th}\), for the parametric AP3 form with the thermodynamic \(K_{0}^{th}\), and for a best mix.

<table>
<thead>
<tr>
<th>(T(K))</th>
<th>(V_{o}(100\text{ pm}))</th>
<th>(K_{o}^{eff}(\text{GPa}))</th>
<th>(K'_{oth})</th>
<th>(K'_{coeff})</th>
<th>(c3_{eff})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.6724</td>
<td>445.7</td>
<td>3.66</td>
<td>3.64</td>
<td>−0.31</td>
</tr>
<tr>
<td>100</td>
<td>5.6724</td>
<td>445.6</td>
<td>3.66</td>
<td>3.64</td>
<td>−0.31</td>
</tr>
<tr>
<td>200</td>
<td>5.6728</td>
<td>445.3</td>
<td>3.67</td>
<td>3.65</td>
<td>−0.35</td>
</tr>
<tr>
<td>300</td>
<td>5.6742</td>
<td>444.4</td>
<td>3.68</td>
<td>3.65</td>
<td>−0.43</td>
</tr>
<tr>
<td>400</td>
<td>5.6766</td>
<td>442.9</td>
<td>3.70</td>
<td>3.67</td>
<td>−0.53</td>
</tr>
<tr>
<td>500</td>
<td>5.6805</td>
<td>440.8</td>
<td>3.72</td>
<td>3.68</td>
<td>−0.65</td>
</tr>
<tr>
<td>600</td>
<td>5.6852</td>
<td>438.5</td>
<td>3.74</td>
<td>3.69</td>
<td>−0.78</td>
</tr>
<tr>
<td>700</td>
<td>5.6905</td>
<td>436.0</td>
<td>3.76</td>
<td>3.71</td>
<td>−0.93</td>
</tr>
<tr>
<td>800</td>
<td>5.6965</td>
<td>433.3</td>
<td>3.79</td>
<td>3.72</td>
<td>−1.09</td>
</tr>
<tr>
<td>900</td>
<td>5.7031</td>
<td>430.5</td>
<td>3.82</td>
<td>3.74</td>
<td>−1.26</td>
</tr>
<tr>
<td>1000</td>
<td>5.7101</td>
<td>427.5</td>
<td>3.85</td>
<td>3.76</td>
<td>−1.45</td>
</tr>
<tr>
<td>1100</td>
<td>5.7175</td>
<td>424.5</td>
<td>3.88</td>
<td>3.78</td>
<td>−1.64</td>
</tr>
<tr>
<td>1200</td>
<td>5.7253</td>
<td>421.4</td>
<td>3.91</td>
<td>3.80</td>
<td>−1.84</td>
</tr>
<tr>
<td>1300</td>
<td>5.7333</td>
<td>418.3</td>
<td>3.94</td>
<td>3.82</td>
<td>−2.05</td>
</tr>
<tr>
<td>1400</td>
<td>5.7416</td>
<td>415.1</td>
<td>3.98</td>
<td>3.84</td>
<td>−2.27</td>
</tr>
<tr>
<td>1500</td>
<td>5.7502</td>
<td>411.8</td>
<td>4.01</td>
<td>3.86</td>
<td>−2.49</td>
</tr>
<tr>
<td>1600</td>
<td>5.7590</td>
<td>408.5</td>
<td>4.04</td>
<td>3.89</td>
<td>−2.72</td>
</tr>
<tr>
<td>1700</td>
<td>5.7680</td>
<td>405.1</td>
<td>4.09</td>
<td>3.91</td>
<td>−2.96</td>
</tr>
<tr>
<td>1800</td>
<td>5.7772</td>
<td>401.6</td>
<td>4.13</td>
<td>3.94</td>
<td>−3.20</td>
</tr>
<tr>
<td>1900</td>
<td>5.7866</td>
<td>398.1</td>
<td>4.18</td>
<td>3.96</td>
<td>−3.45</td>
</tr>
<tr>
<td>2000</td>
<td>5.7961</td>
<td>394.6</td>
<td>4.22</td>
<td>3.99</td>
<td>−3.71</td>
</tr>
<tr>
<td>2100</td>
<td>5.8059</td>
<td>390.9</td>
<td>4.27</td>
<td>4.02</td>
<td>−3.98</td>
</tr>
<tr>
<td>2200</td>
<td>5.8159</td>
<td>387.2</td>
<td>4.32</td>
<td>4.05</td>
<td>−4.26</td>
</tr>
<tr>
<td>2300</td>
<td>5.8260</td>
<td>383.5</td>
<td>4.37</td>
<td>4.08</td>
<td>−4.54</td>
</tr>
<tr>
<td>2400</td>
<td>5.8363</td>
<td>379.7</td>
<td>4.42</td>
<td>4.11</td>
<td>−4.84</td>
</tr>
<tr>
<td>2500</td>
<td>5.8469</td>
<td>375.8</td>
<td>4.47</td>
<td>4.14</td>
<td>−5.14</td>
</tr>
<tr>
<td>2600</td>
<td>5.8576</td>
<td>371.9</td>
<td>4.53</td>
<td>4.18</td>
<td>−5.46</td>
</tr>
<tr>
<td>2700</td>
<td>5.8685</td>
<td>367.8</td>
<td>4.59</td>
<td>4.21</td>
<td>−5.79</td>
</tr>
<tr>
<td>2800</td>
<td>5.8796</td>
<td>363.8</td>
<td>4.65</td>
<td>4.25</td>
<td>−6.13</td>
</tr>
<tr>
<td>2900</td>
<td>5.8910</td>
<td>359.6</td>
<td>4.72</td>
<td>4.29</td>
<td>−6.49</td>
</tr>
<tr>
<td>3000</td>
<td>5.9025</td>
<td>355.4</td>
<td>4.78</td>
<td>4.33</td>
<td>−6.88</td>
</tr>
</tbody>
</table>

V. CONCLUSION

Theoretical calculations of the static lattice pressure for diamond and its phonon spectra under strong compressions up to about 3 TPa allow for a sensitive comparison of different EOS forms with the result that only the form AP3 gives a perfect representation of the static lattice pressure in this extended range of pressure. The strong dispersion in the mode Grüneisen parameters from the theoretical work can be taken into account in the complete thermodynamic modeling of all the thermophysical properties of diamond in a simple

FIG. 19. (Color online) Relative pressure differences between thermodynamic and parametric representations of the 3000 K.
model with one effective Debye temperature for the acoustic phonons and an additional Einstein temperature for the optical phonons. This opDE2 model results in a strong temperature dependence of the thermobaric Grüneisen parameter and in a very weak thermal expansion of diamond under strong compression at moderate temperatures (<3000 K).

Limitations in the modeling of the thermophysical properties with the use of the Barton–Stacey approximation result in interesting hints for the use of more sophisticated models. The less constraint volume dependences of a free average Grüneisen parameter must be taken with great caution, because this form may result in good fits of the available low pressure data. However, strong deviations may be expected under high pressure and high temperature as indicated by differences in the effective values of $K'_0(T)$. The results of the full thermodynamic modeling are finally represented by parametric EOS forms of the AP3 type with effective parameters for $K'_0(T)$ and $c\beta(T)$, the best mix AP3 form with the parameters from Table III.