Shock Compression of Condensed Matter – 1991

Proceedings of the American Physical Society Topical Conference held in Williamsburg, Virginia June 17-20, 1991



Williamsburg '91

Edited by: S. C. SCHMIDT R .D. DICK J.W. FORBES D. G. TASKER

North-Holland

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PREFACE

The Seventh American Physical Society Topical Conference on Shock Compression of Condensed Matter was held in Williamsburg, Virginia, June 17 - 20, 1991. Previous conferences were held in 1979 at Washington State University, Pullman, Washington; in 1981 at SRI International, Menlo Park, California; in 1983 at Santa Fe, New Mexico; in 1985 at Spokane, Washington; in 1987 at Monterey, California; and in 1989 at Albuquerque, New Mexico. The Eight Conference is scheduled for June 28 - July 2, 1993 at Colorado Springs, Colorado.

The purpose of this conference as for past symposia, was to provide a forum where scientists and engineers studying the response of condensed matter to dynamic high pressures and temperatures could exchange ideas and technical information. During the conference, papers describing the mechanical, chemical, electro-magnetic, and optical response of condensed phase materials to shock stimuli were presented. Theoretical, computational, and experimental results were discussed. The abstracts of these papers were published in the June 1991 issue of the Bulletin of the American Physical Society.

Three hundred and thirty-seven scientists and engineers from fourteen countries registered at the conference. The countries represented included the United States (264), France (15), the United Kingdom (13), the Union of Soviet Socialist Republics (13), the People's Republic of China (7), Japan (6), Israel (6), the Federal Republic of Germany (5), South Korea (3), Canada (2), and India, Mexico and The Netherlands (1 each). There were 260 technical presentations with 239 of the presentations appearing as written contributions in this volume.

Lev V Al'tshuler was the recipient of the bienniel award presented by the American Physical Society Topical Group on Shock Compression of Condensed Matter for outstanding contributions to the field of shock wave physics. To commemorate the award, he gave a plenary talk entitled, "Shock Waves and Extreme States of Matter."

John W. Shaner was the Master of Ceremonies for the conference banquet, which was attended by three hundred and seventy-five conference participants and guests. Ivor Noel Hume, renowned archaeologist in the Williamsburg area and author, presented a keynote address, " 'Us New Virginians:' The Search for Martin's Hundred."

The Organizing Committee for the conference comprised the following people:

Conference Chairman - Richard D. Dick, University of Maryland

Conference Vice-Chairman and Local Arrangements Chairman - Douglas G. Tasker, Naval Surface Warfare Center

Technical Program Committee Chairman - Jerry W. Forbes, Naval Surface Warfare Center Publication Chairman - Stephen C. Schmidt, Los Alamos National Laboratory Secretary/Treasurer - E. Ray Lemar, Naval Surface Warfare Center

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The Organizing Committee would like to express its appreciation to the many people who contributed to the success of the conference: the session chairpersons, the authors, the plenary and the invited speakers, and the participants. The editors are especially grateful to the session chairpersons and other persons who reviewed the manuscripts. They are T. J. Ahrens, M. U. Anderson, J. R. Asay, R. R. Bernecker, S. J. Bless, N. S. Brar, R. J. Clifton, C. S. Coffey, M. Cowperthwaite, D. R. Curran, D. P. Dandekar, W. E. Deal, R. D. Dick, J. Ding, M. L. Elert, D. J. Erickson, J. W. Forbes, J. N. Fritz, D. E. Grady, R. Grover, Y. M. Gupta, B. Hammant, P. J. Haskins, M. Held, W. F. Hemsing, W. Herrmann, N. C. Holmes, W. H. Holt, A. Kusubov, E. L. Lee, M. A. Meyers, P. J. Miller, R. S. Miller, T. R. Neal, W. J. Nellis, M. Nicol, D. L. Paisley, R. L. Rabie, M. Ross, J. S. Rottler, S. A. Sheffield, D. J. Steinberg, D. G. Tasker, M. van Thiel, J. S. Wark, R. R. Whitlock, W. H. Wilson.

Special thanks are given to the many people who willingly gave their time and talents to organize and conduct this conference. These are Wanda J. Morat, Debbie Russell, Ruthie Maticic, Felicia Harley, Beverly McLean-King, Linda Lemar, Robert Hay, Richard J. Lee, Gerrit Sutherland, William H. Wilson, Michael Furnish, Alita M. Roach, William E. Deal, and Jo Ann Brown. We appreciate the interesting and popular companion program coordinated by Micki Dick with consultation from Nancy Cole. The conference committee thanks Janet M. Neff and Wanda J. Morat, with early help from Mary Ann Lucero, for their superb assistance and skill in coordinating the review and the correction of the manuscripts. Global Associates Ltd. from Arlington, Virginia prepared many of the manuscripts. The conference logo was the artwork of Dottie Tasker. Eric Dick assisted with publicity announcements and William Lawhon of Colonial Images Ltd. provided audio/visual support. We especially appreciate the cooperation and help of Lucille Strickler of the Williamsburg Hilton Conference Center.

S.C.SCHMIDT R. D. DICK J. W. FORBES D. G. TASKER

FOREWORD

In the middle 1940s, scientists of the Union of Soviet Socialist Republics were, as in the United States, actively developing the use of shock waves as a tool for high pressure physics research. It was their intent, using the shock compression technique, to investigate the properties of materials at high pressures and temperatures. By so doing, they created and advanced a new scientific discipline - the physics of high energy densities. Among the notable figures of this effort was Lev V. Al'tshuler, the recipient of this year's "Shock Compression Science Award." This award, sponsored by the American Physical Society Topical Group on Shock Compression of Condensed Matter, recognizes the significant contributions to shock compression science of this man and his associates. It has been the continuing dedication of Lev Al'tshuler as well as his many colleagues world wide to study the extreme states of matter, that leads us to this year's Topical Group Conference.

As with previous conferences, the spirit of this year's meeting was to associate shock wave phenomenology and data with fundamental understanding. This volume embodies the most recent thoughts of the shock wave community toward this goal. Included are sections on equations of state, phase transitions, material properties, explosive behavior, measurement techniques, and optical and laser studies. Receiving increased attention are studies of impact and penetration phenomenology, the development of materials, especially ceramics, and molecular dynamics and Monte Carlo simulations. Investigations of the shock compression of superconducting and geological materials received less attention this year. These latest advances, in addition to the many other results and topics discussed by an international contingent of authors, serve to make this volume the latest authoritative reference source for the shock wave physics community.

As with previous volumes, the diversity of the subject matter treated in this volume makes it difficult to assimilate. However, an extensive index provides ready entry into various technical subjects. All manuscripts received by the editors have been published in this volume. The editors apologize for any errors that may have occurred, technical and editorial, as part of the publication process.





In recognition of seminal and major contributions in the development of the field of shock wave compression of condensed matter.

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CHAPTER I

PLENARY

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SHOCK WAVES AND EXTREME STATES OF MATTER

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The use of shock waves in physics research has made extreme states of matter and processes of superhigh-speed deformation an object of laboratory experiments.¹⁻⁴ Intensive development of dynamic methods is closely related to our civilization's entry into the atomic age. The official birthdate of the atomic project in Russia was March 1943.⁵ The July 1945 tests in the USA⁶ revealed the main secret of atomic weapons—the possibility of accomplishing in practice the explosive release of energy contained within the atom in fission chain reactions.

The first, rather primitive design of a Soviet atomic bomb was tested in August 1949. To complete the bomb's development and create new, more efficient designs, as well as to perform the necessary scientific research, a large institute isolated from the outside world was established away from Moscow. Yuliy Borisovich Khariton, an eminent scientist and future academician, became its permanent scientific director. So that his work would culminate successfully in flashes "brighter than a thousand suns,"6 it was necessary to investigate the properties of many substances at high and superhigh pressures and temperatures, and to create and advance a new scientific discipline-the physics of high-energy densities. In the first ten years, brilliant, substantive chapters were contributed to the new discipline^{1,2} by Yakov Borisovich Zeldovich; Andrey Dmitrievich Sakharov; David Albertovich Frank-Kamenetskiy, the founder of the theory of combustion; Veniamin Aronovich Tsukerman, the founder of the method of pulse radiography; and many of the institute's experimentalists, including the author of this

report. After the appearance of publications in the western scientific literature (in the mid-1950s), it became clear that our researchers were in competition with outstanding American scientists. At that time in the USA, at Los Alamos, equations of state of many metals⁷ and of water⁸ had been investigated in the range of several hundred kilobars, the phase transition in iron had been identified,⁹ and the detonation pressure of a powerful explosive composition¹⁰ and the structure of its detonation front¹¹ had been determined.

In the designs that were under development, gaseous products of the detonation of chemical explosives played the role of a "working medium," similar to steam in turbines and other heat engines. Therefore, the institute's main task became the measurement of detonation pressures of powerful explosive compositions consisting of blends of TNT and RDX. Theoretical predictions were contradictory in the extreme, and the results obtained in 1945 by American researchers were not known. In the institute's laboratories in 1947-48, three methods (Fig. 1) were proposed and developed² that remain important even today: (1) pulse radiography of the propagating detonation front and of metal foils placed in the high explosive charge; (2) velocity measurements of conductors carried by the explosion products as they move in a static magnetic field (method of Evgeniy Konstantinovich Zavoyskiy) and; (3) measurement of "spall" velocities and of shock wave velocities in metal plates with different thicknesses after the reflection of incident detonation waves. After the initial





Methods of determining Jouguet states:^{2,12,13} 1—plane-wave lens; 2—explosive charge; 3—foil gauges for pulsed radiography;² 4—electromagnetic gages;² 5—free-surface velocity measurements of spalled plate;² 6—manganin pressure transducers;¹³ 7—gauge for the axial magnetic method;¹² 8—layered transparent anvil for shock velocity measurements by laser diagnostics.¹³

period of adoption, followed by unavoidable failures and heated arguments, by 1949 similar results were obtained by different methods. The green light was given for testing of the first Soviet nuclear device.

Chemical explosives continued to be investigated intensively in the following decades. Much about this complex phenomenon was explained by the American scientist W. C. Davis' concept of the two-stage detonation, which was advanced in 1976.12 In the Soviet Union,13 the classical ZND (Zeldovich, Neuman, Doering) mode of detonation in desensitized compositions was discovered together with a steady-state. incompletely compressed detonation (Fig. 2) and an exotic mode of decomposition on the shock discontinuity of agatized RDX and HMX (Fig. 3). By now the detonation pressure of most explosives has been established within 2-3% accuracy. In accordance with the remarkable scientific foresight of Landau and Stanyukovich,14 the isentropic index of explosion products that determines detonation pressures proved to be close to 3 (Fig. 4). Hence, Jouguet pressure is $P_1 \simeq \frac{1}{4} r_0 D^2$, where r_0 is the initial density of the explosive, and D is the detonation velocity.



Steady-state, incompletely compressed detonation of desensitized PETN compositions¹³—shock wave velocities (U_s) in layered plexiglass (PMMA) plate vs PMMA thickness (x) for charge lengths (L). 6% desensitizer: 1—L = 10 mm; 2—L = 20 mm; 3—L = 40 mm.

10% desensitizer: 4-L = 50 mm.



FIGURE 3

Detonation of agatized hexogen (RDX)¹³—shock wave velocities (U_s) in layered plexiglass (PMMA) plate vs PMMA thickness (x) for charge lengths (L). 1—L = 20 mm; 2—L = 50 mm.

The study of the behavior of metals and other materials at high and superhigh dynamic pressures is based on experimental



Detonation pressures and isentropic indices of powerful explosives.¹³

o -traditional measurements.

 —derived from experiments with supercompressed detonation.

measurements of their kinetic parameters: the shock wave propagation rate, Us, and the mass velocity, Up, of the substances behind the shock front for shock waves of different amplitudes. Thus, from conservation equations known since the end of the last century, the pressures (P_H), densities (r_H), and specific internal energies (E_H) of shock compression are determined. The first stage, now largely completed, in the megabar pressure range, consisted of recording the Hugoniot adiabats of standard materials. Such measurements were performed in the Soviet Union in 1948¹⁵ for iron using a collision method that we proposed. The measured values were the velocities of the impactor (W) and of shock wave velocities in targets. If the impactor and the target are made of the same material, then behind the shock-wave front in the target, $U_p = \frac{1}{2}W$. Mass

and shock wave velocities according to wellknown formulas determine pressure density and internal energy:

$$P_{H} = \frac{1}{2} \rho_{0} U_{S} W, \quad \rho_{H} = \rho_{0} \frac{2U_{S}}{2U_{S} - W}$$
$$E_{H} - E_{0} = \frac{1}{8} W^{2} .$$

After determining the shock adiabat of a standard material, a simpler method of "reflection" or "matching of impedances" can be used. The parameters measured here are the rates of subsequent passage of the shock wave through a layer of a "standard" material and through an adjoining sample that is being studied.

In the Soviet Union, the acceleration of impactors was accomplished by using supercompressed detonation waves proposed by Altshuler, Zababakhin, Zeldovich, and Krupnikov. The first data on shock compressibility of several metals in the range of 5 Mbar were obtained in 1948,¹⁵ and they were subsequently used by theoreticians and mathematicians for designing devices that were under development. Later on, these results were refined¹⁶ and the experimental range was extended to 10 Mbar.^{17,18}

In the USA, in addition to explosive-driven systems with capabilities up to 2 Mbar,^{19,20} there was wide use of two-stage light-gas guns,²¹ which accelerated tantalum impactors to velocities near 9 km/s, and which created pressures in targets, depending on their specific weight, from 1 to 6 Mbar. Using such guns over the past 12 years, US scientists have recorded Hugoniot adiabats for different substances and completed a large number of diverse experiments.

The high degree of accuracy and precision of dynamic measurements can be seen in Fig. 5 and 6, which compare results obtained in the Soviet Union in 1960 and 1963, Refs. 16 and 18 respectively, and the USA in 1981, Ref. 21. The Hugoniot adiabats for copper, and tantalum (Fig. 5) are given in experimental U_s , U_p coordinates, and for copper and aluminum (Fig. 6), in thermodynamic P, V variables. Within the first few megabars, the Hugoniot adiabats allow the "room-temperature" isotherms and the cold-compression curves at T = 0 degrees K to be found with good accuracy. Therefore the metals investigated in the dynamic experiments, if they do not undergo phase transitions or electron transfers, become accurate reference standards for dynamic and static pressures, occupying the upper level in the metrological hierarchy.

To understand the properties of metals in extreme conditions, it is not enough to know just the shock adiabat. In the phase diagram in Fig. 7,



FIGURE 5 Experimental Hugoniot adiabats for copper and tantalum—shock vs mass velocity.



FIGURE 6 Experimental Hugoniot adiabats for copper and aluminum—thermodynamic P, V variables.



Schematic of phase diagram (dotted curves) with several experimental trajectories.³

which is borrowed from the survey in Ref. 3, the shock adiabat can be likened to a path leading through an uncharted jungle. For many years, the efforts of Soviet researchers were directed at obtaining additional information, in line with an extensive program outlined by Zeldovich and subsequently published.²² For this purpose, Kormer's group measured the speed of sound behind the front of intense shock waves for four metals.²³ Pursuing another direction, groups headed by Krupnikov²⁴ and Kormer,²⁵ and more recently Trunin,^{26,27} investigated the shock compressibility of metallic powders. Trunin's coworkers, jointly with the laboratories of Altshuler and Fortov, recorded isentropes of expansion for copper and lead from high-energy states.28

Fig. 8 presents the set of shock-wave measurements for copper, together with the Hugoniot adiabats and the phase boundaries calculated from the Bushman equation of state.²⁸ An important achievement of American researchers was the recording of melting pressures on Hugoniot adiabats of metals by observing the decrease of longitudinal acoustic perturbation velocities. The measured shock melting pressures were 2.8 Mbar for iron,²⁹ 1.25 Mbar for aluminum,³⁰ 2.95 Mbar for tantalum,³¹

and 4.0 Mbar for molybdenum.³² The methods that were developed during this effort also made it possible to predict a new body-centered phase in iron at pressures of approximately 2 Mbar ³³.

In experiments reported in Refs. 34 and 35, and in subsequent studies described in Refs. 36 and 37, a large group of elements was identified which, when subjected to pressure, underwent previously unknown rearrangement of their electron structures. For alkali-earth elements (Ca, Sr, Ba), pressure causes a transfer of outer selectrons to unfilled d-levels. In rare-earth elements, there occur transfers of 6s-electrons to inner 5d or 4f shells.38 In praseodymium, moreover, an interesting effect of collectivization of 4f electrons is observed.39 As a result of the electron transfers, low-compressibility electron configurations are formed. Their appearance at the completion of electron transfers causes an abrupt discontinuity in the Hugoniot adiabats (Fig. 9).

In many transparent dielectrics, unlike in metals, important characteristics of compressed and heated media other than density can be recorded: temperature and conductivity, refractive index and Raman spectra, melting and metallization. Kormer, Sinitsyn, and Yushko were the first to perform temperature measurements and to determine refractive indexes and the reflecting power of shock waves.⁴⁰ In the last ten years, investigators using new techniques⁴¹ have measured shock-compression temperatures for many minerals,⁴² water,⁴³ quartz,⁴⁴ periclase,⁴⁵ and cesium iodide.⁴⁶ An attempt also was made to measure the shock compression temperature of iron.⁴⁷

Of special interest are results of experiments dealing with xenon metallization properties⁴⁸ and the dissociation and ionization of nitrogen.^{49,50} These processes are manifested by deflections of shock adiabats, and in nitrogen, moreover, in a paradoxical effect of cooling in shock waves of

L.V. Altshuler



Hugoniot adiabats of copper for different initial densities $\rho_{00} = \frac{\rho_0}{m}$. "Porosity" of samples $m = \frac{\rho_0}{\rho_{00}}$. Phase boundaries and Hugoniot adiabats calculated by the Bushman equation of state.²⁸

repeated compression (Fig. 10). For water (Fig. 11), in addition to the Hugoniot adiabat,^{51,52} temperatures⁴³ and conductances⁵² were determined in the megabar range. For a long time, the physical nature of the break in the adiabat at 10 GPa was unknown. Recording of spontaneous Raman radiation⁵³ showed that at these pressures there occurs intensive breakup of intermolecular hydrogen bonds and transformation of water into a simple weakly-ionized liquid.

The dynamic experiments had a special importance for geophysics. Our planet is a natural pressure vessel of great dimensions. Pressures reach 3.5 Mbar at its center, and 1.4 Mbar at the boundary separating the core and the mantle. The Soviet data obtained on the compressibility of metals and minerals led to the first realistic assessments^{54,55} of the mantle being composed of ferromagnesium silicates and the core being composed of an iron-nickel alloy with an addition of lighter elements—sulfur, oxygen, or silicon.

Beginning in 1968,⁵⁶ further movement into the Terapascal pressure range was accomplished in experiments with shock waves in near-range zones of nuclear explosions.⁵⁷⁻⁶¹ The main result of this research was the determination of the relative compressibility of many metals, as well as of quartz, water, graphite, and lithium deuteride. The greatest pressures—several hundred megabars—were reached in measurements of the relative compressibility of iron, lead, and aluminum.⁶⁰ With this technique, unique experiments were made to measure the absolute



FIGURE 9 Effect of electron transfers³⁴⁻³⁷ on shock

compressibility of lanthanides (Sm, Eu, La).

shock compressibility of molybdenum,⁶² aluminum,⁶³ and porous copper⁶⁴ at pressures of 2 TPa.

Analysis⁶⁵ showed that the use of quantumstatistical models with "corrected" semiempirical "cold compression" curves provides a satisfactory description for most of the experiments (Figs. 12 and 13). As shown by these diagrams, data⁶¹ for molybdenum and copper that were obtained in the region near the nuclear explosion differ somewhat from Hugoniot adiabats calculated in Ref. 65. For data analysis of these experiments, aluminum, which has an equation of state that tends to increase the absolute values of the experimental data,⁶⁰ was used as the standard material.



FIGURE 10

Dissociation and ionization of nitrogen in shock waves. 49,50

Pressure-volume curve (principal Hugoniot) is shown as the solid black line. Each pair of identical symbols corresponds to single and double-shocked points in the same experiment. This illustrates the fact that $(\partial P/\partial T)_V < 0$ in the dissociative transition region. Shock-induced cooling is observed as one double-shocks from the lower to the higher "diamond" points.

For chemical elements, the range of absolute and relative measurements of dynamic compression is shown in Fig. 14, where the outline of the shaded areas shows the upper boundaries of laboratory experiments. The investigated states of several elements are shown on a generalized phase diagram in Fig. 15. The x coordinate shows molar concentration (moles/litre), and the y coordinate shows specific internal energies (kJ/g). Regions 1–3 were determined by dynamic compression of metallic powders^{24-27,64} of



Hugoniot adiabats for water; 51,52 and temperatures 43,77 and conductances 52 of water during shock compression. The break in the adiabat at 10 GPa is caused by the breaking of intermolecular hydrogen bonds. 53

tungsten, copper, and nickel, and the two regions labeled 4 were determined by experiments with xenon^{66,67} in shock tubes. The large shaded area of dense plasma has almost no experimental data, except for Experiment 5 with uranium,⁶² and data²⁸ for isentropic release of copper and lead.

For theoretical description of dense plasma at temperatures T > 5 eV, a quasiclassical shell model, QM, developed by Kirzhnits, Shpatakovskava, and Kuzmenkov⁶⁸⁻⁷⁰ was used, serving as a physical interpolation between the Saha plasma and the region adequate for the TFC model.71,72 At lower temperatures and for stronger interparticle interaction, new perspectives are given by the Confined Atom Model (CAM) developed by Gryaznov and Fortov.73 Using this model, one could satisfactorily describe near critical states of xenon and cesium, as well as Region 3 in Fig. 15. Another effective approach developed by M. Ross⁷⁴ is based on the use of a liquid metal model for partially ionized plasma.

The creation of wide-range equations of state for elements and chemical compounds that adequately describe their extreme characteristics constitutes the main direction of further theoretical and experimental research. An urgent problem for



FIGURE 12 Hugoniot adiabats of Mo, Fe, and Pb according to absolute and relative measurements. • —absolute measurements; ^{16-18,21}

- ⊢→ —underground absolute measurements in molybdenum.⁶²
 ■ —relative measurements in zones near
- underground explosion.^{56-59,61}
- - - calculated data from Ref. 59.

theoreticians is to formulate adequate hightemperature zone models and models of strongly nonideal plasma. New experimental results can be obtained from underground nuclear explosions programmed for scientific research and carried out within a framework of international cooperation. The method of pulsed isochoric heating⁷⁵ makes it possible to reach the region of dense plasma. A similar experiment was accomplished in Ref. 62 for other purposes.

Another urgent problem is the development of linear gas-electrodynamic accelerators capable of accelerating impactors to hypercosmic



Hugoniot adiabats of W, Cu, Cd, and Be. For legend see Fig. 12.

velocities without heating them. Many unsolved problems involve the propagation of shock waves in crystalline media. They include the mechanism of tangential stress relaxation in the front of shock waves, which is still not fully understood, as well as processes of superhigh-speed crystallization of high-pressure phases, measurement of viscous and rigid resistance to hypervelocity deformation, and the kinetics of spall failure. The arsenal of methods for studying superhigh-speed processes would include wide use of pulsed x-ray structural analysis.

A powerful stimulus to the investigation of extraordinary states of matter in the initial decades after the World War II in the Soviet Union was generated by defense requirements—the need to restore a world balance of forces. In this respect, science not only served defense, but defense served science as well. Today, a global task of utmost importance is the pursuit of energy projects that hold promise for the development of powerful,



FIGURE 14

Ranges of absolute and relative dynamic measurements for elements. Shaded area indicates laboratory absolute measurements. + —absolute measurements in molybdenum.⁶² × —absolute measurements in aluminum.⁶³ • —relative measurements.⁵⁶ • —relative measurements.⁵⁷

- I -- relative measurements.60
- relative measurements.⁶¹

ecologically clean sources of energy. These problems can be solved by common efforts of the international scientific society.

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FIGURE 15

Generalized phase diagram—C (mol/liter) vs E(kJ/g) of metals. 1—tungsten;²⁴ 2—copper and nickel;^{25,26,27} 3—copper;⁶⁴ 4—xenon;^{63,66} 5—uranium;⁶² 6—copper isentrope.²⁸ Regions of model validity include: Saha, QM^{68,69,70} and TFCK.^{71,72,76}

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Experimental approaches to understanding shock compression of condensed materials at the microscopic level are reviewed. Representative successes and difficulties in relating continuum measurements to atomic/molecular changes are outlined. Results from recent work on ruby crystals and liquid carbon disulfide are summarized to demonstrate the usefulness of time-resolved, spectroscopic measurements for understanding shock induced deformation and chemical reactions at the microscopic level. Directions for future work are indicated.

1. INTRODUCTION

Plane shock wave experiments provide a well controlled method to examine the response of condensed materials to large, rapid compressions that are macroscopically well defined. Scientific studies related to condensed matter response under plane wave loading have their origin in the pioneering work at the Los Alamos Laboratory in the United States¹ and comparable efforts in the Soviet Union² during the years following World War II.

Although well characterized shock wave measurements have now been carried out for forty years and the use of these measurements to study high pressure equations of state is an established discipline in condensed matter physics,³⁻⁷ a detailed understanding of shock induced changes and processes at the atomic/molecular level remains an outstanding problem. The usual methods for probing atomic/molecular mechanisms in other areas of condensed matter physics and chemistry are not easily incorporated in shock wave experiments. In addition, the time-honored practice in experimental physics and chemistry is to probe changes in material response when only one external parameter (e.g., pressure, temperature, magnetic field, etc) is being varied. The complexity of the shock experiments, discussed in Section II, does not permit this simplification.

The objective of this paper is to review briefly the progress toward understanding the microscopic mechanisms characterizing shock compression in condensed materials, summarize recent experimental developments and results, and indicate future directions that hold promise for examining shock compression at the atomic/molecular level.

The idealized problem shown in Figure 1 is helpful in defining the scientific issues of interest to the present paper. A half-space of a homogeneous material is instantaneously and uniformly loaded at time, t=0. The resulting shock wave propagates through the material and the stress-time profile recorded by an idealized (infinitely thin) in-material, stress gauge at a particular location is as shown in Figure 1.



The following questions then arise: what is the cause of the observed wave structure; what is the state of the material through points ABCDEFG; in particular, what are the atomic/molecular structures and processes corresponding to

ABCDEFG; how can we "watch" the evolution of the changing atomic/molecular structure. Because the wave structure changes with propagation distance, these same questions need to be addressed at different locations in the sample. Answers to these questions, relating to atomic/molecular mechanisms, are quite difficult and require development of diagnostics with sufficient spatial and temporal resolution to probe the samples at the microscopic level of interest.

An important limitation of the present paper should be pointed out. I was asked to prepare a presentation in which our spectroscopic work, at Washington State University, would serve as the core of an overview regarding atomic/molecular mechanisms in shock compression experiments. This goal coupled with the page requirement has resulted in a paper which is very broad in content but extremely abbreviated. I have, however, attempted to indicate the key physical ideas and to provide a good, though not complete, list of references for more detailed examination by interested readers.

CONTINUUM MEASUREMENTS AND ANALYSIS Governing Equations

The conservation equations, in the absence of heat conduction and radiation, for uniaxial strain loading shown in Figure 1 are expressed as:⁸

$$\rho_o \left(\frac{\partial u}{\partial t}\right)_h = - \left(\frac{\partial \sigma}{\partial h}\right)_t \tag{1}$$

$$\rho_o \left(\frac{\partial V}{\partial t} \right)_h = \left(\frac{\partial u}{\partial h} \right)_t \tag{2}$$

$$\rho_o \left(\frac{\partial E}{\partial t} \right)_h = -\sigma \left(\frac{\partial u}{\partial h} \right)_t \tag{3}$$

where h represents distance in Lagrangian or material coordinates, t is time, ρ_0 is initial density, V (= 1/ ρ) is specific volume, σ is mechanical stress along the direction of propagation, and E is specific internal energy. For a given initial condition (e.g. prescribed stress or particle velocity pulse on the upper boundary in Figure 1), the

above equations can be used to relate shock wave measurements to material response by two related approaches.

In the first, a material constitutive description is assumed or developed using a first principles or an alternate method depending on the material.⁹ The material description is then used to integrate the governing equations, for a given initial condition, and the calculated results are compared with the experimental data. The other approach^{10,11} is to measure a dependent variable like $\sigma(t)$ or u(t) at several sample locations and then use this information to integrate the above set of partial differential equations to provide the remaining dependent variables. These approaches, though straightforward in principle, are difficult to implement in most situations and the analysis of large amplitude stress wave profiles in condensed materials is a subject of ongoing study.

With regard to the objectives of this paper, it is important to emphasize the following points. The continuum measurements can only provide the longitudinal stress - volume - energy (σ - V - E) relation for a particular loading condition (uniaxial strain). Furthermore, these variables are, in general, dependent on h and t. The continuum variables in Equations (1) - (3), which are the only variables that can be obtained from the mechanical measurements, provide an incomplete constitutive description of the shocked state for both fluids and solids even when the shocked state is assumed to be in thermodynamic equilibrium.

In liquids, the lack of temperature data in the shocked state is an important shortcoming. In recent years, optical pyrometry has been used increasingly to obtain temperature data in shock wave experiments.¹² Although temperature results have been reported for a number of materials, the data are not always unambiguous. Further work to improve pyrometry measurements is currently underway at the Lawrence Livermore National Laboratory.¹³ In solids, the issue of temperature measurements is even more complicated¹⁴ and purported temperature data in shocked solids need to be viewed with caution.

The stress state in a shocked solid is also not defined completely because lateral stresses cannot be inferred from the conservation equations for uniaxial strain loading. The ability to specify the complete stress state in shocked solids is an important need. Although there have been some recent developments,¹⁵⁻¹⁷ this area merits further study. The very recent work by Wong is noteworthy.¹⁸

Finally, it should be pointed out that the use of continuum measurements to determine microscopic mechanisms or discern between different mechanisms is an inherently difficult problem. There are many more parameters in the theory than experimental constraints. Only those microscopic variations which lead to measurable differences in the σ -V response can be examined in detail. The many successes in understanding material changes at the extreme conditions of shock wave experiments speak highly of the scientists engaged in these studies.

2.2. Analysis of Peak States

For the case of steady or discontinuous waves, the conservation equations can be integrated to give the Rankine-Hugoniot jump conditions.¹⁹ Measurements of two experimental variables (most often shock velocity and particle velocity) provide the σ , V values in the peak state or P, V values if material strength is negligible at the conditions of interest; the neglect of material strength is discussed later in this subsection. It is commonly assumed that peak states correspond to thermodynamically equilibrated states. The locus of the P, V states at different compressions constitutes the Hugoniot curve and is the starting point for much of the thermodynamic and theoretical analysis of shock wave measurements.²⁰

The measurements by Minshall and coworkers^{21,22} in iron and bismuth in the fifties are noteworthy in that they related the shock wave data to phase transitions in these materials and demonstrated the use of shock wave experiments to explore structural changes in condensed materials. Since then shock induced phase transformations have been reported in a large number of materials. The paper by Duvall and Graham²³ provides a good review of the work till 1976. As pointed out by these authors and others,²⁴ despite the extensive studies to date, the detailed atomic mechanisms governing the transitions are not well established. The principal method for inferring structural phase changes under shock loading consists of comparison with the static high pressure, P-V, data. Some of the outstanding questions regarding structural changes are summarized at the end of this section.

Since the work by Ross²⁵ in the sixties, electronic band structure calculations have been used extensively to calculate the high pressure equations of state for a large number of materials. This is a subject of considerable activity and the reader is referred to the review articles cited in References 7 and 26. The use of such calculations for phase transformation studies may be seen in the paper by S. C. Gupta in this volume.

Despite the difficulties stated in the previous subsection, there have been notable successes in inferring structural changes using continuum methods.^{23,27} As examples, results from two recent efforts are summarized below.

The first example is the extensive investigation $^{28-30}$ on shocked liquid nitrogen carried out at Livermore and summarized in several papers at the 1987 Topical Conference at Monterey.³¹ This work shows that liquid nitrogen retains the molecular phase to 30 GPa and 7000 K. Above these pressure and temperature values, N₂ undergoes a continuous dissociative phase transition. Ross has modeled this dissociation³⁰ and obtained good agreement with the experimentally measured P-V states and the temperature measurements reported by Radousky.³¹ A very interesting aspect of this work is the phenomenon of shock-induced cooling in double shock experiments. The dissociation transition at higher pressures and densities results in sufficient absorption of the internal energy that the temperature of the second shocked state is lower than the first shocked state. Both the calculations by Ross and the experiments by Radousky make a strong case for this interesting phenomenon. The success of the nitrogen work demonstrates the need for a comprehensive investigation to develop a detailed microscopic understanding of shocked materials.

A second example, though not as extensive as the nitrogen work, is the work by Aidun on polycrystalline calcium carbonate (CaCO₃).³² Using the developments by Gupta and coworkers,³³⁻³⁵ shear wave measurements were used to characterize the shocked state.³⁶ An important aspect of this work was the determination of the bulk

modulus in the shocked state³² that permitted a direct comparison with the static data.³⁷ The shock data showed the characteristic drop in the bulk modulus associated with the I \rightarrow II transition³⁷ and the subsequent increase at higher compression. What is most interesting is that at higher compression the bulk modulus values under shock loading are significantly lower than the static values. This difference suggests that, under shock loading, phase III is either not obtained or it transforms to another phase (likely aragonite). Recent static pressure measurements, at high temperatures, by Hess have reported the transformation to aragonite.³⁸

Two potential problems regarding the use of peak states to infer microscopic changes should be recognized. First, the theoretical calculations, though quite sophisticated, ignore any time-dependent response and the material is assumed to be in equilibrium. This assumption though consistent with the assumptions used to also analyze the free surface data may not be correct if the kinetics associated with shock induced changes are comparable to experimental time-scales. A second problem in much of the analysis of shock wave data in solids concerns the neglect of material strength at stresses beyond 10 GPa (the exact value will depend on the material in question). It is reasonable to assume that at stresses approaching several tens of GPa, the numerical error introduced by neglecting a strength of 0.1 to 0.5 GPa is not significant. Hence, for the purposes of assigning P - V values to the peak state, fluid like behavior can be assumed for many materials. However, it should be recognized that even at stresses approaching 100 GPa, the material in the shocked state, in general, is not a fluid. It is likely a solid with large density of defects. For many properties that are sensitive to the details of the crystal structure at the atomic level, the fluidlike approximation may be quite inappropriate. Graham, though using different terminology, has made the same point in an earlier paper.39

2.3. Analysis of Wave Profiles

The use of time-resolved shock wave measurements to probe material response can be understood by considering the conservation equations along with the following identity: σ_{mm}

$$\sigma_{ij} \equiv \frac{\sigma_{mm}}{3} + \sigma_{ij}$$
 (4)

It is easy to see that discontinuities in the mean stressvolume ($\sigma_{mm/3}$ - V) relation or in the stress deviatorvolume (σ_{ii} V) relation can lead to multiple waves.* The discontinuities in the first relation are often associated with pressure induced phase transitions, and the discontinuities in the second relation are generally associated with inelastic deformation. Hence, wave profile measurements provide a convenient method to examine time-dependent, phase transitions and yield behavior. It should be emphasized that only those phenomena that produce wave instabilities or changes in the wave shape can be examined by analyzing wave profiles. Second order phase transitions or other microscopic changes that do not alter the shock wave structure cannot be examined using these methods. Finally, if the wave structure is used to examine condensed matter changes then the role of sample thickness on wave evolution needs to be considered carefully, otherwise phenomena of interest may be neglected because of inadequate wave resolution.

To date, time-resolved stress or particle velocity measurements at different sample thicknesses have provided the maximum information regarding kinetics associated with shock induced changes. Duvall and coworkers have examined extensively the role of timedependent phase changes and inelastic deformation on shock wave propagation in crystalline materials.⁴⁰ An example of their work is the comprehensive investigation that has been carried out to examine the micromechanisms responsible for yielding in shocked LiF single crystals.⁴¹⁻⁴⁶ Although this work has provided a great deal of information about shock induced yielding including the role of slip systems, defects, defect clustering, surface preparation, temperature effects, a definitive micromechanism that explains consistently all observed phenomena has not emerged. It is unlikely that continuum measurements alone will resolve this problem.

2.4 Conclusions from Continuum Studies

Continuum measurements and related theoretical analyses comprise almost all of the available real-time results in shock compression of condensed matter. These

^{*} The case of over-driven shocks is not being considered

studies have provided a great deal of thermodynamic data and contributed immensely to an understanding of condensed matter response at extremely high pressure and temperature conditions. For many of the metals, the agreement between the calculated P-V data and the experimental measurements is impressive.⁴⁷ The ability of the calculations to provide off-Hugoniot results is valuable. The recent work on electronic transitions²⁷ and nitrogen dissociation³¹ is noteworthy.

Despite the many successes, the underlying micromechanisms that control shock induced changes are not well understood. Some outstanding questions for nonreacting materials are: (i) What atomic mechanisms control inelastic deformation in shocked crystals? (ii) What atomic mechanisms control shock induced structural changes? (iii) What structural properties govern transition kinetics? (iv) What is the precise role of microscopic defects on structural changes? (v)Is the fluid-like approximation for shocked solids at large compression valid for understanding microscopic changes?

The study of shock induced chemical reactions and detonation represents a related area in which structural and electronic changes are intimately related to dynamic mechanical deformation.⁴⁸ All of the questions indicated above transfer directly to the chemical reaction problem. In addition, there is the very important and difficult issue of identifying chemical species at different times in the shock compression process. It is unlikely that continuum data can provide details regarding the microscopic changes in condensed materials. To address these questions, current approaches to microscopic measurements are indicated in the next section.

3. MICROSCOPIC MEASUREMENTS

Experimental measurements to achieve a microscopic understanding of shock induced changes can be considered in two broad categories as discussed below.

3.1 Post Shock or Recovery Experiments

Examination of recovered samples, that have been subjected to shock wave loading, has been carried out since the 1950's and this area of research is a field in itself. It is not possible to do justice to this large body of work in a paragraph and the interested reader is referred to the following representative Refs. 49-51.

The principal advantage of these experiments is that the recovered samples can be subjected to a wide variety of material characterization studies: metallurgical (microscopy at different scales), x-ray diffraction, electrical, magnetic, chemical and spectroscopic measurements. Hence, a great deal of information can be obtained about permanent changes at the microscopic level. The work by Decarli and Jamieson⁵² on the graphite to diamond conversion is one of the earliest examples of such studies. In recent years, there has been considerable interest in shock recovery experiments for materials synthesis applications.⁵⁰ Graham and coworkers have emphasized the detailed analysis of such measurements for understanding solid state chemical reactions under shock loading.53 Recent work by Syono and coworkers, summarized at the 1987 Topical Conference at Monterey, has demonstrated the use of electron microscope measurements on obtaining information about phase transition mechanisms in shockrecovered materials that undergo permanent changes.54

Despite the usefulness for understanding material synthesis and permanent changes under shock loading, there remain serious difficulties in relating end results to changes that occur in different parts of the stress pulse.^{55,56} Without very good correlation between stress profiles and microstructural details in recovered samples, it is difficult to establish the microscopic mechanisms responsible for observed changes.

3.2 Real Time Examination of the Shocked State

In terms of understanding atomic/molecular mechanisms under shock loading, real time measurements are expected to be the most useful. However, as discussed later, these experiments are difficult to conduct and to analyze in detail. Two types of experimental measurements have been carried out: x-ray diffraction and optical spectroscopy.

(a) X-Ray Diffraction Measurements: In the early 1970's, Johnson, et al., carried out an impressive set of experiments in which they obtained x-ray diffraction data in shocked single crystals.⁵⁷⁻⁵⁹ These results established the presence of crystalline order behind the shock front and

opened up the possibility of a direct examination of shocked crystal lattices.

More recently, Wark, Whitlock and coworkers have pursued similar measurements using laser driven shock waves. 60,61 A noteworthy aspect of their work is the ability to make time-resolved measurements with subnanosecond resolution. The ability to examine crystal structures directly with such time-resolution offers significant benefits for understanding atomic mechanisms in shocked crystals.

Two aspects of these experiments need further refinement. The spatial uniformity of loading needs to be improved to ensure uniaxial strain, and the separation of compression and tension effects needs to be carried out in rear surface measurements. More data and analysis are needed to determine the full potential of this interesting method for examining structural changes. These experiments, because of their potential to examine lateral strains at the atomic level, are expected to be useful in understanding the nature of inelastic deformation in shocked crystals.

(b) Optical Spectroscopy Measurements: During the 1980's, optical spectroscopy methods to examine the shock response of condensed materials were developed at several organizations: CEA(France), Livermore, Los Alamos, Naval Research Laboratory, Sandia, and in our laboratory at Washington State University. These measurements can be divided into the following two categories: electronic spectroscopy (absorption, emission, fluorescence and reflection) and vibrational spectroscopy (CARS, TRISP, Spontaneous Raman). A noteworthy aspect of the work at Washington State University has been the development of time-resolved measurements for both electronic and vibrational spectroscopies.^{62,63} This feature is important for understanding the mechanisms and kinetics under dynamic loading.

A recent review by Moore and Schmidt⁶⁴ provides a good discussion of spectroscopic techniques in shock compressed materials and the reader is referred to their paper for a discussion of spectroscopic methods. Additionally, the review by Renlund and Trott⁶⁵ is recommended for a discussion of various spectroscopic methods (emission, Raman, TRISP) to examine the response of high explosives. In the next two sections, some of the electronic spectroscopy results obtained in our laboratory are summarized. Therefore, some comments regarding vibrational spectroscopy measurements are presented in the remainder of this section.

Much of the vibrational spectroscopy work to date has consisted of experimental developments to demonstrate the applicability of a particular method to the problem and/or material of interest. The most comprehensive vibrational spectroscopy effort to date is the work on liquid N₂ and O₂ at Los Alamos.^{66,67} These coherent anti-stokes Raman scattering (CARS) measurements by Moore and Schmidt represent an impressive experimental achievement. Unlike spontaneous Raman data, strong signals can be obtained using the CARS method.

Schmidt, Moore and coworkers have provided direct evidence for molecular N₂ up to pressures of 17.5 GPa and 4000 K under single shock loading⁶⁶ and their results support the continuum measurements of Nellis, et al.³¹ The CARS work has resulted in measurements of vibrational relaxation times and vibrational temperatures. These data are rich in detail, and the Raman shifts provide valuable benchmarks for a detailed understanding of interand intra-molecular potentials under shock loading. Because shock compression leads to simultaneous increase in pressure and temperature, these data coupled with static high pressure data are useful in separating pressure and temperature effects.

It should be emphasized that CARS experiments and associated data analysis are non-trivial undertakings. In deciding between a nonlinear optical technique like CARS and a linear technique like spontaneous Raman scattering, the need for stronger signals has to be weighed against the complexity of the experiments and resulting data analysis for a particular problem.

Finally, the time-resolved Raman measurements in α quartz by Gustavsen and Gupta, reported at this meeting,⁶⁸ have provided information about the role of nonhydrostatic stresses on compression at the atomic level. In this study, shift of the A₁ (466cm⁻¹) line is shown to increase significantly in the presence of nonhydrostatic stresses for a given density compression. Shift of the A₁ line in quartz is known to correlate with the decrease of the Si-O-Si bond angle which is the primary compression mechanism in quartz.⁶⁹ Extension of this work to higher compressions is expected to be valuable in understanding the shock compression of quartz.

4. SHOCK RESPONSE OF RUBY CRYSTALS

The wavelength shift of luminescence R-lines of ruby $(Al_2O_3 : Cr^{3+})$ is commonly used for pressure calibration in diamond anvil cell (DAC) experiments.⁷⁰ In 1985, we undertook an effort to determine the feasibility of measuring R-line shifts under shock loading. The feasibility experiments were successful⁷¹ and since then we have had an ongoing effort with two broad objectives: (i) to develop a comprehensive and detailed understanding of the R-line shifts under arbitrary deformation, and (ii) to examine the use of R-lines as a probe of the microscopic environment around Cr³⁺ ion during elastic and inelastic deformation of shocked sapphire. The second objective is related to the questions posed in connection with the idealized problem in Figure 1. In the following paragraphs, a brief summary of our work over the past several years is presented. Details may be seen in Refs. 72-76.

Ruby has a corundum structure with Cr^{3+} replacing $A1^{3+}$ substitutionally. In our samples, there was approximately one chromium ion per 15-20 unit cells. The first-neighbor oxygen-ions form almost an octahedron with respect to the Cr^{3+} ion; strictly speaking, the site symmetry is trigonal and this results in the two R-lines (692.9nm and 694.3nm) at ambient condition. The optical properties of ruby, which arise from the localized nature of the d-electrons, are dominated by the nearest neighbor interactions. Relating the site-symmetry changes to the imposed deformation is essential to meeting the two objectives indicated above.

The mechanical response of sapphire (or ruby), based on acoustic and shock wave data, is nearly isotropic. For example, the end states in shock wave experiments for both elastic and inelastic deformation appear to be independent of crystal orientation;⁷⁷ a plot of all available sapphire data to a longitudinal stress of 40 GPa is the basis for this finding.⁷⁸ Additionally, σ - u plots for elastic compression along cand a-axes, based on third order constants, differ by less than 0.4 percent up to 12.5 GPa.^{75}

A typical experimental setup used in our work⁷² is shown in Figure 2. The ruby thickness (nominally 200 μ m) has been exaggerated for clarity. The incident light and the outgoing luminescence signal are transmitted on the same optical fiber and separated using a dichroic beam splitter. The luminescence signal is dispersed in wavelength and time, and the raw data consist of intensity - wavelength time plots as shown in Figure 3. The spectra shown in Figure 3





were for uniaxial compression along the c-axis and were obtained every 30 ns. Time-resolution to 10 ns can be obtained easily and work for achieving even better time-resolution is currently underway. The precision in wa clength measurements is ± 1 Å.



We have carried out an extensive set of experiments in which ruby crystals have been shocked along both the cand a-axes.^{72,75} Data have been obtained for both compression (to 12.5 GPa longitudinal stress) and tension (to -10.5 GPa longitudinal stress) during elastic loading. The wavelength shifts are completely reversible and there is no change in the quality of the spectra during shock loading; no line-broadening was observed. All of the data showed a red shift in compression and a blue shift in tension. Details of the experimental results may be seen in Refs 72 and 75.

Unlike the continuum results indicated earlier, the Rline data show strong anisotropy. The changes in R_1 - R_2 line splitting, shown in Figure 4, clearly demonstrate both nonhydrostatic and anisotropic effects. Recall, that for hydrostatic loading there is no change in R_1 - R_2 splitting; this result will be manifested as a horizontal line through $\Delta(R_1-R_2) = 0$ in Figure 4. Not only are the two sets of data different numerically, they are qualitatively very different. The c-axis data can be understood in terms of the changes in the trigonal field magnitude but the a-axis data show direct evidence for site-symmetry changes under uniaxial strain loading.⁷³ These results show that the local symmetry at the Cr3+ ion is not preserved under uniaxial compression along the a-axis. This is an important finding because it opens up the possibility for examining symmetry changes under shock loading.73



FIGURE 4

The R-line data from shocked ruby provide a more sensitive indicator of nonhydrostatic and anisotropic response in contrast to continuum measurements. Additionally, the shifts of the two R-lines represent two distinct pieces of information and these can be related to the mean stress and the stress deviators in the ruby. Thus, these data provide a direct measure of the stress difference in the shocked state in ruby; this need was discussed in Section 2.

To relate the macroscopic deformation under shock loading to microscopic changes, a theoretical approach to analyzing ruby R-line data has been developed by Sharma and Gupta.⁷³ In this approach, a symmetry-adapted representation of the various loading conditions in conjunction with crystal field theory (but no point-ion model) is used to relate the shift of the R lines to deformation. The parameters needed in the model are obtained from shock wave compression data along the cand a-axes. Without further iteration, these parameters provide a consistent analysis of all other available data: shock wave tension results, hydrostatic results and uniaxial stress results for both c- and a-axis orientations. The recent work by Shen and Gupta has extended the theoretical work in Ref.73 to analyze more arbitrary deformations.75 The $R_1 - R_2$ splitting data shown in Figure 4 can be modeled quite precisely using the theoretical developments in Refs.73 and 75.

More recently, Shen and Gupta have examined the use of R-lines to probe inelastic deformation in shocked ruby.⁷⁶ These results, the first of their kind, have shown the considerable potential of time-resolved luminescence measurements to probe inelastic deformation in a brittle material like sapphire. As in elastic deformation, the inelastic results show considerable anistropy. These data clearly show the occurrence of inelastic deformation, relaxation of stress deviators, and subsequent residual stresses. A detailed analysis of these results is currently underway and will be published in the near future. The principal findings from the ruby work may be summarized as follows:

(i). The ability to do fast time-resolved spectroscopic measurements in shocked solids was demonstrated.

(ii). The role of nonhydrostatic stresses, crystal orientation and state of loading on R-line shifts has been quantified. Unlike continuum results, the R-line data show strong anistropy and are rich in detail.

(iii). A theoretical model has been developed that explains quantitatively all available R-line data in a consistent manner. Site symmetry changes around the Cr^{3+} ion have been related to macroscopic deformation; the crystal field is altered for uniaxial strain along the crystal a-axis.

(iv). R-line data provide a novel approach to examine shock-induced inelastic deformation at the microscopic level. These data have provided a quantitative measure of stress deviators, relaxation kinetics, strain distribution, and residual stresses beyond the HEL. We are still learning how to analyze these data.

5. SHOCK RESPONSE OF LIQUID CS2

Since 1980, a comprehensive investigation has been underway in our laboratory to understand the electronic and chemical changes in shocked liquid CS₂. Results from these investigations have been published in the literature⁷⁹⁻⁸² and a good review of this work was presented by Yoo at the 1989 Topical Conference in Albuquerque.⁸³ Here, I will review certain aspects of the CS₂ work to address questions relevant to the present paper. Additionally, new results from the reflection spectroscopy work by Gustavsen will be used to link the continuum and absorption studies.^{84,85}

Continuum measurements in liquid CS₂ have been obtained by Dick (single shock)⁸⁶ and Sheffield (double shock).⁸⁷ On the basis of these data and the calculated temperatures (using an equation of state developed by Sheffield and Duvall),⁸⁸ a shock induced chemical reaction has been inferred in CS₂. The end states in these experiments lie in that part of the CS₂ phase diagram (see Figure 1 in Ref. 83) where the CS₂ is known to decompose under static conditions.⁸⁹ The question then arises: what is the nature of the chemical changes in shocked CS₂ over the μ s time scale of these experiments; based on kinetic considerations, the end states in the shock and static high pressure experiments are expected to be different. Continuum measurements alone cannot resolve these issues and spectroscopic data are needed.

Duvall and coworkers have carried out an extensive set of absorption experiments in liquid CS₂ (100-200µm thick) in which shock induced changes to the V-band $({}^{1}\Sigma_{g}^{+}\rightarrow {}^{1}B_{2})$, centered at 320 nm, were used to probe the chemical reaction in CS_2 .⁹⁰ Because of the step-wise-loading (SWL) in these experiments, the measured pressure threshold (8.9 GPa) for irreversible changes was different from the values reported by Dick⁸⁶ and Sheffield.⁸⁷ This observation agrees with the lower calculated temperature in step-wise-loading.⁷⁹ It was demonstrated that a concerted reaction was occurring under shock loading and a case was made for shock induced polymerization by Yoo et. al.⁸¹

Yoo and Gupta have recently reported absorption results⁸² in very thin CS₂ samples (~1 μ m) and a pressure threshold of 11 GPa was determined for irreversible changes. Two noteworthy findings of this study are: (i) the growth of a new band (likely T-band) which could not be seen in the previous, thicker sample, results, and (ii) time-dependent increase in absorbance that suggests molecular rotation. The latter results needs to be confirmed by more direct evidence.

Because of the strong absorption in the CS₂ and because of the need to relate Sheffield's results (doubleshock-loading)⁸⁷ to the absorption measurements (stepwise-loading),90 Gustavsen developed a method for doing time-resolved reflectance measurements (300-500 nm range) in shocked CS₂.⁸⁴ Both double-shock and SWL experiments were conducted. A comprehensive account of the reflection work may be seen in a recent paper by Gustavsen and Gupta.⁸⁵ Some of the results may be summarized as follows: (i) Between 300-500 nm, large reflectance changes are observed under step-wise-loading, (ii) Unlike absorption data, reflectance changes in SWL experiments were reversible over the range of pressures (to 10.5 GPa) examined; this result is a consequence of probing a very thin layer of CS₂ next to the sapphire window, (iv) Unlike Sheffield's results,⁸⁷ the doubleshock experiments show no evidence of a chemical change below 9 GPa; above 9.5 GPa these experiments show evidence of a chemical change and a complicated reflection history.

A phenomenological model was developed to calculate the complex refractive index of CS_2 .⁸⁵ This model, in conjunction with Fresnel's equations, can be used to analyze the SWL reflection and absorption data in a consistent manner. A consistent analysis of the doubleshock and SWL experiments requires that pressure and wavelength dependence of the attenuation length of CS_2 , and temperature effects due to heat conduction be incorporated properly into the data analysis. In general, the results from the reflection experiments support the findings of the absorption results. The reflection data have provided considerable insight into relating electronic and chemical changes under different thermodynamic conditions: double and multiple shock loading.

The overall picture that emerges from the CS_2 work is that the shock wave aligns the molecules and causes intermolecular compression which results in growth of the absorption bands due to increasing overlap of the electronic wave functions of neighboring molecules. This overlap is likely a precursor to an associative chemical reaction resulting in CS_2 multimers. Despite the considerable success in the CS_2 spectroscopic studies, the chemical species on the sub-microsecond time-scale have not been identified. This objective will require time-resolved vibrational spectroscopic measurements and even then it will be a difficult task.

6. CONCLUSIONS AND FUTURE NEEDS

Although time-resolved optical spectroscopic methods provide the most promising approach for addressing the idealized problem in Figure 1, some brief comments regarding the difficulties associated with such measurements are in order.

Under shock wave loading, conducting optical spectroscopy measurements with high time and spectral resolution is a non-trivial undertaking. Practical constraints limit the spectral information that can be obtained in a single experiment; the spectral region of interest has to be chosen in advance. Only the strongest lines or bands can be observed with nanosecond resolution. Achieving high spatial and temporal resolution simultaneously is an outstanding problem. Examination of the shock front continues to be an important need. It is likely that many of these problems will be resolved with improved instrumentation and with further developments.

A good understanding of the shocked state at the microscopic level will require a combination of continuum and quantum mechanical analyses. The interdisciplinary nature of these problems represents a challenging opportunity. Analyses of optical data when "interesting" changes (e.g. inelastic deformation, structural changes, chemical reactions) take place will require considerable skill because the spectral details may be difficult to discern.

As demonstrated by specific examples (N_2 , ruby and CS_2), spectroscopic studies provide a unique method to probe shocked materials at the microscopic level. The use of time-resolved measurements is necessary for achieving an understanding of the microscopic mechanisms controlling shock induced changes. As with any new undertaking, sustained efforts along with a careful choice of materials are crucial for success. Spectroscopic measurements should be viewed as a complement to, but not a substitute for, continuum measurements. Given the complexity of the shock wave experiments, there is no one ideal experiment. Data from different experiments have to be pieced together carefully to form a consistent picture.

In closing, I want to emphasize two final points: First, there exists a strong need to examine theroetically the role of atomic deformation and defects on shock induced processes and kinetics. To date, theoretical developments in terms of calculating P-V curves have been impressive. With availability of increased microscopic results from the spectroscopic experiments, there is a strong need to carry out calculations that provide "microscopic" results and can be related to these data. Second, studies of shock compression of condensed matter are at an exciting stage because of the experimental developments in the past ten years. We are now able to obtain results that can be related more directly to atomic/molecular changes. Hence, there exist considerable opportunities to make important scientific contributions toward understanding condenserd matter response under shock loading.

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STATIC COMPRESSION TO MULTIMEGABAR PRESSURES

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Diamond-cell techniques now permit detailed studies of the physical properties of materials, including dense solid hydrogen, under static conditions to multimegabar pressures (to 300 GPa). Recent diamond-cell experiments in this pressure range are reviewed, with particular emphasis on studies of the crystal structure, vibrational dynamics, and optical properties of hydrogen at very high densities. The continued investigations of pressure calibration standards and characterization of the diamond anvils at very high stresses are examined, and the results of relevant shock-wave studies are compared. Recent hydrogen results include further characterization of the 150-GPa transition, observations of changes in optical properties at higher pressures, and evidence for new transformations.

1. INTRODUCTION

The field of static ultrahigh-pressure research has been developing at an accelerating rate during the past few years. As a result of advances in. diamond-cell techniques, experimental studies at static pressures up to 300 GPa are now possible. This research has now advanced beyond the initial stages of reaching and calibrating pressure.¹ In this new phase of study, detailed investigations of physical and chemical properties of matter under extreme pressure conditions can now be performed. One of the longstanding goals in this research has been the successful pressurization of hydrogen under multimegabar conditions, together with measurement of the unusual properties predicted theoretically for this material at very high densities.² Progress in this field during the past three years has been particularly rapid.³

In this paper we review recent static highpressure investigations carried out to multimegabar pressures, focussing on advances in the study of dense hydrogen. We begin with a brief review of pressure calibration using both ruby fluorescence and x-ray diffraction. Recent x-ray diffraction measurements on hydrogen, which provide crucial information on the crystal structure and equation of state (EOS) are then discussed. We then review spectroscopic studies to ~300 GPa, including studies of the 150-GPa phase transition and changes in optical and electronic properties at higher pressures. Recent observations of stress-induced changes in optical properties of diamond are reviewed. Finally, we present recent observations of new transformations in diamond-cell studies of hydrogen above 150 GPa.

2. MULTIMEGABAR DIAMOND-CELL TECHNIQUE

The attainment of pressure under static conditions in the several hundred gigapascal range with the diamond-cell is now well established, despite early predictions that 100 GPa was not possible with such devices. In fact, these advances were made possible by the single bevel design of the diamond cell over 15 years ago. The basic single bevel design remains the most useful configuration in this range.⁴ A critical development in the evolution of these techniques was the extension of the R_1 ruby fluorescence pressure scale to 100 GPa,⁵ which is currently calibrated to 180 GPa,⁶ This pressure scale is derived from 300 K, *P-V* isotherms of metal standards determined from shock-wave experiments. Pressure calibration of R_1 ruby fluorescence under quasihydrostatic conditions represents an important refinement and has been carried out to 110 GPa.^{7,8} It should be emphasized that the non-hydrostatic scale is the appropriate ruby scale for x-ray diffraction experiments with the same geometry as that used in the calibration. For optical measurements and the studies of hydrogen and related materials, the quasihydrostatic scale is more accurate.

The ruby pressure gauge has been used extensively in megabar studies primarily because of its convenience. It was noted some time ago that ruby measurements above 100 GPa can be complicated by changes in the relative intensities and relative pressure shifts of sidebands of the ruby R_1 (and R_2) peaks.⁹ As shown in Fig. 1, the splitting between R_3 ' and R_1 decreases with pressure, and the intensity of R_3 ' approaches that of R_1 . This could complicate determination of pressure at higher pressures.^{9,10} However, a crossing or hybridization of the levels does not appear to occur to at least 248 GPa (quasihydrostatic scale), although the splitting is small. Measurements in hydrogen samples showed that well-defined ruby R_1 peaks could be measured to this pressure at 77 K.11 Measurements at higher pressures in these experiments have been complicated by the growing intensity of diamond fluorescence.

In all such experiments on hydrogen (and other materials above 100 GPa), the excitation wavelengths of the lasers were varied between 457.9 and 514.5 in order to maximize both the sharpness and intensity of the R_1 luminescence. At lower pressures, 488.0-nm excitation was used; with increasing pressure, the bluer lines (*e.g.*, 476.5 and 457.9 nm) become more efficient. However, above 150 GPa, excitation with the 488.0 nm line again becomes stronger, and this remains the optimal wavelength for excitation above 200 GPa. This has also been found recently by Eggert *et al.*, ¹² who have modelled this behavior in terms of pumping of the *B*-lines in ruby. Measurements of the change in the absorption edge of diamond (see below) indicate that the optimal pumping involves a trade-off between the shift of the effective absorption edge to longer wavelengths and the shift of the ruby absorption bands to shorter wavelengths. These pressure shifts (and excitation energy dependence) should be calibrated further in order to improve the accuracy of pressure calibration above 250 GPa. Ruby R_1 fluorescence is a secondary standard, and other approaches, including the use of primary x-ray standards, are a preferred alternative at higher pressures.



FIGURE 1

R-line fluorescence spectra of ruby at high pressure (hydrogen medium) at 300 K. The wavenumbers are relative to the R_1 line at each pressure, which is determined using the scale of Mao et al.⁷ N and V refer to Cr^{+3} pair and vibronic bands.

3. MULTIMEGABAR X-RAY DIFFRACTION

X-ray diffraction provides the most definitive means of determining pressure in multimegabar experiments. Recently, synchrotron x-ray diffraction experiments at pressures above 200 GPa have been performed to evaluate different pressure standards.¹³⁻¹⁷ Much of this work has involved the use of Pt, which has been recently calibrated to 600 GPa by Holmes *et al.*¹⁸ using both shock-wave techniques and first-principles theory. A large number of experiments indicate that pressures in excess of 300 GPa can be achieved, and these experiments provide cross checks on diamond-cell pressure calibration. The materials examined so far in our laboratory include CsI, Fe, Fe-Ni, FeO, Pb, Re, W, and I₂.¹³⁻¹⁷

The diffraction studies of CsI to 302 GPa provide a useful example of both the cross-check between techniques and interesting high-pressure behavior (Fig. 2).^{13,20} These measurements demonstrated that the discrepancy²¹ between the EOS determined by shock-wave and that found in previous diamond-cell experiments arose from an incorrect assignment of the crystal structure in the latter. The new x-ray data indicated that the solid transforms to an hcp-like structure in its highpressure metallic form, which is also structurally isomorphous with, and has a high-pressure density nearly identical to, solid Xe.²²⁻²⁵

4. HIGH-PRESSURE X-RAY DIFFRACTION OF OF SOLID HYDROGEN

The crystal structure of hydrogen at high densities and its P-V EOS are central to understanding details of its high-density behavior, including metallization. The first structural studies by x-ray diffraction on hydrogen in the diamond-cell were performed at 5.4 GPa in 1987.²⁶ These measurements were followed by singlecrystal diffraction using synchrotron radiation to pressures of 26.5 GPa for hydrogen²⁷ and 14.5 GPa for deuterium²⁸ (300 K). The latter were close to the neutron diffraction results reported by Glazkov *et*



FIGURE 2

P-V equation of state for CsI (Mao et al.¹³) compared with that of Xe (Jephcoat et al.,²² solid triangles; Reichlin et al.,²³ open triangles). The solid line is the result of the APW (Ross and McMahan).²⁵ The dashed line is the 300 K equation of state for CsI calculated from exp-6 potential determined from lower pressure shockwave data (Radousky et al.²⁴)

 $al.^{29}$ These studies have established that the crystal structure of the two isotopes is hexagonalclose packed (hcp) over the measured pressure range.

We have recently extended these measurements to 38 GPa, which corresponds to a relative density of $\rho/\rho_0 = 5.6$, using synchrotron radiation from a superconducting wiggler source.^{30,31} The *P*-V results, shown for deuterium in Fig. 3, are consistent with our previous lower pressure data and the EOS calculated from them. The x-ray and neutron data²⁹ are in good agreement over the pressure range where the two data sets can be compared. However, the volumes obtained in the neutron data appear to be systematically lower than those obtained by x-ray diffraction. This difference is small in comparison to the discrepancy between both diffraction results and the EOS determined optically by van Straaten and Silvera,³² in which the pressure is significantly overestimated. Previously, we showed that there is a need to modify effective pair potentials determined from shock-wave data³³ to fit the x-ray diffraction data for the solid.²⁹ Comparison between the calculated EOS and the experimental data illustrate the need for further refinement of intermolecular potentials for the dense solid.



FIGURE 3

P-V equation of state for solid D₂ (300 K). The new single-crystal x-ray data^{30,31} are compared with the earlier x-ray results from Hemley et al.²⁸ and neutron diffraction data of Glazkov et al.²⁹ The EOS fit (solid line) is the fit reported in Ref. 28 with V_0 =19.94 cm³/mol, K_0 =0.35 GPa, and K_0 '=6.64 and the thermal contribution calculated from a Debye model. The exp-6 curve (dashed) shows the results of lattice dynamics calculations with α =10.9, ε =36.4 K and r*=3.43 A (Ref. 28). The equation of state determined optically by van Straaten and Silvera³² is also shown (dotted line).

5. VIBRATIONAL DYNAMICS OF HYDROGEN AT HIGH PRESSURES

The characterization of solid hydrogen at higher pressures, in the megabar and multimegabar range, has relied exclusively on spectroscopic techniques used in conjunction with the diamond cell. Vibrational Raman spectroscopy has been particularly useful because this technique can be used to probe the intramolecular stretching vibration (vibron), which is a sensitive measure of the state of bonding in the solid. The first diamondcell measurements were carried out by Sharma et $al.^{34}$ who documented the turnover of the intramolecular stretching mode in studies carried out to 60 GPa. Subsequent measurements showed that this trend continues to 147 GPa (300 K).³⁵ Later experiments showed that samples of hydrogen in the diamond cell appear to be more stable at low (e.g., liquid-nitrogen) temperatures. As a result, the pressure range of diamond-cell experiments was extended to approximately 300 GPa.^{11,36}

Measurements of the Raman-active vibron in this ultrahigh pressure range showed that the molecular solid is stable to ~250 GPa, although the weakening of the molecular bond indicated by the decrease in the vibron frequency with pressure continues over this range (Fig. 4).¹¹ At the highest pressures for which accurate measurements were made for the vibron, evidence for resonance enhancement was found. This corresponded to vibron frequencies below 3725 cm⁻¹ (Fig. 5). The vibron peak could not be measured at the highest pressures (>250 GPa). This could be indicative of a phase transition, either to a new molecular phase with a significantly different vibron frequency or even to a non-molecular phase. However, this interpretation remains speculative, since the measurements were complicated by the onset of strong luminescence bands and perhaps structural changes in the diamond anvils (see below).

Bands in the low-frequency Raman spectrum (<1000 cm⁻¹) arise from rotational and lattice mode excitations. These peaks are characteristic of the

state of rotational ordering and the symmetry of the crystal structure. As such, measurements in this range complement the direct structural studies by x-ray diffraction.^{37,38} Detailed lowfrequency Raman measurements have confirmed that the underlying hexagonal structure persists to pressures above 150 GPa.³⁷ Moreover, the spectroscopic results suggest that the molecules do not order abruptly within this structure but continue to undergo large amplitude vibrational motions in the very high density state.

6. THE 150-GPa TRANSITION

The high-pressure Raman measurements also revealed a major discontinuous shift in the vibron frequency of ~100 cm⁻¹ at 150 GPa (77 K), which was identified as a phase transition in the molecular solid (Fig. 4).¹¹ Considerable work has been directed at understanding the nature of this phase transition since its discovery in 1988. A number of different transitions are possible in this pressure range, including orientational ordering, structural transitions, an electronic transition, includ-



FIGURE 4

Pressure dependence of the Raman-active vibron of hydrogen at 77 K.¹¹



FIGURE 5 Raman spectrum of the hydrogen vibron at 77 K and >200 GPa.³⁶

ing both metallization itself or the formation of a (localized) excitonic state.³ The first measurements showed that the character of the transition was compatible with an order-disorder transition expected at these *P*-*T* conditions.¹¹ A series of experiments on deuterium revealed a similar transition at a higher pressure in the heavier isotope.³⁹ These results demonstrated that the transition is distinct from the orientational ordering observed at lower pressures.³⁹ Support for this interpretation was subsequently reported by Lorenzana *et al.*⁴⁰ on the basis of measurements of the temperature dependence of the transition (to 167 GPa).

Further information on the nature of this transition has been obtained from measurements of the low-frequency Raman spectrum.^{37,38} A gradual broadening of the rotational or librational bands was observed in both isotopes with increasing pressure above 100 GPa. Remarkably, the character of the bands appeared to be little affected by the vibron transition, which confirmed that the principal changes occur in the intramolecular bonds and are not orientational. Direct measurements as a function of temperature between 77 and 300 K show evidence for critical behavior in the transition with a $T_c \leq 150$ K.⁴¹ (Fig. 6). Lorenzana et al.⁴² subsequently reinterpreted their earlier results and found agreement with our direct observations in the vicinity of the critical point. Recent measurements reveal critical behavior in the D₂ transition, providing additional support for the observations in H₂ and a determination of the isotope effect on $T_c.^{43}$

Lorenzana et al.⁴⁴ have identified the 150-GPa transition as one of orientational ordering. The featureless spectra reported in that study, however, can be interpreted in other ways.^{3,37} On the basis of band calculations, Garcia et al.⁴⁵ have proposed that the transition is associated with ordering and further that the ordered highpressure phase is metallic. However, Kaxiras et al.⁴⁶ have found by similar theoretical methods that there are lower energy structures based on hcp that have wider band gaps than the previously considered ordered structure; hence ordering transitions can actually increase rather than decrease the band gap. Transitions among these closely related structures could occur with



FIGURE 6 Frequency-temperature plot at the vibron discontinuity showing evidence for critical behavior in the hydrogen 150-GPa transition.⁴¹

increasing pressure and hence be associated with the vibron discontinuity.⁴⁶ A detailed, quantitative description of the transition that explains the lowand high-frequency spectra, temperature dependence, critical behavior, and changes in optical spectra above 150 GPa requires further study.

7. OPTICAL SPECTRA OF HYDROGEN ABOVE 150 GPa

In principle, the transition to the predicted metallic phase could be determined from measurement of the onset of dc electrical conductivity or a change in magnetic properties. Measurements of this type have been performed on other materials only at comparatively low pressures (<30 GPa).47 At higher pressures, absorption and reflectivity measurements can reveal the onset of Drude-type behavior diagnostic of metallization. A few studies of pressure-induced insulator-metal transitions have been reported above 100 GPa, all of which show relatively small changes in reflectivity (e.g., <5% in the near-infrared).^{23,48,49} Such measurements at multimegabar pressures are complicated by the small size of the samples (<20 microns), changes in the intrinsic optical properties of diamond anvils, and physical optical effects associated with deformation of the anvils.

Optical measurements carried out on ~5-micron samples demonstrated that samples remained essentially transparent to at least ~200 GPa and that no large-scale changes in optical properties in the visible occur at the 150-GPa transition.³⁶ Ruby fluorescence in the hydrogen experiments could not be measured above ~250 GPa, but in a number of experiments, the load could be increased further and optical spectra measured. At pressures estimated to be 250-300 GPa, the samples darkened. This interpretation was supported by the results of a series of control experiments on other materials compressed in the same range. No direct evidence for the closure of the band gap was obtained, although it was suggested that if the band gap is indirect as predicted by theory⁵⁰ then band overlap could occur at lower pressures without resulting in large changes in the visible spectrum (see also, Refs. 45, 46).

More recently, we have performed a series of experiments on larger samples at pressures up to 200 GPa and over a wider wavelength range in order to understand these changes in more detail, and specifically to examine possible changes in the optical properties in the vicinity of the 150-GPa transition.⁵¹⁻⁵³ Extension of the lower energy limit of the spectra in the near infrared (from 1.5 to 0.5 eV) was crucial in these measurements. These studies showed that there is a systematic rise in both the reflectivity and absorption below 0.7 eV. Further, these changes were observed in four separate experiments on hydrogen samples.

The results could be fit with a Drude-type model with relaxation time as expected if the system indeed underwent a transition to a conducting state. The specific values for the parameters obtained from analyses of the spectra, however, strongly depend on assumptions concerning the index of refraction and dispersion of the diamond anvils under these conditions, which have not been determined independently.51,52 For example, the analysis showed that the amount of absorption measured below 0.7 eV is smaller than that expected from simple fits to the reflectivity if the index of refraction of the hydrogen $n_{\rm H}$ is assumed to be greater than that of diamond n_{d} . However, it is possible to fit both the absorption and reflectance spectra to a dielectric model if $n_{\rm H} < n_{\rm d}$. The measurements show that the absorption strength is insufficient to attenuate interference fringes measured in one sample.⁴⁵ This result was also analyzed by Eggert *et al.*, 54 who also found that the absorption remains low, although they were unable to measure the changes in the near infrared because of the limited wavelength range of their measurements. In addition, careful measurements⁵³ of the index of refraction to 170GPa demonstrate that the dielectric catastrophe

predicted previously⁵⁵ at 150 GPa by pressure extrapolation does not exist.

Other factors to be considered are contributions from vibrational or interband transitions, preferred orientation effects (e.g., if the material is highly anisotropic at these pressures), or the formation of a thin conducting layer of material at the diamond-hydrogen interface (which would be highly reflecting and weakly absorbing), or by diffusion of impurities into the hydrogen from the gasket. These possibilities could be tested by extending the infrared measurements to still lower energies and extending the structural x-ray studies to still higher pressures (e.g., >100 GPa).⁵²

Ruoff and Vanderborgh⁵⁶ speculated that the changes in reflectivity were due to reduction of Al₂O₃ by hydrogen to form Al metal in a composite. We have recently shown that this hypothesis is incorrect, because the changes in near-infrared spectra are independent of the amount of ruby present and occur, in fact, when no ruby is present.⁵⁷ Also, no abrupt changes in the intensity of the ruby fluorescence were observed (*e.g.*, Fig. 1). Finally, the proposed model⁵⁶ applies to a sample consisting of at least 60% (volume) of submicron-sized (0.1 μ m) ruby particles, whereas in the experiments in question, the ruby consisted primarily of 1-3 μ m grains with maximum volume fraction of <5% at high pressures.

8. OPTICAL TRANSITIONS IN DIAMOND

In order to effectively discriminate between the properties of hydrogen (and other materials) at high pressures and those of the anvils, it is essential that the optical properties of diamond itself be examined.⁵⁸ It was clear from the first studies of hydrogen above 150 GPa that significant changes in the optical properties of the diamonds can occur at these pressures,^{11,36} the same pressure range in which new phenomena in hydrogen are observed. The changes in diamond were ascertained by making detailed comparisons of the results from a large number of runs on

hydrogen, related materials, oxides, and metals having a wide range of material properties. A total of over 30 different experiments terminating at pressures above 150 GPa were performed. The large number of experiments was essential because of the natural variability in the impurity content of diamond anvils and different optical response of the diamonds due to differences in stress conditions from one experiment to the next.

A large shift in the absorption edge in diamond and the appearance of new fluorescence bands with visible laser excitation have been observed.⁵⁸ The shift in the absorption edge with increasing sample pressures is similar in both Type I and II diamonds above 100 GPa. Since it appears to be independent of the impurity content, we suggest that this shift represents a change in electronic structure intrinsic to diamond. The effective absorption edge is lower in weaker (e.g., hydrogen) samples. This suggests that the shift is largely an effect of non-hydrostatic stresses in the diamond, perhaps as a result of stress concentration as the diamond deforms at the interface of the strong gasket and weak sample. At the very highest stresses, a sudden onset of yellow to brown coloration at the anvil tip is typically observed.

Measurements of spatially resolved Raman spectra at the tips of the anvils under these conditions reveal additional changes (Fig. 7). Measurements of the T_{2g} phonon of diamond at the anvil tips show the elastic response documented in the early studies to ~40 GPa continues well above 200 GPa. However, in some runs new Raman transitions are observed at 140-150 GPa at low frequencies (590 cm^{-1}). When measurements are carried out with visible lasers (476.5-514.5 nm), relatively sharp fluorescence bands are observed, but careful studies, including those carried out at longer wavelengths, show that Raman features are also present. The observation of this peak in numerous experiments with a variety of samples indicates that the peak is not associated with the samples. Experiments with hydrogen samples at

higher pressures have shown evidence for additional peaks in the anvils at 1950-2000 cm⁻¹ (Fig. 7) and at 900 cm⁻¹. It is not known whether the new peaks are associated with the incorporation of hydrogen in the anvil. No evidence for the formation of C-H bonds (peaks at ~3000 cm⁻¹) has been found.

9. EVIDENCE FOR NEW TRANSFORMATIONS

Recently, we have extended measurements of the low-frequency Raman spectrum to higher pressures and have obtained evidence for new transformations at 150-250 GPa.⁵⁹ Raman spectra of hydrogen as a function of pressure at 77 K from one of our experiments are shown in Fig. 8. The low-frequency region is characterized by broadened bands identified as large-amplitude librational bands that correlate with the $S_0(0)$ and $S_1(0)$ rotational envelopes observed at low pressure.³⁷ The weak, but sharper, band associated with the



FIGURE 7

Examples of Raman spectra of diamond at the sample-anvil interface. a. Zero-pressure. b. 160 GPa (nitrogen sample). c. >250 GPa (hydrogen sample). d. ~300 GPa (neon sample).

Raman-active optical phonon at 950 to 1000 cm⁻¹ is also observed. No significant change in the lowfrequency region is observed at the phase transition,³⁷ as noted earlier. When the pressure is increased further, however, an intense peak at 240 cm⁻¹ grows in over a small pressure interval. The band shifts with pressure, reaching 280 cm⁻¹ at 190 GPa. The peak also appears to be asymmetric, being slightly skewed to the high-frequency side. Study of the temperature dependence of the band reveals that the intensity weakens appreciably with



FIGURE 8 Low-frequency Raman spectra of diamond-cell samples of hydrogen at 77 K showing the appearance of the new feature at 240 cm⁻¹.

increasing temperature, becoming very weak above approximately 180-200 K. Further experiments have shown that the onset pressure of the peak can occur over a wide range (150 to above 180 GPa). Also, the new feature exhibits a large hysteresis, with the band present at sample pressures as low as 50 GPa before disappearing (at low temperature). We find that the band is present even when the vibron is very weak or in fact has disappeared.

From these observations and measurements, we conclude that the 240 cm⁻¹ band is associated with a new pressure-induced transformation in the diamond-cell sample. Three possible interpretations are proposed. First, the new band is a vibrational mode signalling a transformation in bulk hydrogen associated with ordering or crystallographic change. According to this assignment, the band arises from a librational mode (libron) in an ordered structure, as discussed above. A series of experiments on the heavier isotope performed to test this assignment has shown that the new peak occurs in D_2 samples within at most 5 cm⁻¹ of that observed in H_2 . The similar frequencies in experiments with the two isotopes suggests that the peak is not associated with a simple librational mode and that the transition does not involve simply orientational ordering.

Second, the band is a vibrational mode in a new phase of diamond forming at the tip of the anvil. The new band, however, does not appear to correlate with any known bands in carbon phases, nor does it match stress-induced changes that we documented in diamond anvils under similar conditions with other samples, as described above. We have not observed the peak in experiments with samples of Ne, NaCl, and Al₂O₃ in this pressure range; however, we cannot rule out changes in diamond due to the presence of hydrogen (or deuterium) either bound chemically or in contact physically as a distinct phase. The lack of an isotope shift indicates that the mode does not involve hydrogen or deuterium motions, and no other