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High pressure–high temperature equations of state of neon and diamond

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We report accurate measurements of the equation of state of diamond and neon, measured by x-ray diffraction in a resistively heated diamond-anvil cell. The atomic volume of single crystals of diamond embedded in neon pressure-transmitting medium has been measured between 0 and 80 GPa and from 300 to 900 K. The atomic volume of neon is reported in the same *P*-*T* range and also up to 208 GPa at room temperature. The crystal structure of neon remains face-centered cubic over the domain of investigation. We show that a Mie–Grüneisen–Debye formalism reproduces very well the present *P*-*V*-*T* data for neon as well as low pressure–low temperature data available in the literature. This makes neon a well calibrated x-ray pressure gauge, suitable for high pressure–high temperature studies. The thermal behavior of diamond is more complex and cannot be completely described by a Mie–Grüneisen–Debye model. Its thermal expansion decreases faster with increasing pressure than the predictions of simple thermodynamic models.

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I. INTRODUCTION

There is a current interest in the high pressure (HP) and high temperature (HT) physical properties of diamond.[1–7] These properties are important for planetary physics (diamond is proposed to be a component of the interior of some giant planets[8]) and for HP technology (diamond is used as a pressure gauge in diamond-anvil cells: a small crystal can be placed in the pressure chamber in contact with chemically reactive sample[2] or the Raman signal of the tips of the anvils can be directly used at very high pressure[9]).

On the one hand, measuring the equation of state (EoS) and Raman signal of diamond in quasihydrostatic conditions up to 140 GPa in a diamond-anvil cell confirmed the covalent bonding of this material up to strong compression.[4] It has also allowed a critical test of the HP–room temperature metrology: An update of the ruby pressure sensor calibration has been proposed to reconcile this EoS with ultrasonic measurements[6] or *ab initio* predictions.[5] On the other hand, by laser-shock compression of diamond, the very HT-HP region of its phase diagram (above 500 GPa) has been recently reached and a domain in which the Clapeyron melting slope is negative has been evidenced.[7] Between these two domains, the predictions of the thermodynamic behavior of diamond, based on heuristic models[10,11] or density-functional perturbation theory calculations,[3] have been made and need to be experimentally tested.

The goal of this study has been to measure the HP-HT EoS of diamond in the following range: $0 \leqslant P \leqslant 100$ GPa and $298 \leqslant T \leqslant 1000$ K. It corresponds to the conditions where diamond is likely to be used as a HT-HP pressure gauge, using its Raman[2] or x-ray diffraction signal. To date, only HP–room temperature[4] and HT–ambient pressure[12,13] EoS data were available to establish the calibration of this gauge up to 100 GPa. The small thermal expansion coefficient of diamond ($\alpha \simeq 4 \times 10^{-6}$ K^{-1} under ambient conditions) imposes the need for very accurate measurement of volume, pressure, and temperature to obtain reliable constraints for the HT-HP EoS. For instance, an overestimate of 2 GPa of the measured pressure around 40 GPa and 750 K will result in a doubling of the estimated average thermal expansion coefficient between 298 and 750 K. We have thus chosen a well-controlled way of heating up homogeneously the sample by resistive heating in a diamond-anvil cell, which prevents temperature and pressure gradients, and a pressure metrology ($SrB_4O_7:Sm^{2+}$ gauge[14,15]) that has been repeatedly tested by our groups under HP-HT[16–18] to perform the present measurements. Moreover, the HP-HT EoS of neon, which is used as the pressure-transmitting medium in this study, confirms the validity of this pressure metrology (see below). The data set obtained in this study, together with ambient pressure thermoelastic data, is then used to test the EoS formalisms available in the literature for diamond.[12,13,19] Anharmonic effects are clearly evidenced.

This paper is organized as follows. In Sec. II, we describe our experimental method. In Sec. III, we present the EoS of neon based on the present experimental data and those obtained in a recent study of iron.[20] We show that the HP-HT EoS of neon can be accurately described by a Mie–Grüneisen–Debye formalism under HP, with parameters obtained from a theoretical model. In Sec. IV, the diamond data are analyzed.

II. EXPERIMENTAL PROCEDURE AND DATA

Five experimental runs have been carried out. The experimental method for runs 1–4 has been described elsewhere.[16] During these runs, a few single crystals of diamond of size ranging from 3 to 5 μm were loaded into the pressure chamber of a diamond-anvil cell, along with ruby or $SrB_4O_7:Sm^{2+}$ as pressure sensors. Neon was the pressure-transmitting medium. Membrane diamond-anvil cells designed for HT operation were used. The cells were heated by a ring-shaped resistive heater up to 750 K and an additional heater was placed around the diamond anvils to reach higher temperatures. A *K*-type thermocouple fixed to the diamond anvil was used to measure the temperature within 5 K of the sample temperature. In run 5, P-V data for neon were measured when this rare gas was used as a pressure-transmitting medium in an experiment devoted to the measurement of the EoS of iron up to 200 GPa at room temperature.[20] In all these runs, care was taken in order to position the samples and the pressure sensors within a few micrometer distance to each other and at the center of the pressure chamber. Pressure was determined using the pressure shift of the luminescence lines of ruby (at 298 K, run 1), $SrB_4O_7:Sm^{2+}$ (Ref. 14) (above 298 K, runs 2–4), or using the EoS of tungsten[11] (run 5). For consistency with our previous report,[18] the pressures follow Holzapfel's 2005 ruby scale,[21] hereafter denoted H05. The calibration of the $SrB_4O_7:Sm^{2+}$ (Ref. 14) and tungsten[11] gauges were also modified to match the H05 scale.

Angular-dispersive x-ray diffraction experiments were performed on beamlines ID27 and ID09 of the European Synchrotron Radiation Facility (ESRF) (Grenoble, France). The monochromatic beam ($\lambda \simeq 0.3738$ Å) was focused to $\simeq 7\times 10$ μm^2. Diffracted x ray were collected by a MAR345 image plate, while the MDAC was rotated about the ϕ axis by $\pm 20°$. The images were integrated using the FIT2D program.[22] For diamond, between five and nine single-crystal reflections could be observed depending on the sample. The lattice parameter a was calculated from the measured d spacings of all observed reflections. The uncertainty on a was on average 5×10^{-4} Å. For neon, a few single crystals were initially formed in the pressure chamber by pressure-induced solidification; these crystals broke progressively on pressure increase, leading to a textured powder at ultrahigh pressure. For runs 1–4, the analysis of different d spacings did not evidence any sign of nonhydrostaticity (see the method presented in Refs. 23 and 24). The lattice parameter deduced from all the d spacings is thus used in this work. During run 5, neon was compressed at ambient temperature up to 208.8 GPa. Above $\simeq 100$ GPa, the x-ray diffraction peaks broadened considerably. Only the (111) diffraction peak position could be measured accurately. These observations suggest that neon was nonhydrostatically compressed in this run. It is thus possible that the volume of neon measured above 100 GPa was overestimated in this run, as it usually happens under nonhydrostatic compression. However, the (111) peak is expected to be the least affected by nonhydrostatic effects (like other materials with $C_{44} > (C_{11} - C_{12})/2$,[23–25] where C_{ij} denotes the elastic constants). Table I summarizes the lattice parameters measured for diamond and neon as a function of the pressure P_{H05} and temperature.

III. HIGH PRESSURE AND HIGH TEMPERATURE EQUATION OF STATE OF NEON

The room temperature and HP EoS of solid neon has been experimentally studied by Finger *et al.*[26] up to 14.4 GPa and by Hemley *et al.*[27] up to 110 GPa. Fei *et al.*[28,29] measured neon volume along the 1000 K isotherm between 24 and 56 GPa. The present measurements extend the P-V-T database for neon to 208.8 GPa at room temperature and 86 GPa at HT. For rare-gas solids, a face-centered-cubic (fcc) to a hexagonal-closed-packed (hcp) transition has been predicted to occur on cold compression[30] and a stability domain for a body-centered-cubic (bcc) phase is also expected along the melting line at HP. In the P-T range studied here, there was no evidence for the formation of an hcp or a bcc phase of neon. It could mean that three-body interactions, which are the likely cause of the fcc → hcp transition,[30] are weaker in neon than in other rare-gas solids. Also, no changes of the neon electronic structure are expected in the studied P-T range.[31] Our data set, which includes data up to $V/V_0 = 0.24$, thus allows a good test of isothermal equations of state, which describe compression of systems without phase changes. To describe HP-HT EoS, the quasiharmonic Mie–Grüneisen–Debye model has often been used.[28,32] "Quasiharmonic" means that the effect of temperature on the vibrational modes (phonons) is taken into account only through the volume change associated with thermal expansion. However, intrinsic anharmonic effects, which cause departure from the Mie–Grüneisen–Debye model, have been reported and discussed for several substances.[11,33,34] These effects are caused by the anharmonicity of individual phonons (associated with the anharmonicity of the interatomic potential shape) and by phonon-phonon interactions. The present P-V-T database, together with other measurements (calorimetric, volumetric, and ultrasonic), provides a test of the Mie–Grüneisen–Debye approximation in the case of neon.

The Mie–Grüneisen–Debye EoS is formulated as

$$P(V,T) = P_V(V,0\ \mathrm{K}) + P_{TH\ \mathrm{Debye}}(V,T). \tag{1}$$

$P_V(V,0\ \mathrm{K})$ can be expressed using several formalisms, in particular, the so-called Vinet EoS,[35]

$$P_V = 3K_0 x^{-2}(1-x)\exp[(1.5K_0' - 1.5)(1-x)]. \tag{2}$$

In Eq. (2), $x = (V/V_0)^{1/3}$. This equation has three parameters: V_0 the atomic volume and K_0 and K_0' the bulk modulus and its pressure derivative in the reference state (here, chosen as ambient pressure, including zero-point pressure and $T=0$ K). The reference volume of neon has been fixed to the value deduced from accurate measurements down to 4 K (Ref. 33): $V_0 = 22.234$ Å^3/at.

Zero-point vibration pressure being included in $P_V(V,0\ \mathrm{K})$, only one term remains for the Debye thermal pressure,

$$P_{TH\ \mathrm{Debye}}(V,T) = \frac{9RT\gamma_D}{V}\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{z^3 dz}{e^z - 1}. \tag{3}$$

The characteristic Debye temperature θ_D is assumed to only vary with volume: $d\ln\theta_D/d\ln V = -\gamma_D$, with γ_D the Debye–Grüneisen parameter. Under reference conditions, $\theta_D = \theta_0 = 75.1$ K. This value has been obtained from specific heat measurements at ambient pressure.[33] The volume dependence of θ_D has been expressed as[26,27]

$$\theta_D = \theta_0 x^{-1.5} \exp[\gamma_1(1 - x^{3q})/q]. \tag{4}$$

This corresponds to the following volume dependence of γ_D:

$$\gamma_D = \gamma_1 x^{3q} + 1/2.$$

To estimate the parameters γ_1 and q, we have used a

TABLE I. EoS data for diamond and neon obtained during five experimental runs. For each run, neon was used as pressure-transmitting medium. T was measured within 5 K. P has been measured using the signal from a luminescence gauge (Ruby, $SrB_4O_7:Sm^{2+}$) or the signal from an x-ray gauge (tungsten: W). H05 (Ref. 19) pressure scale has been used. Uncertainty on P_{H05} increases from 0.05 GPa at 1 GPa to 3 GPa at 200 GPa, if the H05 pressure scale is assumed to be correct. a_C and a_{Ne} are the lattice parameters of diamond and neon, measured with a relative uncertainty of $\simeq \pm 3 \times 10^{-4}$. The atomic volumes are $V_C = a_C^3/8$ and $V_{Ne} = a_{Ne}^3/4$. The missing points for neon correspond to the P-T conditions at which neon is fluid.

Run	P gauge	T (K)	P_{H05} (GPa)	a_C (Å)	a_{Ne} (Å)
1	Ruby	298	4.53	3.5534	3.7981
1	Ruby	298	7.55	3.5474	3.6658
1	Ruby	298	9.38	3.5426	3.6019
1	Ruby	298	11.2	3.5372	3.5533
1	Ruby	298	13.6	3.5324	3.4996
1	Ruby	298	15.5	3.5278	3.4664
1	Ruby	298	17.9	3.5221	3.4277
1	Ruby	298	19.8	3.5179	3.4008
1	Ruby	298	22.5	3.5115	3.3672
1	Ruby	298	24.5	3.5077	3.3463
1	Ruby	298	26	3.5044	3.3312
1	Ruby	298	28.6	3.4987	3.3051
2	SrB_4O_7	298	57.6	3.4435	3.1179
2	SrB_4O_7	298	53.1	3.4512	3.1371
2	SrB_4O_7	298	48.4	3.4603	3.1617
2	SrB_4O_7	298	43.6	3.4704	3.1912
3	SrB_4O_7	298	13	3.5342	3.5088
3	SrB_4O_7	298	21.5	3.5142	3.3800
1	SrB_4O_7	298	0	3.5666	
4	SrB_4O_7	298	1.3	3.5626	
4	SrB_4O_7	298	2.92	3.5591	
4	SrB_4O_7	298	3.94	3.5554	
4	SrB_4O_7	298	17.9	3.5216	3.4248
2	SrB_4O_7	500	2	3.5621	
2	SrB_4O_7	500	9.76	3.543	
2	SrB_4O_7	500	13.9	3.533	3.5137
2	SrB_4O_7	500	21.6	3.5149	3.3886
2	SrB_4O_7	500	25.1	3.5072	3.3481
2	SrB_4O_7	501	44.5	3.4681	3.1912
2	SrB_4O_7	501	46.5	3.4643	3.1805
3	SrB_4O_7	600	39.3	3.4778	3.2277
3	SrB_4O_7	600	47.9	3.462	3.1744
3	SrB_4O_7	600	56.5	3.4458	3.1328
3	SrB_4O_7	600	66.8	3.4297	3.0852
3	SrB_4O_7	600	76.8	3.4126	3.0476
3	SrB_4O_7	600	86		3.0185
2	SrB_4O_7	750	4.59	3.5584	
2	SrB_4O_7	750	7.58	3.5507	
2	SrB_4O_7	750	8.19	3.5494	
2	SrB_4O_7	750	13.9	3.5347	
2	SrB_4O_7	750	18.7	3.5239	3.4544
2	SrB_4O_7	750	34.7	3.4893	3.2777
2	SrB_4O_7	750	35.7	3.4876	3.2675
2	SrB_4O_7	750	42	3.4745	3.2205
2	SrB_4O_7	750	49.5	3.4605	3.176
2	SrB_4O_7	900	54.8	3.4515	3.1517
4	SrB_4O_7	900	7.31	3.5547	
4	SrB_4O_7	900	9.68	3.5482	
4	SrB_4O_7	900	14.4	3.5365	
4	SrB_4O_7	900	17.7	3.5267	
4	SrB_4O_7	900	20.9	3.5203	
4	SrB_4O_7	900	27.2	3.507	3.3589
4	SrB_4O_7	900	32.2	3.4959	3.3038
4	SrB_4O_7	900	35.7	3.4875	3.2722
4	SrB_4O_7	900	38.7	3.4813	3.2467
4	SrB_4O_7	900	42.5	3.4736	3.2226
4	SrB_4O_7	500	4.59	3.5562	
4	SrB_4O_7	750	5.64	3.556	
5	W	298	53.4		3.1363
5	W	298	91.2		2.9934
5	W	298	107.8		2.9504
5	W	298	129.9		2.9034
5	W	298	135.8		2.8913
5	W	298	146.5		2.8706
5	W	298	157.7		2.8514
5	W	298	166.6		2.8357
5	W	298	175.9		2.8216
5	W	298	185.0		2.8087
5	W	298	193.4		2.7988
5	W	298	199.0		2.7911
5	W	298	206.1		2.7818
5	W	298	205.2		2.7806
5	W	298	208.8		2.7762

self-correlated cell model calculation,[36] with the exponential–six interatomic potential proposed for neon in Ref. 37. This calculation gives a correct description of the EoS of neon measured up to 209 GPa (with less than 2% difference in volume at the maximum pressure reached). The characteristic Debye temperature was then calculated in the Domb–Salter approximation.[38] It assumes that the Debye temperature of the system can be expressed as a function of the second moment of the eigenfrequencies of the dynamical matrix, which can be exactly calculated using the interatomic potential V of the system (R_i is the position of the ith atom of mass M in the cell),

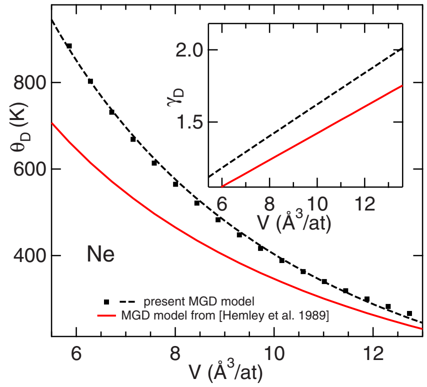

FIG. 1. (Color online) Evolution of the Debye temperature θ_D and the Grüneisen parameter γ_D for two Mie–Grüneisen–Debye (MGD) models (see text).

$$\theta_D = \left(\frac{5\hbar^2}{3k_B^2}\langle\omega^2\rangle\right)^{1/2} = \left(\frac{5\hbar^2}{9k_B^2 M}\sum_i \Delta V(R_i)\right)^{1/2}. \qquad (5)$$

In Eq. (5), ω is the vibration frequency of one mode. The variation of θ_D with compression calculated using Eq. (5) has been fitted with Eq. (4). This leads to the following parameters: $\theta_0=75.1$ K (fixed), $\gamma_1=2.442$, and $q=0.97$. Another set of parameters has been proposed in Refs. 26 and 27: $\theta_0=75.1$ K, $\gamma_1=2.05$, and $q=1$. The corresponding parameters θ_D and γ_D are compared with the present ones in Fig. 1: θ_D predicted by the two models differ by more than 20% at high compression.

TABLE II. Parameters for the equation of state of neon using a Mie–Grüneisen–Debye model (see text). Vinet (V) (Ref. 35), third-order Birch–Murnaghan (BM) (Ref. 39), and Holzapfel (H02) (Ref. 40) formulations have been tested for the $P(V,T=0)$ static part of Eq. (1). Thermal pressure is calculated using Eq. (3). The following parameters have been fixed during the fitting procedure: $V_0=22.234$ Å^3/at., $\Theta_0=75.1$ K, $\gamma_1=2.442$, and $q=0.97$. The numbers in parentheses are the fitting standard deviations (95% confidence interval) on the last or last two digits. χ^2 is an indication of the quality of the fit (lower for a better fit).

EoS	K_0 (GPa)	K'_0	χ^2
V	1.070(16)	8.40(3)	8.9
BM	1.420(83)	8.03(29)	23.3
H02	1.397(26)	7.43(3)	13.3

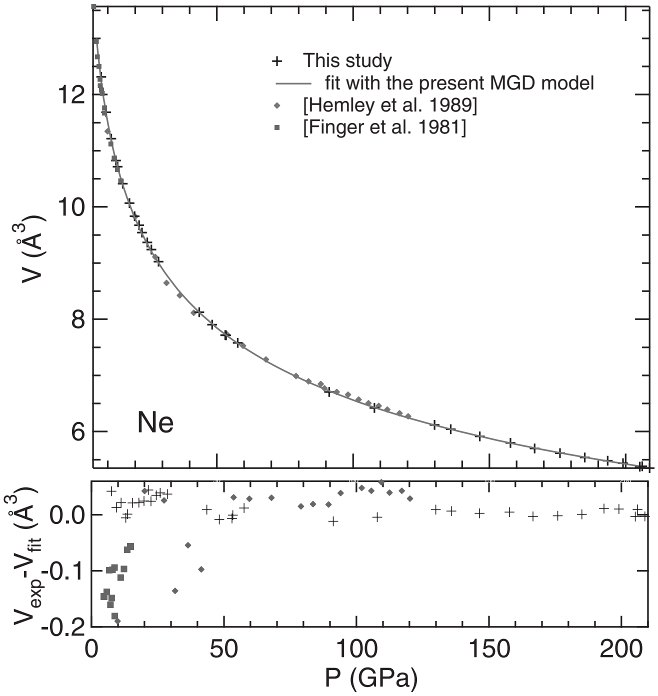

FIG. 2. Top: Atomic volume of neon at 298 K as a function of pressure [H05 scale (Ref. 21)]. The solid line is a fit to the current experimental data with the MGD model presented in the text. The data from Refs. 26 and 27, modified to follow the H05 pressure calibration, are represented for comparison. Bottom: Difference in volume between the experimental data points and the fit.

A least-squares fit of the present data, using the present Mie–Grüneisen–Debye model, leads to the following parameters: $K_0=1.070(16)$ GPa and $K'_0=8.40(28)$. Figure 2 represents the 298 K P-V points measured in this study and found in the literature, and the difference between the data and the fit. For our data, this difference remains smaller than $\Delta V/V=0.2\%$ in the spanned pressure range. The scatter of the data of Hemley *et al.*[27] is slightly larger, but overall, they are in good agreement with ours. Volumes of Finger *et al.*[26] exhibit a deviation from the present data, which corresponds to an underestimation of pressure of 0.2–0.5 GPa. High pressure elastic constants of neon have been measured recently by Brillouin spectroscopy.[25] At 6 GPa and ambient temperature, the Brillouin K_T is 27.5 GPa,[25] close to the value of 26.0 GPa which can be estimated using the present EoS.

We have also tested other forms of isothermal EoS on the present data, namely, the Birch–Murnaghan[39] and H02[40] EoS (see Table II). The goodness of the fit is the highest (the lowest χ^2) for the Vinet EoS. It should be noted, however, that the values of χ^2 are also sensitive to the chosen pressure scale. The bulk modulus under reference conditions (0 K, 1 atm) obtained by fitting our data with a Vinet EoS [1.070(16) GPa] is in good agreement with the bulk modulus measured in the same conditions [1.12(3) GPa (Ref. 33) or 1.097 GPa (Ref. 41)]. The agreement is much poorer if Birch–Murnaghan or H02 EoS are used instead ($K_0=1.420$ and 1.397 GPa, respectively). It thus seems that the Vinet EoS is, among the three parameter EoS tested here, the one that gives the most reasonable fitting parameters (i.e., parameters that correspond to their physical definition). Vinet EoS also allows reproducing the data with the highest accuracy in the full compression range.

The volumes and bulk modulus calculated using Eqs. (2) and (3), with the parameters listed in the first row of Table II, are compared with room pressure measurements reported by Batchelder *et al.*[33] in Fig. 3. The agreement is good up to $\simeq 18$ K. In fact, anharmonic effects have been reported to become important in neon just below its melting point.[33] These anharmonic effects are expected to strongly decrease

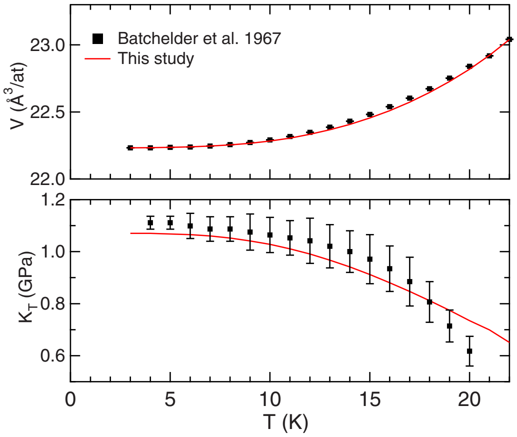

FIG. 3. (Color online) Volume and isothermal bulk modulus measured in Ref. 33 and calculated using the present Mie–Grüneisen–Debye model.

when pressure increases to several gigapascals. This is due to an extension of the temperature domain where zero-point vibrations are larger than thermal vibrations; in this domain, the apparent behavior of neon is quasiharmonic.[33] Statistical calculations have also predicted that intrinsic anharmonic contribution to the free energy is suppressed at high compression.[42] The Mie–Grüneisen–Debye EoS should thus become more and more accurate at HP and HT. The present data set, together with the data of Fei *et al.*,[28] allows testing these predictions.

We have plotted the data points measured for neon in these two studies, together with the isotherms predicted by the Mie–Grüneisen–Debye model described above in Fig. 4(a). The thermal expansion of neon decreases upon pressure increase because the number of excited phonons at a given temperature diminishes as the Debye temperature increases. The present EoS is in good agreement with the collected data. The difference in volume between this EoS and data points corresponds to pressure differences within ±0.5 GPa for the present data and $-2/+0.5$ GPa for the data of Fei *et al.* [see Fig. 4(b)]. No anharmonic effects can be evidenced from the present data, even close to the melting curve. The isotherms corresponding to a Mie–Grüneisen–Debye EoS based on the parameters of Refs. 26 and 27 ($\gamma_1=2.05$, $q=1$) is also plotted in Fig. 4(a). The close agreement between the two EoS could appear surprising because the Debye temperatures and Grüneisen parameters used in these two models are rather different (10%–25%, see Fig. 1). However, these differences compensate to a large extent in the calculation of the thermal pressure. The final EoS is thus quite insensitive to reasonable variations of the Debye parameters.

There is a satisfactory agreement between the EoS proposed here and the EoS of Fei *et al.*,[28,29] except in the low pressure range at room temperature ($\Delta P \simeq 0.5$ GPa for $P \simeq 7$ GPa) and at very HT and high compression. These disagreements can be explained as follows. At low pressure, Fei *et al.* had only a few data points to constrain their EoS. At very high pressure, the large decrease of thermal expansion coefficient predicted by their EoS is due to the expression used for the Grüneisen parameter ($\gamma \rightarrow 0$ when $V \rightarrow 0$). At high compression, this leads to a nonphysical behavior.

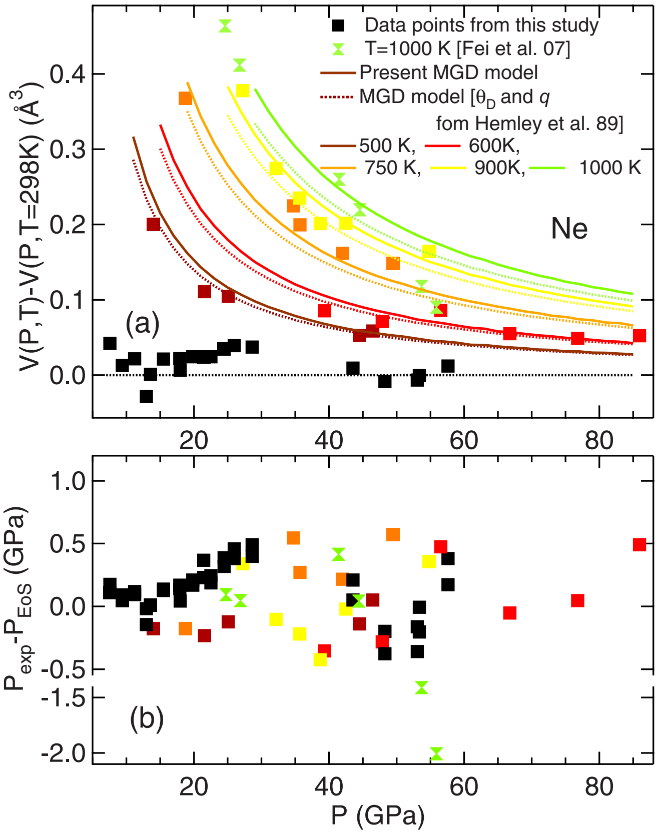

FIG. 4. (Color online) (a) Variation of the atomic volume of neon with temperature and pressure along six isotherms: 298, 500, 600, 750, 900, and 1000 K. The isotherms have been stopped at the melting point (Ref. 17). The 298 K compression curve (see Fig. 2) has been subtracted from the measured volumes in order to emphasize the temperature effect. The squares represent the present data points. The double triangles represent the data points measured by Fei *et al.* (Ref. 28) at 1000 K. The lines are the volumes calculated using the two Mie–Grüneisen–Debye models considered in this study (see text). (b) Difference between the measured pressure and the pressure calculated using the first Mie–Grüneisen–Debye model (the vertical axis has been split).

To sum up, a single Mie–Grüneisen–Debye formalism allows reproducing the present *P-V-T* data points for neon (Fig. 4), down to a compression ratio of 0.24, and the low pressure–low temperature thermoelastic data (Fig. 3). Since the highest temperature reached in our experiments exceeds the Debye temperature ($\simeq$600 K at 100 GPa), it is likely that the present EoS can be extrapolated and used for temperatures outside the range scanned here. An extrapolation to higher pressures should also be possible because the electronic structure of neon has been predicted to remain unchanged at higher compression.[31] We thus believe that this thermal EoS can provide an accurate estimate of pressure when neon is used as a pressure transmitting medium for resistive-heating or laser-heating diamond-anvil cell experiments.

As a side result, the very good consistency displayed by our experimental data for neon, where the pressure is read from the $SrB_4O_7:Sm^{2+}$ sensor, gives further evidence that the calibration of this sensor, based on the independent de-

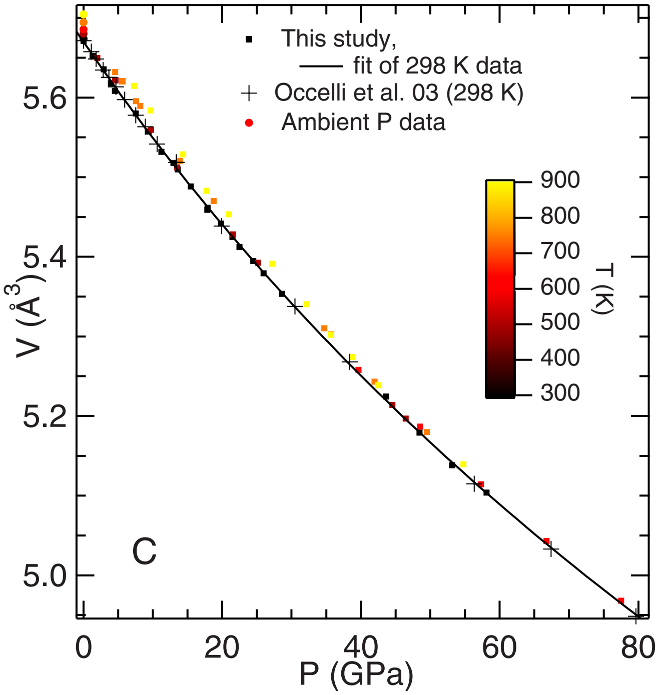

FIG. 5. (Color online) P-V-T data points for diamond as measured in this study and as reported in Refs. 4 and 12. The continuous line corresponds to a Vinet EoS with $V_0=5.6693$ Å^3/at., $K_0=444.5$ GPa and $K_0'=4.18$.

termination of the pressure and temperature coefficients,[14] is valid at HP-HT conditions. In other words, $\partial^2\lambda/\partial P\partial T$ is too small to be detected within experimental uncertainties in the presently covered P-T range.

IV. HIGH PRESSURE AND HIGH TEMPERATURE EQUATION OF STATE OF DIAMOND

The diamond EoS data points given in Table I are plotted in Fig. 5, together with the available literature data: the room temperature compression curve measured in helium pressure-transmitting medium by Occelli *et al.*[4] and the room-pressure thermal expansion data of Ref. 12. The agreement between our room temperature data and those of Occelli *et al.* is excellent. A similar accuracy is thus achieved, in the case of diamond, using neon or helium pressure transmitting medium up to 80 GPa. We have fitted our data with a Mie–Grüneisen–Debye formalism, with a reference temperature of 298 K, at which a large number of experimental data is available (EoS and ultrasonic data). It is expressed in the following form:

$$P(V,T) = P(V,298\text{ K}) + [P_{TH\text{ Debye}}(V,T) - P_{TH\text{ Debye}}(V,298\text{ K})]. \quad (6)$$

$P_{TH\text{ Debye}}(V,T)$ is expressed using Eq. (3). We have chosen the following empirical form for the variation of γ_D with volume: $\gamma_D=\gamma_0 x^{3q}$. This form has the advantage of being very simple, with only two parameters, and is expected to correctly describe the behavior of the Grüneisen parameter in a moderate compression range. The corresponding expression for θ_D is $\theta_D=\theta_0\exp[-\gamma_0/q\times(x^{3q}-1)]$.

As a first step of analysis, the present 298 K P-V data points have been fitted with the most popular EoS formulations.[35,39,40] To prevent overfitting, K_0 was fixed to the value measured recently by Brillouin scattering experiments:[43] $K_0=444.5$ GPa (the adiabatic to isothermal conversion of the value reported in Ref. 43 has been performed). Here, the reference conditions are ambient pressure and $T=298$ K. We found that all tested forms gives very similar values of K_0', which is the expected behavior as the compression range spanned here for diamond remains small ($V/V_0>0.85$). We will thus limit our report to the results obtained with the Vinet EOS [Eq. (2)] for homogeneity with the previous section. The fitted parameters are $V_0=5.6693\pm0.0016$ Å^3/at. $K_0'=4.18\pm0.15$. These parameters are within error bars of the parameters obtained by fitting the data of Occelli *et al.*,[4] after modification of the measured pressure from the scale of Mao *et al.*[44] to H05 scale[21] (see Table III). As a second step, all P-V data points presented in Table I have been fitted using the Mie–Grüneisen–Debye EoS presented in Eqs. (6), (2), and (3). θ_0 has been fixed to 1860 K, a value based on heat capacity measurements.[19] The Grüneisen parameter under reference conditions γ_0 has been fixed to 0.85, based on ambient pressure thermal expansion data.[12] The single parameter adjusted using our HP-HT measurements was thus $q=3.6\pm1.5$. A similar value of the parameter q ($q=4\pm1.5$) has been obtained for c-BN.[16] It corresponds to a large decrease of thermal expansion coefficient with pressure, the thermal expansion coefficient being proportional to the Grüneisen parameter. At 70 GPa, a temperature increase of 300 K would lead to a volume expansion

TABLE III. Parameters of the EoS of diamond [see Eqs. (6), (2), and (3)] obtained by least-squares fit of the experimental data. The H05 (Ref. 21) pressure scale was chosen. The bold values have been fixed during the fitting procedure. Numbers in parentheses are published error bars or fitting error bars (95% confidence interval) on the last or the two last digits.

Data set	V_0 (Å^3/at.)	K_0 (GPa)	K_0'	θ_{D0}	γ_0	q
Occelli *et al.* (data at 298 K)	5.6724(19)	**444.5**	3.98(4)			
This study (data at 298 K)	5.6693(16)	**444.5**	4.18(15)			
This study, Mie–Grüneisen–Debye model (all data)	**5.6693**	**444.5**	**4.18**	**1860**	**0.85**	3.6(1.5)
Raman-based Debye model (after Occelli *et al.*)	**5.6693**	**444.5**	**4.18**	**1860**	**0.97**	**0**

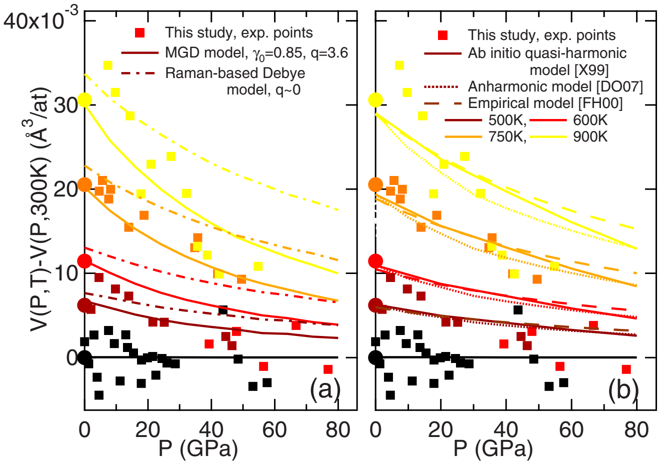

FIG. 6. (Color online) Variations of the atomic volume of diamond with temperature and pressure along five isotherms: 298, 500, 600, 750, and 900 K. The 298 K compression curve (parameters presented in Table III) has been subtracted from the measured volumes in order to clearly represent the temperature effect. The squares represent the present data points. The circles are the volumes measured at ambient pressure (Ref. 12). (a) Comparison between experimental data points and the EoSs presented in this study. The solid lines labeled "MGD model" have been calculated using Eqs. (6), (2), and (3), with the parameters determined from least-squares fit of the present data (Table III, third row). The dashed-dotted lines are the volumes calculated using the Raman-based Debye model (Table III, fourth row). (b) Comparison between experimental data points and the EoSs published in the literature. The solid line corresponds to the quasiharmonic model X99, with *ab initio* calculated vibration modes frequencies (Ref. 3). The dotted line corresponds to the semiempirical anharmonic model DO07 (Ref. 11). The dashed lines correspond to the empirical model FH00 (Ref. 10).

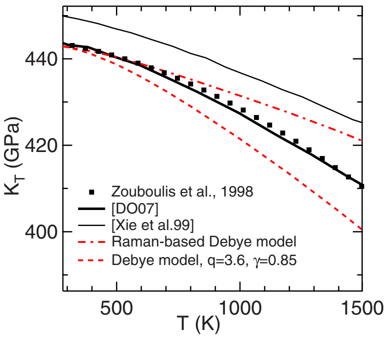

FIG. 7. (Color online) Bulk modulus of diamond as a function of temperature at ambient pressure. The thick black line corresponds to the DO07 EoS (Ref. 11), which perfectly reproduces the Brillouin scattering data up to 1600 K (Ref. 13). The thin black line corresponds to X99 *ab initio* model (Ref. 3). The red (gray) dashed-dotted line corresponds to the Raman-based Debye model, while the red (gray) dashed line corresponds to the Debye model that reproduces at best our *P*-*V* data points (Table III, third row).

smaller than 0.1%. As a consequence, if diamond is used as an x-ray pressure gauge for an HP-HT experiment, and if the temperature is overestimated by 300 K at 70 GPa, the pressure will be overestimated by 0.5 GPa.

Figure 6 represents the temperature effect on the volume of diamond measured in this study during runs 1–4. For each point, the volume at 298 K [calculated using Eq. (2) with the parameters listed in Table III, second row] has been subtracted from the measured volume. For each HT run, at least two room temperature measurements of diamond volume have been performed, and these measurements agree with the room temperature EoS within $\pm 5\times 10^{-3}$ Å^3/at. (see Fig. 6). The volume increase predicted by several models, including the Mie–Grüneisen–Debye model presented above, is also plotted in Fig. 6 with different line symbols. Xie *et al.*[3] (X99) calculated the thermodynamic behavior of diamond under HP in the quasiharmonic approximation based on phonon frequencies calculated using density functional perturbation theory in the local density approximation. The semiempirical EoS proposed by Dorogokupets and Oganov[11] (DO07) has been established on the basis of calorimetric,[19] acoustic,[13] and thermal expansion[12] data at ambient pressure, and static[4] and dynamic[45] compression data at HP. Intrinsic anharmonicity is included in their formulation. Fried and Howard[10] proposed an empirical model based on the compilation of thermodynamic data (FH00) for different phases of carbon. We have also plotted the isotherms predicted by a Mie–Grüneisen–Debye EoS that uses the parameters γ and q corresponding to the longitudinal-transverse optical vibration mode of diamond (its only Raman-active mode). These parameters have been determined at 298 K by Occelli *et al.*[4] Their use to generate an HP-HT EoS implies two assumptions: (i) All vibrational modes have the same Grüneisen parameter: and (ii) the solid behaves quasiharmonically. We call this model the "Raman-based Debye model."

All models and the present data exhibit the expected decrease of thermal expansion with increasing pressure (see Fig. 6). The Raman-based Debye model is the less predictive: Its thermal expansion is larger than the measured one at all pressures. In fact, this model does not take into account the acoustic vibration modes, which have a smaller Grüneisen parameter than optical modes[3] and thus decrease the thermal expansion. This illustrates the inadequacy of the use of Raman data alone to predict HP-HT thermodynamic properties of materials. The model FH00 slightly overestimates the thermal expansion at high pressure. X99[3] EoS underestimates the thermal expansion at HT and ambient pressure. This can be due to the errors in the calculation of Grüneisen parameters in the local density approximation or of the neglected anharmonic effects. Even if anharmonic effects are expected to diminish with compression,[11,33,34] it is difficult to tell wether X99 model will become more accurate at HP. The decrease of thermal expansion measured here is larger than in the X99 model; yet, the difference is only slightly above our estimated error bars. An interesting effect was evidenced by X99 work, that is, the large decrease of acoustic Grüneisen parameters at large compression. However, this would reduce the thermal expansion at pressures higher than the ones investigated here. The difference between DO07[11] heuristic EoS and X99 EoS is small in the studied *P*-*T* range, DO07 being closer to our data. The decrease of thermal expansion predicted by DO07 is also smaller than the measured one above ≃20 GPa. It should be noted that no experimental data in the *P-T* range scanned here have been included in this model. As a matter of fact, the Hugoniot curve of diamond, which is the only HP-HT information included in DO07 model, remains below $\simeq$400 K up to 80 GPa.[7] In this domain, all models plotted in Fig. 6 have similar thermal expansions.

Figure 7 presents the isothermal bulk moduli calculated using the present Mie–Grüneisen–Debye EoS, X99, and DO07 models, together with experimental data.[13] DO07 model has been adjusted on these data and reproduces them very well. X99 model overestimates the bulk modulus at all temperatures, which is the expected bias in the local density approximation. The temperature dependence of K_T is also slightly underestimated, which strengthens our observation that X99 model underestimates $(\partial\alpha/\partial P)_T$, since the latter quantity and K_T are linked by the thermodynamic relation: $(\partial\alpha/\partial P)_T = 1/K_T^2(\partial K_T/\partial T)_P$. The Mie–Grüneisen–Debye model which fits at best the present *P-V-T* data underestimates the bulk modulus at HT. This proves that a more sophisticated model is needed to reproduce all thermodynamic properties of diamond under HP and HT. In particular, the very different behavior of acoustic and optic modes with respect to compression should be taken into account. This can be done in a model such as DO07, which contains several characteristic Grüneisen parameters and temperatures. The data obtained here, maybe coupled with information obtained by modern *ab initio* calculations, should be included now in these models. It would also be useful to measure the pressure effect on thermal expansion of diamond in a wider temperature range (e.g., up to 2000 K), between 0 and 60 GPa.

V. CONCLUSION

We have measured the thermal expansion of diamond in the pressure-temperature range of 0–80 GPa and 300–900 K. These conditions had not been scanned before for this material. A Mie–Grüneisen–Debye EoS has been fitted to our data, which led to the parameters given in Table III. The comparison of our data with recently published EoS[3,11] suggests that the latter might underestimate the pressure effect on thermal expansion; however, this effect is at the limit of the present experimental accuracy. The lack of consistency between our Mie–Grüneisen–Debye EoS and the ambient pressure measurement of bulk modulus suggests that this formalism is too simple to fully describe the thermodynamic behavior of diamond at HP and HT. This can be due to the different sensitivities of acoustic and optical vibrational modes to compression. Extrapolation of our Mie–Grüneisen–Debye model out of the conditions scanned here should thus be done with caution. The present data should be included in more advanced HP-HT EoS models (with several vibrational behaviors) of diamond.

The *P-V-T* data taken for neon, in the same range, show that the EoS of this rare-gas solid can be very accurately described by a Mie–Grüneisen–Debye formalism. The good consistency between low pressure–low temperature heat capacity and EoS measurements, HP–room temperature measurements of bulk modulus, and the present HP-HT EoS measurements proves that the present EoS (see Table II) can be used with confidence even outside the pressure and temperature range scanned here. This EoS is accurate within 0.5 GPa. Neon can now be considered as a well calibrated x-ray pressure gauge for HP-HT diamond-anvil cell studies. This is particularly advantageous when neon is used as a pressure-transmitting medium in diamond-anvil cell studies.

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