

Preface

This volume, belonging to the series “High-Pressure Shock Compression of Solids”, focuses on the utility of static-compression studies of energetic materials to understand shock processes such as detonation. Static compression, initially based on P. W. Bridgman’s work during the first half of the 20th century, launched into its own science in 1959 when the diamond anvil cell (DAC) was developed and subsequently utilized as a primary tool to achieve very high pressures. One motivation for this book is to document the history of the development of the DAC and its associated analytical techniques to the study of energetic materials at static high pressures. Another incentive is to present recent work utilizing the DAC in several areas relevant to understanding the behavior of energetic materials at high static pressures.

In the late 1960s, three scientists at the National Bureau of Standards (NBS) in Washington, DC, S. Block, C. E. Weir, and G. J. Piermarini (the co-editor of this book), were actively involved in the development of a single crystal x-ray diffraction technique utilizing the DAC. Several papers describing the progress they were making in that area had been published, demonstrating promising results. However, one major obstacle had not been overcome, and that was the ability to measure accurate sample pressure in the DAC in a simple, routine, and rapid way. Research scientists at the Explosives Laboratory, Picatinny Arsenal, Dover NJ, were aware of the NBS work and were following its progress with great interest. In 1969, the Picatinny scientists approached the NBS group and asked if they would try the new high-pressure single-crystal x-ray diffraction technique on several inorganic azides that were of interest to them. They desired information on pressure-induced polymorphism and anisotropic compressibility of these azides, data that were unavailable at that time.

The NBS scientists initial response, to say the least, was not very enthusiastic, because they pointed out that such data required a knowledge of sample pressure and also a hydrostatic pressure environment due to the desired anisotropic properties of the crystals. Both pressure and hydrostaticity were quite unreliable at that time because of the lack of exact measurement capabilities with respect to those properties. The Picatinny scientists were more optimistic than the NBS group and suggested that they undertake the study to see where it would lead. After some deliberation, the NBS group agreed to take a look at these azides, but only when they

could fit the work into an already busy schedule. They cautioned the Picatinny scientists that it might take months before they could get meaningful results, if at all. The Picatinny scientists presented a convincing argument to study these materials. They noted that little work on explosive materials at very high pressures and also at elevated temperatures had been published because of the nature of the experimental conditions available at that time, i.e., relatively large volume presses had to be used to generate the pressures needed to obtain useful data such as compressibility, thermal stability, pressure-induced polymorphism, etc. Few contemporary experimental scientists were willing to conduct such experiments owing to the danger of the sample detonating inside the anvils of the press, jeopardizing the safety of the researchers. So it was that the NBS scientists were introduced to studying energetic materials at high pressures in a DAC. Little did they know or appreciate the far-reaching consequences of their decision to study pressure effects on these azides.

In 1970, the DAC was an unsophisticated piece of equipment and the technology associated with it for pressure measurement was rudimentary (known freezing pressures of the pressure-transmitting media were used to define the pressure), but nevertheless the NBS scientists were able to obtain useful data with it, and, in the case of the azides, some of the data were reported for the first time. Since then, DAC technology and the means for measuring sample pressure in the instrument (e.g., the ruby fluorescence method and now other more recently developed techniques) have dramatically progressed. The DAC has been transformed from a rather crude qualitative instrument to the sophisticated quantitative research tool that it is today, capable of routinely producing and measuring sustained static pressures in the multi-megabar range and readily adaptable to numerous scientific measurement techniques because of its optical window, miniature size, and portability.

Today, the DAC is the premier instrument of choice for conducting experiments of all kinds and in all disciplines which utilize the static high pressure and temperature variables. Indeed, for static high pressure/temperature studies on energetic materials, the DAC has become a widely used indispensable tool especially for studying these very sensitive energetic materials with multiple phase transitions at small pressure/temperature changes. Common energetic materials such as ionic ammonium nitrate, ammonium perchlorate, sodium perchlorate, and the molecular solids, NM, TNT, HMX, RDX, and TATB when initiated, undergo rapid decomposition resulting in a high-pressure high-temperature shock wave or detonation. This is a complex process to accurately describe, being a combination of almost-instantaneous chemical, mechanical, and physical changes, requiring estimations of high-pressures, high-temperature thermodynamic properties, chemical kinetics, and reaction mechanisms. Fortunately, as described in this book, DACs allow the design of well-defined static experimental conditions with accurate analytical measurements, leading to a much better understanding of the behavior of energetic materials with respect to initiation, reaction, and detonation processes. The various chapters in this book will attest to this fact, because much of the experimental data represented in these chapters were obtained with the DAC.

Because of its enormous popularity in the scientific community, and because many users of the DAC are unaware of its origin due to its many modifications,

the history behind the invention of the DAC at NBS is presented in Chapter 1. This chapter highlights the development of the original lever-arm type DAC together with a description of four other generic types of DACs developed later. Also described are several analytical techniques – optical polarizing light microscopy, infrared absorption spectroscopy, and powder- and single-crystal x-ray diffraction – that were applied successfully for the first time to the study of energetic materials at static high pressures.

In addition, Chapter 1 describes a process of invention, which illustrates a concept that unique and original research often is not planned by the organization, but originates from the scientists themselves, who must be highly qualified and motivated to do research. Planned research assumes that certain predictable results will be achieved, and therefore, funding can be justified by the institution. Unfortunately, this line of reasoning frequently produces mediocre scientific results. The quintessential message proffered in Chapter 1 is that the development of the DAC was not planned in advance; but, after its conception by the scientists themselves, the work was allowed to simply progress, until ultimately its importance was recognized and financially supported.

Chapter 2 explains the utility of static high pressures to synthesize energetic materials. The ultimate intent of the research described in this chapter is to create high-nitrogen or polymeric nitrogen materials. Thus, it describes the creation of single-bonded crystalline nitrogen, synthesized from N_2 at $P > 100$ GPa and $T > 2,000$ K. The material has a cubic-gauche (cg-N) structure, which was determined from x-ray diffraction and Raman measurements.

Chapter 3 elucidates experimental measurements of the pressure–volume equations of state of energetic materials and their phase transitions at high pressure and temperature, while Chapter 4 explains the same for binders and polymers used in the formulation of explosives. The adaptation of the DAC for x-ray diffraction experiments, Raman and Brillouin spectroscopy, and other analytical techniques is detailed. The influence of nano- to micron-scale features of binders and polymers, on the equation of state of formulated explosives is explained.

Chapter 5 highlights dynamic techniques with the DAC, utilizing time-resolved spectroscopy to study complex processes of rapid mechanical, physical, and chemical changes that occur during the detonation of an energetic material. Chapter 6 discusses static experiments that allow a detailed understanding of these complex processes at the molecular level to illustrate the interplay between static and shock experiments.

Chapter 7 describes molecular dynamics simulation methods and applications to energetic materials under high compression. Applications using both electronic-structure-based methods and conventional molecular dynamics methods employing empirically derived force fields are given, as well as a discussion on advantages and limitations/deficiencies of the various methods and models. Chapter 8 addresses how defects affect the initiation and detonation of energetic materials. Ab initio modeling of several energetic materials is used to elucidate the effect of electronic and spatial structure of defects and their complex involvement in initiation of the explosion process.

The editors wish to acknowledge the demanding efforts of all the contributing authors to this book, and also to recognize their personal contributions to static compression and its utility in studying energetic materials. This is a dynamic and diverse field with many questions still to be investigated, leaving exciting possibilities for future work.

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