Electrical conductivities of methane, benzene, and polybutene shock compressed to 60 GPa (600 kbar)

3 authors, including:

W. J. Nellis
Harvard University
325 PUBLICATIONS   **7,869** CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Project   Ultra-compressed matter by dynamic compression - the book   View project

Project   Dynamic compaction of nanocrystalline powders   View project

Electrical conductivities of methane, benzene, and polybutene shock compressed to 60 GPa (600 kbar)

W. J. Nellis, D. C. Hamilton, and A. C. Mitchell
Lawrence Livermore National Laboratory, University of California, Livermore, California 94550

Electrical conductivities were measured for methane, benzene, and polybutene shock compressed to pressures in the range 20 to 60 GPa (600 kbar) and temperatures in the range 2000 to 4000 K achieved with a two-stage light-gas gun. The data for methane and benzene are interpreted simply in terms of chemical decomposition into diamondlike, defected C nanoparticles and fluid H_2 and their relative abundances ($C:H_2$), 1:2 for methane and 2:1 for benzene. The measured conductivities suggest that conduction flows predominately through the majority species, H_2 for methane and C for benzene. These data also suggest that methane is in a range of shock pressures in which dissociation increases continuously from a system which is mostly methane to one which has a substantial concentration of H_2. Thermal activation of benzene conductivities at 20–40 GPa is probably caused by thermal activation of nucleation, growth, and connectivity of diamondlike, defected C nanoparticles. At 40 GPa the concentration of these C nanoparticles reaches a critical density, such that further increase in density does not have a significant affect on the cross-sectional area of conduction and, thus, conductivity saturates. The electrical conductivity of polybutene (1:1) is very low. While the mechanism is unknown, one possibility is that the electronic bandgap of whatever species are present is large compared to the temperature. Electrical conductivity measurements are proposed as a way to determine the melting curve of diamondlike C nanoparticles at 100 GPa pressures. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1379537]

I. INTRODUCTION

The nature of hydrocarbons at high pressures and temperatures is a question of ongoing scientific interest. Methane is a major constituent of the ''ice'' layers in Uranus and Neptune, where pressures range between 20 and 600 GPa and temperatures range between 2000 to 8000 K.[1,2] The electrical conductivity of methane at these conditions is important for understanding its contribution to planetary magnetic fields, which are caused by convective dynamo action of electrically conducting fluids.[3]

At sufficiently high pressures and temperatures, hydrocarbons, including methane, are thought to decompose into H_2 and diamond.[4] However, at lower pressures and temperatures near the onset of decomposition a more complex mixture of H_2, C, and various hydrocarbons probably forms. Single-shock compression (Hugoniot) experiments achieve high pressures and temperatures which induce decomposition but have relatively short lifetimes ($\sim$100 ns). Such a lifetime is long enough for nucleation and growth of diamondlike nanoparticles, C polymers, molecular hydrogen, and/or nanoclusters of heavy hydrocarbons, such as higher-order alkanes. The exact pressures and temperatures required for decomposition are unknown.

On the methane Hugoniot[5] shock conditions required for decomposition have been suggested to range from 20 GPa and 2000 K based on chemical equilibrium calculations,[6] up to 33 GPa based on tight-binding molecular dynamics with a 54-molecule simulation cell,[7] and up to $\sim$100 GPa based on quantum molecular dynamics with a 16-molecule simulation cell.[8] Both of the latter simulations were run for $\sim$1 ps. The latter molecular dynamics simulations indicate that the dissociation products at pressure below $\sim$100 GPa and temperatures of $\sim$4000 K are a mixture of hydrocarbons, which separate into hydrogen and carbon only above 300 GPa. Methane decomposes at high static pressures and temperatures in a diamond-anvil cell,[9] in qualitative agreement with Ree's prediction.[4]

Benzene, in contrast to methane, decomposes at 13 GPa on its Hugoniot.[10–14] At much higher shock pressures chemical equilibrium calculations of decomposed benzene suggest that the dominant reaction products are diamond and H_2, with the possible inclusion of small concentrations of high molecular weight species, such as alkanes.[15] Molecular dynamics simulations of shock-compressed benzene are in good agreement with the onset of decomposition observed at 13 GPa and with the Hugoniot measured at higher pressures.[16]

Because at sufficiently high pressures and temperatures hydrocarbons are thought to decompose simply into diamondlike C and H_2,[4] we have measured electrical conductivities of three hydrocarbons with varying relative concentrations of C and H_2 to see if, in fact, the data could be understood simply in terms of the conductivities of diamondlike C and H_2. High pressures and temperatures were achieved by single-shock compression. This approach has been made possible by conductivity measurements on fluid H_2 shocked to pressures of 10 to 180 GPa[17–19] and on graphite shocked into the diamond phase.[20] Scaling relationships have been developed to estimate electrical conductivities of fluid hydrogen over this extensive range of pressures, densi-

TABLE I. Electrical conductivities σ of singly shocked-compressed benzene (CBZ), methane (CH4), and polybutene (PBC). u_l is impactor velocity, P is pressure, ρ is density, and T is temperature. Initial densities were 0.874, 0.428, and 0.89 g/cm^3, respectively. Initial temperatures were 298 K for benzene and polybutene and 110 and 106 K for CH4-C3 and CH4-C4, respectively. Impactors struck Al baseplates in all cases. Shock temperatures were obtained by interpolation or extrapolation of the data in Ref. 15 for benzene and polybutene and in Ref. 29 for methane. Pressures, densities, and temperatures have absolute uncertainties of 3%, 5%, and 10%, respectively.

Shot	Impactor	u_l (km/s)	P (GPa)[a]	ρ (g/cm^3)	T (K)	ρ (ohm-cm)$^{-1}$
CBZ-7	Al	4.798	21.4	1.97	2200	$(2.3 \pm 0.2) \times 10^{-3}$
CBZ-14	Al	5.505	26.8	2.06	2600	$(5 \pm 4) \times 10^{-2}$
CBZ-6	Al	6.112	31.7	2.12	2900	2.4 ± 0.4
CBZ-4	Al	6.801	37.8	2.18	3300	50 ± 30
CBZ-10	Al	7.073	40.4	2.21	3400	30 ± 6
CBZ-11	Al	7.083	40.5	2.21	3400	20 ± 5
CBZ-15	Ta	5.405	50.1	2.29	3900	46 ± 10
CBZ-16	Ta	6.119	61.4	2.35	4300	36 ± 8
CH4-C3	Al	7.510	26.3	1.10	3200	$(2.7 \pm 0.5) \times 10^{-4}$
CH4-C4	Ta	6.151	36.5	1.21	3900	0.3 ± 0.2
PBC-2	Ta	7.4	45	1.8	2300	$<10^{-5}$

[a]1 GPa=10 kbar.

ties, and temperatures.[21,22] Since diamondlike nanoparticles are shock synthesized in ~100 ns, they are expected to be heavily defected. The conductivity of shock-synthesized diamondlike particles is assumed to be roughly constant with pressure and temperature.

Three hydrocarbons were chosen which span a range of C content. Methane (CH$_4$), polybutene (n-C$_4$H$_8$), and benzene (C$_6$H$_6$) have ratios of C to H$_2$ (C:H$_2$) of 1:2, 1:1, and 2:1, respectively. The measured conductivities suggest that conduction flows predominately through the majority species, H$_2$ for methane and C for benzene. The conductivities also suggest that methane undergoes a continuous transition from a fluid at 26 GPa, which is mostly methane, to one at 37 GPa which contains a substantial amount of H$_2$. At the pressures in these experiments benzene is completely decomposed and conduction is probably dominated by conduction through C nanoparticles, although C polymers[16] and other species might be responsible. Polybutene is a very poor electrical conductor at a shock pressure of 45 GPa and the mechanism of its conduction is not known.

II. EXPERIMENT

High pressures and temperatures were achieved by single shock compression obtained by impact of a metal plate onto a target specimen. The metal impactor plate was accelerated to several km/s with a two-stage light-gas gun. Shock pressures, densities, and internal energies achieved in the fluid samples were calculated using the shock impedance matching technique, the measured impactor velocity[23] and the Hugoniot equations of state of the metal impactor,[24] Al base plate,[24,25] and fluid samples.[5,15] Electrical conductivities were determined by measuring the resistance R of the shock-compressed sample and calculating the resistivity ρ (inverse of conductivity σ) from the measured geometrical cell constant C. The cell constant $C = R/\rho$ was determined by measuring the resistance of the cell containing a liquid of known

resistivity prior to the shock experiment. The electrical circuits were described previously.[26–28] Conductivity voltage histories were measured with ~2 ns time resolution. Typical experimental lifetimes were a few 100 ns. The cryogenic cooling system for the liquid methane experiments was described previously.[5,28] Liquid methane samples were condensed from high-purity gas. Mass spectrographic analysis of the reagent-grade benzene showed that the major impurity was N with a concentration of <0.08 mol%. The polybutene was supplied by Chevron Oil Company and was also used to measure the Hugoniot equation of state of polybutene.[15] Shock temperatures of methane,[29] benzene,[15] and polybutene[15] were measured previously. Temperatures achieved in the conductivity experiments were obtained by interpolation in P-T space to the shock pressures achieved in the conductivity experiments. The electrical conductivities measured at various shock pressures, densities, and temperatures are listed in Table I. Electrical conductivities of methane and benzene are plotted versus shock pressure in Figs. 1 and 2, respectively. Only one polybutene conductivity experiment was performed because its conductivity is so low in this shock pressure range.

III. DISCUSSION

A. Methane

The Hugoniot equation of state of methane does not yield any information as to whether shock compressed methane has decomposed or not. That is, essentially the same pressure-density Hugoniot curve is calculated assuming either that methane retains its molecular nature or decomposes into diamondlike C and H$_2$. However, the electrical conductivity might be able to discriminate between the two models. In order to test this idea we compare the measured methane conductivities with the conductivities calculated assuming decomposition into diamondlike C and H$_2$. If the comparison
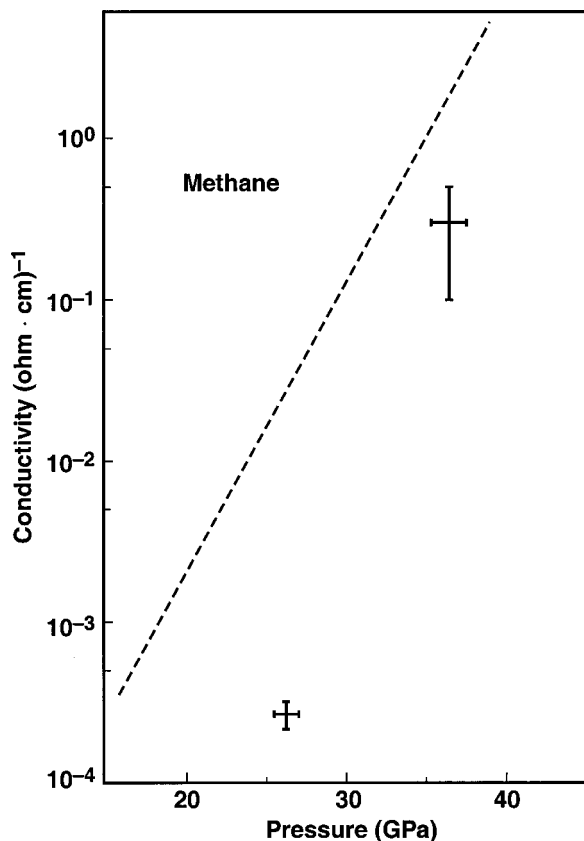
FIG. 1. Electrical conductivity of methane versus shock pressure. Crosses are data points; dashed line is calculated assuming electrical conduction is only through fluid H_2 formed on decomposition of methane into H_2 and diamond-like C nanoparticles.
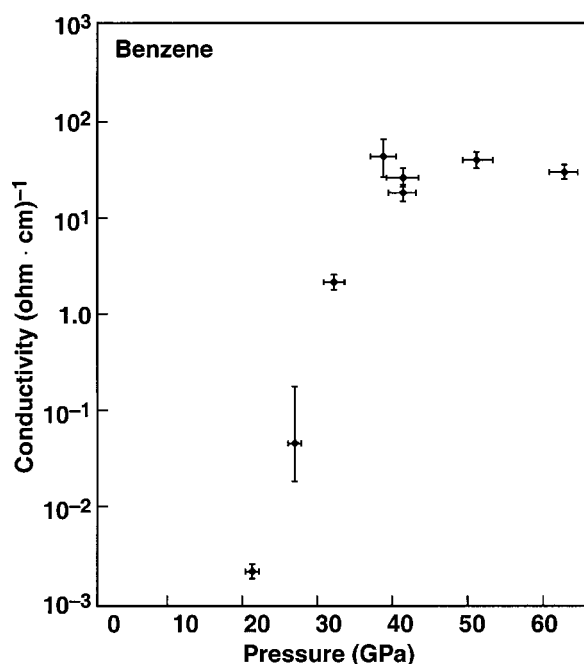

FIG. 2. Measured electrical conductivities of benzene versus shock pressure. Conductivity saturates at $\sim$40 (ohm-cm)$^{-1}$. 40 GPa occurs at a critical density at which connectivity of C nanoparticles becomes sufficiently large that further increase in density has weak affect on the effective cross-sectional area for electrical conduction.

is good, this suggests that methane decomposed; if the comparison is poor, this suggests methane remains molecular.

To examine the likelihood methane decomposes into diamondlike C and H_2, we calculated the conductivity assuming that a given volume of shock-compressed methane is composed only of diamondlike C and H_2 ($CH_4 \rightarrow C + 2H_2$) and that electrical conduction is dominated by conduction through H_2. That is, we assume that since the C concentration in decomposed methane is relatively low and close to the percolation limit, its conductivity is sufficiently low that any conduction through C filaments can be neglected. Because C nanoparticles are expected to be $\sim$5 nm in size,[30] these small C particles are expected to thermally equilibrate with fluid H_2 in a time much smaller than the time resolution of the diagnostics ($\sim$1 ns).

To determine the partial molar volumes of H_2 and C in the event of decomposition, numerical databases for the equations of state of C and of hydrogen were interrogated to find the densities of each at which their pressures and temperatures are equal to those measured in the experiments (Table I). When the partial molar volumes of C and H_2 were added for each CH_4 experiment, their sums agreed with the Hugoniot densities in Table I to within 2%. In the event of decomposition, the methane mass densities in Table I imply molar densities of 0.185 and 0.209 mol of H_2/cm^3, respectively. These H_2 molar densities were used to calculate electrical conductivities.

Conductivity was calculated with a thermally activated semiconducting model:

$$\sigma = \sigma_0(D)\exp[-E_g(D)/2k_B T], \tag{1}$$

where σ is electrical conductivity, $\sigma_0(D)$ is a density-dependent prefactor, $E_g(D)$ is the density-dependent mobility gap, D is molar density of H_2, k_B is Boltzmann's constant, and T is temperature. The mobility gaps and prefactors were calculated with density-dependent scaling relationships for H_2 derived previously: $E_g(D) = 20.3 - 64.7D$ and $\sigma_0(D) = 3.4 \times 10^8 \exp[-44D]$.[22] The calculated electrical conductivities are 3×10^{-2} (ohm-cm)$^{-1}$ and 1×10^0 (ohm-cm)$^{-1}$ for experiments CH4-C3 and CH4-C4, respectively. These two points define the dashed straight line in Fig. 1. At 26 GPa the discrepancy in conductivity between the data point and this simple model is two orders of magnitude, which suggests that little, if any, H2 is present and that most of the methane has not decomposed. At 36 GPa the discrepancy in conductivity between the data point and this simple model is only a factor of 3, which suggests that much of the methane has decomposed into a substantial concentration of molecular hydrogen with C and alkanes. Thus, comparison between the experimental data and the simple model in Fig. 1 suggests that at pressures below $\sim$30 GPa methane retains its molecular nature. As density and temperature increase with Hugoniot pressure, dissociation of methane increases continuously to form an H_2-rich fluid. This interpretation is consistent with tight-binding molecular dynamics calculations of shock-compressed methane which indicate that for pressures below 33 GPa, CH_4 does not decompose and that at pressures of 43 GPa and higher this fluid decomposes into C polymers and H_2.[7]

B. Benzene

Benzene decomposes at ~13 GPa shock pressure.[10–14] The benzene conductivities in Fig. 2 have a thermally activated regime in which the conductivity changes four orders of magnitude from 20 to 40 GPa, followed by a plateau of ~40 $(ohm\text{-}cm)^{-1}$ at pressures up to 60 GPa. Since on a molar basis the concentrations of C and H_2 are (2:1), conduction is expected to be dominated by C. That is, the conductivity and concentration of H_2 are sufficiently low that its conductivity is negligible. At the pressures, temperatures (Table I), and relatively short time durations (100 ns) in these experiments, C is probably in the form of solid, diamondlike,[31] defected, nanoparticles. Carbon particles of this type have been observed in real-time optical scattering experiments on shock-compressed benzene[14] and in the recovered detonation products of C-bearing reacted explosives.[30,32] The effective activation energy of E_g ~11 eV in the pressure range 20–40 GPa was calculated using Eq. (1) and the temperatures in Table I. That is, data at 20 and 40 GPa were assumed to obey $\sigma = \sigma_0 \times \exp[-E_g/2kT]$ and σ_0 and E_g were calculated. To estimate E_g its relatively weak density dependence was neglected. This 11 eV activation energy is unlikely to be an energy gap for bulk conduction because a gap this large cannot be caused by the C itself. The energy gap of well-ordered crystalline diamond is ~5 eV and would be even less with defects and disorder. Hydrogen can be ruled out as the cause of the exponential rise in Fig. 2 because at the H_2 density of 0.22 mol/cm^3 in these experiments, the H_2 activation energy is 6 eV, rather than the observed 11 eV. Hydrocarbons are essentially decomposed at these conditions.[15]

Thermal activation of conductivity at 20–40 GPa is probably caused by thermal activation of connectivity of diamondlike defected C nanoparticles, which themselves have a relatively small electrical conductivity, compared to a metal, which is weakly dependent on density and temperature. The size and proximity of the C nanoparticles depend on density and temperature because of their nucleation and growth. Their connectivity increases with increasing number density and size, which in turn increases electrical conductivity via the effective cross-sectional area for bulk conduction. Thus, the plateau in Fig. 2 is probably caused by diamondlike C nanoparticles reaching a critical density and connectivity, such that further increase in density does not have a significant affect on the cross-sectional area of conduction. Density is continuous through this transition; there is no volume change evident on the Hugoniot at 40 GPa.[15]

The benzene electrical conductivity above 40 GPa is 40 $(ohm\text{-}cm)^{-1}$. The electrical conductivity of pure graphite shock compressed into the diamondlike phase is 13 $(ohm\text{-}cm)^{-1}$.[20] Thus, the magnitude of benzene conductivity on the plateau is what is expected for shock-synthesized diamondlike C.

At 40 GPa the density of shock-compressed C_6H_6 is 2.20 g/cm^3. Assuming decomposition into C and H_2, this implies a C diamond density corresponding to a partial molar volume of about 60%; the rest of the volume is occupied by H_2 which is effectively insulating. At lower shock pressures these C particles would have even lower densities. Thus, the region of shock pressures from 20 to 40 GPa is one in which connectivity between nanoparticles is expected to increase rapidly with an associated rapid increase in electrical conductivity. This result is similar in concept to the results of quantum molecular dynamics calculations[16] for shock compressed benzene, which indicate that long C polymers are formed at these shock pressures which must connect in bulk to conduct. Those quantum calculations, however, yield a much softer equation of state than the experiments. For example, at 2.15 g/cc and 2900 K the data in Table I indicate a pressure of ~35 GPa, in contrast to 23 GPa for the calculation. The higher pressures in the experiments are suggestive of stiffer materials, such as diamond.

At higher pressures, temperatures, and densities beyond the range in Fig. 2, conductivity is expected to vary weakly because it is caused by disordered diamondlike nanoparticles. However, if solid C nanoparticles should melt into the fluid phase at 100 GPa pressures, then metallic C conductivities are expected with values of ~1000 $(ohm\text{-}cm)^{-1}$, as observed for graphite along its melting curve at 5–10 GPa.[33] That is, liquid C is a good nearly-free-electron metal [25 000 $(ohm\text{-}cm)^{-1}$] near atmospheric pressure, 4500 K, and 1.9 g/cm^3.[34,35] As pressure increases from atmospheric in this temperature regime, quantum molecular dynamics calculations indicate that liquid C remains metallic but the liquid is composed of twofold, threefold, and fourfold coordinated C atoms.[36] The density of C conduction electrons decreases by formation of these localized valencelike states but sufficient conduction electrons remain to keep the system metallic. In such a liquid metal, conductivity is expected to have a value of order that at the Ioffe–Regal[37] strong-scattering limit, ~1000 $(ohm\text{-}cm)^{-1}$, which is still large compared to a conductivity of ~40 $(ohm\text{-}cm)^{-1}$. Thus, electrical conductivity is a possible diagnostic to determine the melting curve of nanodiamond particles at 100 GPa pressures by an increase in conductivity of approximately an order of magnitude in going from solid diamondlike nanoparticles to liquid in shock-compressed C-rich hydrocarbons and in graphite and graphite aerogels.

C. Polybutene

The measured electrical conductivity of polybutene is $<10^{-5}$ $(ohm\text{-}cm)^{-1}$ at a shock pressure of 45 GPa. Since the mobility gap is typically ~10 eV for hydrocarbons and hydrogen, at 2300 K (Table I), the calculated conductivity is ~10^{-7} $(ohm\text{-}cm)^{-1}$ whatever the material is, in agreement with the measured upper bound. This value for the fluid is smaller than expected for solid polyethylene (CH_2) based on extrapolation of conductivity data[38] to a shock pressure of 45 GPa. Similarly, polyethylene is essentially an electrical insulator at 100 GPa pressures under compression by a reverberating shock.[39] While the mechanism causing this low conductivity in hydrocarbons with equimolar concentrations of C and H_2 is not known, it might be due to the fact that the electronic bandgap of species present is large compared to the temperature.

ACKNOWLEDGMENTS

[1] W. B. Hubbard, Science **214**, 145 (1980).
[2] D. J. Stevenson, Annu. Rev. Earth Planet Sci. **14**, 257 (1982).
[3] D. J. Stevenson, Rep. Prog. Phys. **46**, 555 (1983).
[4] F. H. Ree, J. Chem. Phys. **70**, 974 (1979).
[5] W. J. Nellis, F. H. Ree, M. van Thiel, and A. C. Mitchell, J. Chem. Phys. **75**, 3055 (1981).
[6] M. Ross and F. H. Ree, J. Chem. Phys. **73**, 6146 (1980).
[7] J. D. Kress, S. R. Bickham, L. A. Collins, B. L. Holian, and S. Goedecker, Phys. Rev. Lett. **83**, 3896 (1999).
[8] F. Ancilotto, G. L. Chiarotti, S. Scandolo, and E. Tosatti, Science **275**, 1288 (1997).
[9] L. R. Benedetti, J. H. Nguyen, W. A. Caldwell, H. Liu, M. Kruger, and R. Jeanloz, Science **286**, 100 (1999).
[10] G. E. Hauver, J. Appl. Phys. **36**, 2113 (1965).
[11] R. D. Dick, J. Chem. Phys. **52**, 6021 (1970).
[12] R. H. Warnes, J. Chem. Phys. **53**, 1088 (1970).
[13] O. B. Yakusheva, V. V. Yakushev, and A. N. Dremin, High Temp.-High Press. **3**, 261 (1971).
[14] N. C. Holmes, G. Otani, P. McCandless, and F. H. Ree, High Press. Res. **5**, 669 (1990).
[15] W. J. Nellis, F. H. Ree, R. J. Trainor, A. C. Mitchell, and M. B. Boslough, J. Chem. Phys. **80**, 2789 (1984).
[16] S. R. Bickham, J. D. Kress, and L. A. Collins, J. Chem. Phys. **112**, 9695 (2000).
[17] W. J. Nellis, A. C. Mitchell, P. C. McCandless, D. J. Erskine, and S. T. Weir, Phys. Rev. Lett. **68**, 2937 (1992).
[18] S. T. Weir, A. C. Mitchell, and W. J. Nellis, Phys. Rev. Lett. **76**, 1860 (1996).
[19] W. J. Nellis, S. T. Weir, and A. C. Mitchell, Phys. Rev. B **59**, 3434 (1999).
[20] A. C. Mitchell, J. W. Shaner, and R. N. Keeler, Physica **139&140**, 386 (1986).
[21] W. J. Nellis, R. Ross, and N. C. Holmes, Science **269**, 1249 (1995).
[22] W. J. Nellis, S. T. Weir, and A. C. Mitchell, Science **273**, 936 (1996).
[23] A. C. Mitchell and W. J. Nellis, Rev. Sci. Instrum. **52**, 347 (1981).
[24] W. J. Nellis and A. C. Mitchell, J. Appl. Phys. **52**, 3363 (1981).
[25] W. J. Nellis and A. C. Mitchell, J. Chem. Phys. **73**, 6137 (1980).
[26] D. C. Hamilton, Ph.D. thesis, University of California at Davis, Lawrence Livermore National Laboratory Report UCRL-53768, 1986.
[27] A. C. Mitchell and W. J. Nellis, J. Chem. Phys. **76**, 6273 (1982).
[28] D. C. Hamilton, W. J. Nellis, A. C. Mitchell, F. H. Ree, and M. van Thiel, J. Chem. Phys. **88**, 5042 (1988).
[29] H. B. Radousky, A. C. Mitchell, and W. J. Nellis, J. Chem. Phys. **93**, 8235 (1990).
[30] N. R. Greiner, D. S. Phillips, J. D. Johnson, and F. Volk, Nature (London) **333**, 440 (1988).
[31] M. van Thiel and F. H. Ree, Int. J. Thermodynamics **10**, 227 (1989).
[32] V. N. Kolomiichuk and I. Y. Malkov, Combust., Explos. Shock Waves **29**, 113 (1993).
[33] M. Togaya, Phys. Rev. Lett. **79**, 2474 (1997).
[34] J. Heremans, C. H. Olk, G. L. Eesley, J. Steinbeck, and G. Dresselhaus, Phys. Rev. Lett. **60**, 452 (1988).
[35] J. Steinbeck, G. Dresselhaus, and M. S. Dresselhaus, Int. J. Thermodynamics **11**, 789 (1990).
[36] G. Galli, R. M. Martin, R. Car, and M. Parrinello, Phys. Rev. Lett. **63**, 988 (1989).
[37] A. F. Ioffe and A. R. Regal, Prog. Semicond. **4**, 237 (1960).
[38] A. R. Champion, J. Appl. Phys. **43**, 2216 (1972).
[39] V. V. Yakushev (deceased), Institute of Chemical Physics, Chernogolovka, private communication, 1998.