Diamond at high pressures: Raman scattering of light, equation of state, and high-pressure scale

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First-order Raman scattering and x-ray measurements of the density of diamond were made at pressures up to 42 GPa, using the diamond anvil technique. The results of the measurements made it possible to calculate "directly" the Gruneisen constant for the LTO(Γ) mode of diamond, which was found to be independent of the density right up to pressures of ~40 GPa. An analysis of the pressure dependences of the density of diamond and of its Raman scattering frequency demonstrated that the present results cannot be reconciled with the data obtained by ultrasonic investigations of diamond or with theoretical calculations without substantial changes in the high-pressure scale. A new scale is proposed on the basis of an a priori equation of state of diamond.

INTRODUCTION

Diamond is an ideal covalent crystal, the hardest and least compressible substance in the known universe. The origin of the unique properties of diamond is not yet fully understood, although several theoretical treatments shedding light on this topic have appeared recently. In particular, the local density formalism and the pseudopotential approximation for the description of the electron-ion interaction have made it possible to calculate a number of quantities characterizing macroscopic and microscopic properties of diamond, silicon, and germanium. The most interesting result of these investigations has been the unusually wide range of stability of the diamond phase of carbon and its resistance to a transition to a metallic phase with the structure of white tin. This conclusion is clearly supported by the modern practice of using diamond to attain ultrahigh pressures greatly exceeding 100 GPa (Refs. 9-11). However, a detailed comparison between the theory and experiment cannot yet be carried out because of the limited experimental data, which undoubtedly holds up further progress in this field.

We shall report the results of an investigation of the equation of state of diamond by x-ray diffraction and Raman scattering at high pressures. Some of the results on the Raman scattering in diamond have been published earlier.

EXPERIMENTS

High pressures were created in a specially developed diamond cell which could be used to study x-ray diffraction in a wide range of angles. The pressure-transmitting medium was compressed helium, which ensured conditions closest to hydrostatic. The investigated sample was a natural single crystal of diamond of dimensions 60×30×15 μm. The pressure was deduced from the shift of the R₁ luminescence line of ruby and the error in the pressure measurements was ~0.05 GPa. The x-ray diffraction study was carried out employing a conventional two-circle DRON 2.0 diffractometer and Mo Kα radiation. We used the layout shown in Fig. 1a. Naturally, these measurements (when diamond was compressed by diamond anvils) were possible only when the crystallographic orientation of the sample was different from the orientation of the anvils. This condition was satisfied in our case because the basal plane of the sample coincided with the (110) plane and the orientations of the axes of the diamond anvils were close to [100]. However, under actual experimental conditions only the (440) reflection was recorded because of the presence of a steel spacer. The lattice parameter of diamond measured under our conditions at atmospheric pressure and room temperature was found to be 3.567 Å, in excellent agreement with the results of precision measurements reported in Ref. 14. However, this did not mean that the reliability of the corresponding measurements at high pressures was equally high, especially as in this range the important factors were not only the precision of the measurements of the lattice parameter, but also the validity of describing the complex stressed state of the sample by means of a single scalar quantity, of pressure.

The situation is illustrated largely in Fig. 2. Figure 2a shows the profiles of the (440) diffraction line obtained at various pressures. Clearly, the intensity of the reflection fell as the pressure increased, whereas its half-width was within the limits of the instrumental half-width at any pressure. The reason for the fall of the intensity of this reflection is made clear in Fig. 2b, which gives the rocking curves obtained by oscillating the sample about the position corresponding to the (440) reflection. It is clear from this figure that the width of the rocking curve increases catastrophically beginning from a pressure ~35 GPa, which implies an equally catastrophic fall of the quality of the crystal. It was natural to attribute the observed effect to a departure from hydrostatic conditions (because helium solidified the pressure of ~12 GPa at room temperature). It was interesting to note that the lattice parameters determined for different positions of a crystal and corresponding to different points on the rocking curve agreed within experimental error. Nevertheless, this observation indicated that the system was no longer hydrostatic as a whole.

The technique used in determination of the first-order spectra of the Raman scattering of light in diamond was described briefly in Ref. 12. We used the experimental geometry shown in Fig. 1b. The precision of the determination of a spectral position of the Raman lines was ~0.3 cm⁻¹. At pressures in excess of ~35 GPa the half-width of the Raman lines became greater than the half-width of the instrumental...
function of the apparatus used (~ 3 cm⁻¹) and at the highest pressures reached the value ~ 5 cm⁻¹. This observation was in agreement with the broadening of the rocking curve of the sample and indicated a deviation from hydrostatic conditions, mentioned above.

The lattice parameter and Raman frequency measurements were made on the same sample for the same readings of the “ruby manometer”, both during loading and unloading of the cell but only after holding a pressure constant for a certain time needed to ensure practical completion of the relaxation processes associated with a change in the external load (usually 1–2 days). All the measurements were carried out at room temperature.

Figure 3 shows the dependences of the reduced first-order Raman scattering frequency obtained in our experiments on the spectral shift Δλ of the R₁ ruby luminescence line. It is clear from Fig. 3 that both dependences were described excellently by linear functions in the range Δλ < 12.5 nm or at pressures P < 35 GPa. At higher pressures the experimental points clearly diverged from the corresponding straight lines, which in our opinion was due to departure from hydrostatic conditions and a consequent possible bending of the sample, which was a fairly thin and large plate (see also Ref. 13). We were therefore forced to limit our subsequent analysis to the range where the density was 1 < p/p₀ < 1.075. The combined error in the measurements of the lattice parameter in this range is estimated to be ~ 0.001 Å, which corresponds to an error of ~ 0.1% in the numerical values of the density.

Bearing in mind the imperfection of the currently used ruby scale of high pressures [several variants of the calibration dependences F(Δλ) are given in Ref. 15], we preferred to express our experimental results in the form of relationships between the measured quantities and the shift of the R₁ luminescence line. The dependences obtained in this way were

\[ \frac{p}{p_0} - 1 = (4.28 \pm 0.03) (3.00 \pm 1.075) \Delta \lambda, \]

(1)

\[ \frac{\nu}{\nu_0} - 1 = (4.00 \pm 0.02) (3.2 \pm 1.2) (2.00 \pm 1.075) \Delta \lambda, \]

(2)

where \( p, \nu, \) and \( \Delta \) are the running values of the density, of the frequency of the LTO(T) mode, and of the wavelength of the R₁ ruby luminescence line; \( p_0, \nu_0, \) and \( \Delta_0 \) are the values of the same quantities at \( P = 0 \). The numerical values of the
errors were estimated at the 65% confidence level. Subsequently, we used reliable information on the dependence $P(M)$ and readily transformed Eqs. (1) and (2) into the pressure dependences $\rho(P)$ and $v(P)$.

**DISCUSSION OF RESULTS**

1. Raman light scattering

Figure 4 shows the dependence of the reduced first-order Raman scattering frequency on the density of a diamond sample, based on the experimental results obtained in the present study. It also includes the results of theoretical calculations. The experimental dependence $v(p)$ makes it possible to calculate "directly" the Grüneisen parameter $\gamma = -\frac{d \ln v}{d \ln V}$ for the LTO($\Gamma$) diamond mode and its dependence on the density without recourse to any information on the equation of state of diamond or on the high-pressure scale. An analysis of the experimental results (for details see Ref. 13) shows that in the range $1 < p/p_0 < 1.075$ we have to assume that $\gamma_{LTO(\Gamma)} = \text{const} = \gamma_0$. A calculation carried out in this approximation gives $\gamma_0 = 0.965 \pm 0.005$. Therefore, the LTO($\Gamma$) mode of diamond obeys the Grüneisen law

$$v = \frac{\gamma_0}{V} (V/V_0)^{\gamma_0}.$$  \hspace{1cm} (3)

We must point out that the relationship (3) makes it possible to reduce measurements of the density of diamond to a fairly simple and accurate procedure for finding the frequency of the first-order Raman scattering. We shall use this approach. Estimates obtained from the experimental data (see Fig. 4 and Ref. 13) demonstrate that application of Eq. (3) gives rise to an error in the calculations of the volume or density of diamond of at most 1% at pressures up to $\sim 150$ GPa.

A comparison of the experimental results with the theoretical data4,5 (Fig. 4) leads to contradictory conclusions, although the excellent agreement between the theory of Ref. 4 and the present results cannot be simply accidental. In this respect the results in Fig. 5 are quite unambiguous: they give the pressure dependences of the frequency of the LTO($\Gamma$) mode found experimentally and theoretically. It is worth noting here that the results of two other experimental investigations6,7 of the dependence $v_{LTO(\Gamma)}(p)$ are in very good agreement with our data plotted in Fig. 5. It is clear from this figure that, in spite of some small discrepancies between the theoretical curves themselves, these curves clearly differ from the experimental dependence. Using only the theoreti-
FIG. 6. Compression isotherms of diamond: (□) static data; (▲) dynamic compression; (▲) our results; (△) our results published earlier; (●) our results published earlier; (●) our results published earlier; (+) symbols and the dashed curve are the results of Ref. 12 with the pressure calculated using the calibration dependence of Ref. 20; the + symbols and the dashed curve are the results of Ref. 12 with the pressure calculated using the calibration dependence of Refs. 19 and 21; the dotted and chain curves give the calculated results reported in Refs. 4 and 5, respectively; the continuous curves are our data after conversion in accordance with the new calibration dependence (see text).

2. Equation of state

Figure 6 shows the compression isotherms of diamond obtained at room temperature in various investigations and it includes also the results of theoretical calculations. Our experimental data and those obtained in our earlier study are converted by means of Eq. (3) and presented here in the form of three separate branches in accordance with the three calibration dependences \( P(M) \) proposed for the ruby manometer in Refs. 19–21. We can see from Fig. 6 that, in spite of indeterminacy of the ruby pressure scale, our results differ considerably from those obtained in static and dynamic experiments, but agree quite well with the calculations of Refs. 4 and 5 at relatively low pressures. At high pressures all the sets of data disagree significantly with one another. Fortunately, there is a fairly objective way of checking the quality of the experimental and theoretical results on the equation of state of low-compressibility substances. In fact, in view of the smallness of the relative compression, the equation of state of diamond can be represented as an expansion of the pressure in powers of the deviation of the density of diamond from the equilibrium value over a wide range of pressures. Retaining the expansion terms of first and second order, we find after elementary transformations that

\[
P/K_0 = -\Delta p/p + 1/2 (K''_0 - 1) \Delta p/p^2,
\]

where \( K_0 \) and \( K'_0 \) are the bulk modulus and its first derivative with respect to pressure at \( P = 0 \). Therefore, the equation of state of a nearly incompressible substance is closely related to its characteristics at \( P = 0 \).

Table I gives the values of \( K_0 \) and \( K'_0 \) calculated from

<table>
<thead>
<tr>
<th>Method</th>
<th>( K_0 ), GPa</th>
<th>( K'_0 )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static compression</td>
<td>500</td>
<td>2.6</td>
<td>Ref. 17</td>
</tr>
<tr>
<td>Dynamic (shock) compression</td>
<td>829</td>
<td>4.6 ( \times 10^7 )</td>
<td>Ref. 19</td>
</tr>
<tr>
<td>Ultrasonic</td>
<td>932</td>
<td>3.5</td>
<td>Ref. 21</td>
</tr>
<tr>
<td>Brillouin scattering</td>
<td>939</td>
<td>4.3</td>
<td>Ref. 5</td>
</tr>
<tr>
<td>Theory</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Static compression in diamond anvils</td>
<td>941</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>945 ( \pm 0.3 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>951 ( \pm 0.3 )</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>955 ( \pm 0.3 )</td>
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</tbody>
</table>

**Calculations based on Eq. (4); the pressure was deduced using the calibration dependences given in Refs. 19–21, respectively.
the experimental and theoretical $P-V$ dependences. This table includes also the values of $K_u$ and $K_u'$, deduced from independent experiments. It is clear from Table I that an analysis of our results gives the same value of $K_u$ irrespective of the nature of the calibration dependence $P(\Delta k)$. This value is in excellent agreement with the very reliable and accurate results of ultrasonic$^{22}$ and Brillouin scattering experiments, in confirming the validity of the initial slope of the dependence $P(\Delta k)$ established in Refs. 19–21 and also showing that our results are quite accurate. On the other hand, our value of $K_u'$ (Table I) depends critically on the nature and magnitude of the nonlinear terms in $P(\Delta k)$ and differs considerably from the average value deduced from ultrasonic measurements.$^{22}$

It therefore follows that a systematic error in the equation of state of diamond obtained from our measurements is practically entirely due to a systematic error of the ruby manometer scale.

3. High-pressure scale

It follows from the equations of state of the type given by Eq. (4) and from the dependence $P(\Delta k)$ of Eq. (1) obtained in the present study, that it is possible to construct a high-pressure scale based on an a priori equation of state of diamond. Unfortunately, the value of $K_u'$ (Table I) required for the derivation of the equation of state of diamond is subject to an error which is far too large to ensure that this procedure is faultless. Nevertheless, there are serious grounds for assuming that $K_u'$ of diamond is considerably larger than that deduced from the calculations based on the known calibration dependences $P(\Delta k)$ (Table I). It is shown in the Appendix that the estimate $K_u' = 4$ for diamond is accurate to within a few percent.

Equations (1) and (4) yield a calibration dependence

$$P = A (\Delta k) + m (\Delta k)^{2/3}$$

(5)

($A = 1892 \pm 13$ GPa, $m = 6.4 \pm 0.5$) which can be extrapolated to the range of pressures $\sim 100$ GPa without a significant loss of precision. However, in the case of these pressures we can calibrate these curves better not by using Eq. (4), but applying the Birch equation of state for $K_u' = 4$ (Ref. 24)

$$P = [\rho/(\rho_0)]^{\gamma_1} = [\rho/(\rho_0)]^{1.7}$$

When the calibration dependence $P(\Delta k)$ is presented in the form proposed in Ref. 20, we find that

$$P = A (\Delta k)^{1.7} - 1,$$

(6)

where $A = 1918 \pm 4$ GPa and $n = 11.7 \pm 0.2$. The coefficients in Eq. (6) were calculated using also the results of measurements reported in Ref. 12 converted by means of Eq. (3). We can see from Fig. 7 that this procedure results in dramatic changes in the ruby scale at pressures exceeding 50 GPa.

It can be seen from Figs. 5 and 6 that the use of the new calibration dependence (5) ensures agreement between the experimental and theoretical $P(\Delta k)$ and $v(\Delta k)$ curves. Naturally, such agreement cannot be regarded as an absolute proof of the reliability of the calibration curve described by Eq. (5) (we still need to determine accurately $K_u'$ for diamond) or of the precision of the theoretical calculations, but it does provide a serious argument. Finally, we shall point out that the diamond itself or, more exactly, the frequency of the LTO ($\Gamma$) mode of diamond can be used in pressure measurements or in calibration of other pressure sensors (see also Ref. 25). In fact, if we expand the pressure as a series in powers of the deviation of the frequency from its value at $P = 0$, we find in second order that

$$P/K_u = \gamma_1 (\nu/\nu_0) + (K_u'/\gamma_1 - 1) (\nu^2/\nu_0^2)^{1/3},$$

(7)

where it is assumed that $(\partial P/\partial P_0) = 0$. Substituting in Eq. (7) the known numerical values $K_u = 4.42$ Mbar, $K_u' = 4.0$, and $\gamma_1 = 0.965$, we obtain a calibration dependence in terms of the frequency of the LTO ($\Gamma$) mode. The dependence (7) with the appropriate numerical coefficients agrees fully with the experimental dependence if the calculations are made using the proposed scale described by Eq. (5) (see Fig. 5).

We shall conclude by noting that the problem of pressure measurements in chambers using diamond anvils is not limited to construction of the "correct" high-pressure scale. It is known that the pressure established in a solid heterogeneous medium is generally a complex function governed by the mechanical properties of each of the phases and by their relative amounts.$^{26-28}$ In the specific case of diamond anvils the pressure experienced by a ruby sensor is not equal to the pressure on the investigated substance unless their bulk moduli are the same. Corrections cannot be always made because of the absence of the necessary information on the mechanical properties of specific substances.

In this situation, bearing in mind also the existence of a complex stress state in a solid, we have to accept that the pressure is not a single-valued and reproducible characteristic of the degree of compression at ultrahigh pressures. Any physical investigation carried out using diamond anvils should be regarded as complete only if it is accompanied by measurements of the density of the investigated substance.

The authors are grateful to I. N. Makarenko for help in this investigation.

FIG. 7. Calibration dependences for a ruby sensor taken from Ref. 19 (chain curve), Ref. 20 (dashed curve), and Ref. 21 (dotted curve). The continuous curve gives our results.
APPENDIX. SIMILARITY AND REDUCED EQUATION OF STATE FOR C, SI, AND GE

We shall write down the energy of a substance at $T = 0$ in the form

$$E = E_0(V/V_0),$$  \hfill (A1)

where $E_0$ and $F_0$ are the energy and volume of the substance at $P = 0$ and $T = 0$. If the function $f(F/V)$ is universal for a certain range of substances, we can plot a series of universal dimensionless relationships between the reduced values of the energy, pressure, bulk modulus, etc., on the one hand, and the dimensionless volume, on the other. We can then use these relationships to calculate readily any unknown properties of a specific substance if the values of the same properties are known for at least one other substance in the same group. These are essentially similarity or scaling relationships. We shall now attempt to establish the essential criteria for the existence of these relationships. Differentiating Eq. (A1) with respect to the volume of a substance, we obtain

$$P = -(E_0/\nu_0) 
\frac{f'(V/V_0)}{V/V_0},$$ \hfill (A2)

or at $P = 0$,

$$K_0 = \frac{E_0}{V_0} V_0,$$ \hfill (A3)

Rewriting Eq. (A4) in the form

$$K_0 = f(V/V_0),$$ \hfill (A4)

we obtain the first similarity criterion. Using Eqs. (A2) and (A3), we then obtain the reduced equation of state which can also be used as one of the similarity criteria:

$$P/K_0 = -(E_0/\nu_0) \frac{f(V/V_0)}{V/V_0}.$$ \hfill (A6)

Finally, differentiating Eq. (A3) with respect to the pressure in the investigated substance, we obtain one more similarity criterion in the form

$$K_0 = \frac{(\partial E/\partial F)}{(\partial F/\partial P)} = (1 + \nu_0 f''/f').$$ \hfill (A7)

Therefore, if at least one of the criteria of Eqs. (A5)-(A7) is satisfied, we should be able to use one universal function $f(F/V)$ for the selected group of substances.

Table II gives the necessary numerical data required in the calculation of the ratio $K_0 V_0/E_0$ for C, Si, and Ge. This table includes also the experimental values of $K_0$ obtained for these substances. We can see from Table II that the values of the ratio $K_0 V_0/E_0$ for the group C, Si, and Ge are quite similar (for C and Si they are practically equal). It is therefore unlikely that the value of $K_0$ for diamond should differ greatly from its average value given in Table II. More specific arguments in support of this conclusion are provided in the analysis given below.

It is known that the main contribution to the energy of a covalent crystal comes from the "covalent" attraction energy and the short-range repulsion energy. These two energy contributions may be represented, at least in a limited range of volume changes, as power functions of the interatomic distance or of the volume of a crystal. We shall write down the energy of a monatomic covalent crystal in the form

$$E = A(V/V_0)^m - B(V/V_0)^n$$ \hfill (A8)

or reducing Eq. (A8) to Eq. (A1)

$$E = [E_0(1 - m - n)] [m (V/V_0)^m - n (V/V_0)^n].$$ \hfill (A9)

Next, using the equilibrium condition at $P = 0$, we readily obtain

$$K_0 V_0/E_0 = mn,$$ \hfill (A10)

and $K_0' = m + n + 2$ \hfill (A11)

and this makes it possible to find the exponents $m$ and $n$ by solving a quadratic equation. It should be noted that within the framework of the representation Eq. (A8) the numerical values of the ratio $K_0 V_0/E_0$ impose stringent restrictions on the value of $K_0'$. For example, if it is assumed that in the case of diamond this value satisfies $K_0' < 4$, the relevant quadratic equation cannot be solved at all. We shall now calculate the value of $K_0$ for diamond on the basis of the existence of a similarity or scaling relationship between diamond and the diamond phase of silicon (because the practical equality of the ratios $K_0 V_0/E_0$ for these two substances makes this hypothesis very convincing). First, we shall use the data of Table II and the relationships (A10) and (A11) to obtain $n = 1.45$ and $m = 0.71$ for Si. These numerical values of the exponents are in full agreement with the theoretical expectations.\footnote{M. T. Yin and M. L. Cohen, Phys. Rev. Lett. 50, 2006 (1983).} Next, assuming that at least one of these exponents (for example $m$, which governs the behavior of the covalent energy) remains the same for diamond, we find then from Eqs. (A10) and (A11) that $n = 1.39$ and $K_0' = 4.1$.

\footnote{M. T. Yin, Phys. Rev. B 30, 1773 (1984).}