Available online at www.sciencedirect.com

ScienceDirect

MATTER AND RADIATION AT EXTREMES

Matter and Radiation at Extremes xx (2016) 1–13

www.journals.elsevier.com/matter-and-radiation-at-extremes

Research article

How far away are accurate equations of state determinations? Some issues on pressure scales and non-hydrostaticity in diamond anvil cells

Lei Liu [a,b], Yan Bi [a,*]

[a] *National Key Laboratory of Shock Wave and Detonation Physics, Institute of Fluid Physics, China Academy of Engineering, Mianyang, 621900, China*
[b] *Department of Earth Science, Uppsala University, Uppsala, SE, 75236, Sweden*

Received 29 March 2016; revised 19 May 2016; accepted 27 May 2016
Available online ■ ■ ■

Abstract

The equations of state (EOSs) of materials are the cornerstone of condensed matter physics, material science, and geophysics. However, acquiring an accurate EOS in diamond anvil cell (DAC) experiments continues to prove problematic because the current lack of an accurate pressure scale with clarified sources of uncertainty makes it difficult to determine a precise pressure value at high pressure, and non-hydrostaticity affects both the volume and pressure determination. This study will discuss the advantages and drawbacks of various pressure scales, and propose an absolute pressure scale and correction methods for the effects of non-hydrostaticity. At the end of this paper, we analyze the accuracy of the determined EOS in the DAC experiments we can achieve to date.

PACS codes: 62.50.-p; 64.30.-t; 07.35.+k

Keywords: Equation of state; Pressure scale; Nonhydrostaticity effect; Diamond anvil cell

1. Introduction

The equations of state (EOSs), which link the thermodynamic variables (pressure, temperature, volume, *etc*.) of materials, are of great interest to condensed matter physicists, material scientists, and geophysicists. The EOSs of materials are appropriate benchmarks for testing the validity of various theoretical models in condensed matter physics. In geophysics, the EOSs of the candidate minerals in the Earth's interior are indispensable for building its compositional model.

Benefiting from the developments of synchrotron X-ray diffraction (XRD) and double-sided laser heating techniques in the past decades, the diamond anvil cell (DAC) is routinely used to determine the EOS of materials up to 100 GPa and 3000 K [1]. The highest pressures and temperatures that can be achieved in DAC are up to ~750 GPa [2] and ~6000 K [3]. In laser heating DAC experiments, the pressure is determined from the pressure scales (*e.g*., known EOSs of materials, the ruby fluorescence pressure scale, or other secondary optical pressure scales); the temperature is determined from the thermal radiation spectrum of samples; and the volume is determined from the X-ray diffraction patterns of samples [1].

In this paper, we focus on EOS determination under ambient temperatures. Currently, the uncertainties of pressure scales and the effects of non-hydrostaticity in DAC prevent us from achieving accurate EOS. We attempt to address the uncertainties of various pressure scales, and analyze the non-hydrostaticity effects quantitatively in volume determination (and subsequently the pressure determination) of materials by XRD technique under high pressures.

* Corresponding author.
E-mail address: biyan@hpstar.ac.cn (Y. Bi).
Peer review under responsibility of Science and Technology Information Center, China Academy of Engineering Physics.

http://dx.doi.org/10.1016/j.mre.2016.06.002

This paper is organized in three parts: various pressure scales and their advantages and disadvantages are summarized and discussed in Section 2; the effects of non-hydrostaticity and methods to correct them in DAC XRD experiments are discussed in Section 3; and in Section 4, we analyze the accuracy of the determined EOSs we can achieve to date.

2. Pressure scale

There are two categories of pressure scales in DAC experiments: (1) the known EOSs of materials derived from experiments (ultrasonic [4–7], shock-wave [8–10], Brillouin scattering and X-ray diffraction [11], etc.) or theoretical calculations (thermodynamic calculations [12,13] and density function theory (DFT) calculations [14,15]); and (2) the pressure scales calibrated against the known EOSs of materials, especially the optical pressure scales (fluorescence of ruby [16,17] and $SrB_4O_7:Sm^{2+}$ (SBO) [18–20], Raman signal of diamond [21–24] and *c*-BN [25–27], etc.). The first category of pressure scales is impractical in bench-top experiments, where high intensity X-ray is often unavailable, whereas the calibrated optical pressure scales are widely used. Generally, pressure standard candidates have simple and stable crystal structures in a wide pressure and temperature range, and are chemically inert to the samples and pressure transmitting media (PTM). This section introduces how various pressure scales were established, and discusses the advantages and disadvantages of each pressure scale. At the end of this section, we propose an absolute pressure scale with refined sources of uncertainty.

2.1. Known EOS of candidate materials

2.1.1. Analytical EOS and ultrasonic determination

The elastic constants and subsequently the bulk moduli of materials can be derived by determining their acoustic wave propagation velocities in single crystals along different directions, with ultrasonic techniques. Fitting the obtained pressure-bulk modulus data provides constrains on the pressure derivative of the bulk modulus. Basically, this is the normal approach to obtain materials' accurate bulk moduli and its pressure derivatives. Unfortunately, traditional ultrasonic techniques are limited in low pressure ranges, usually below 20 GPa [28]. However, recent advances in gigahertz ultrasonic techniques [29], laser ultrasonic techniques [30], and inelastic X-ray scattering techniques [31] in DAC experiments have extended the pressure limit to mega-bar range.

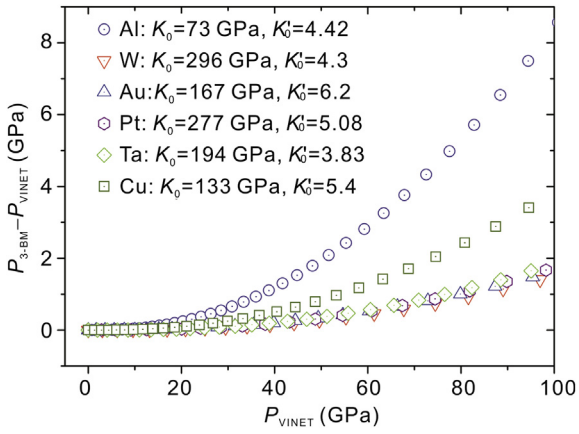

Fig. 1. The pressure difference of Al, W, Au, Pt, Ta, and Cu, when using the same K_0 and K_0' values but different EOS formulas. The K_0 and K_0' values determined by ultrasonic techniques are from Ref. [4] for Al, Ref. [7] for W, Ref. [5] for Au, Ref. [37] for Pt, Ref. [6] for Ta and Ref. [5,38] for Cu respectively.

The obtained bulk modulus and its pressure derivatives are plugged into EOS formulas to describe the compressive behavior of materials under higher pressures. The most widely used EOS formulas are the third-order Birch–Murnaghan EOS (3-BM) [32,33]:

$$P=\frac{3K_0}{2}\left[\left(\frac{V}{V_0}\right)^{-7/3}-\left(\frac{V}{V_0}\right)^{-5/3}\right]\times\left\{1+\frac{3}{4}\left(K_0^{'}-4\right)\left[\left(\frac{V}{V_0}\right)^{-2/3}-1\right]\right\} \quad (1)$$

and the Vinet EOS [34,35].

$$P=3K_0\left(\frac{V}{V_0}\right)^{-2/3}\left[1-\left(\frac{V}{V_0}\right)^{1/3}\right]\exp\left\{\frac{3}{2}\left(K_0'-1\right)\left[1-\left(\frac{V}{V_0}\right)^{1/3}\right]\right\} \quad (2)$$

where V, V_0, K_0 and K_0' are the volume at pressure P, the volume at ambient pressure, the bulk modulus at atmospheric pressure, and the pressure derivative of the bulk modulus, respectively. We are now concerned with the following question: for a material with given volume V, are there any differences in pressure if we use the same K_0 and K_0' values but different EOS formulas to calculate its pressure? We calculated the isotherms of six widely-used pressure standard materials (Al, W, Au, Pt, Ta and Cu) with the 3-BM and Vinet EOS formulas respectively, using the same K_0 and K_0' values. The pressure differences for each material are illustrated in Fig. 1. The 3-BM EOS formula gives a higher pressure for all six materials. Below ~20 GPa, the two EOS formulas give consistent pressures. However, the pressure difference reaches ~8% for Al, ~4% for Cu, and less than 2% for W, Au, Pt and Ta at 100 GPa. These pressure differences cannot be ignored, especially for Al and Cu. This result demonstrates that we must carefully choose appropriate EOS formulas to describe the compressive behavior of materials. The Vinet EOS formula, derived from an empirical inter-atomic potential, is more suitable to describe compressible solids under high pressures [36].

2.1.2. Shock-wave reduced isotherms (SWRIs)

(1) Grüneisen framework

The isotherms reduced from the Hugoniot curve within the framework of the Grüneisen EOS or Grüneisen function [9,16,39] are:

Please cite this article in press as: L. Liu, Y. Bi, How far away are accurate equations of state determinations? Some issues on pressure scales and non-hydrostaticity in diamond anvil cells, Matter and Radiation at Extremes (2016), http://dx.doi.org/10.1016/j.mre.2016.06.002