Reprinted from The Review of Scientific Instruments, Vol. 35, No. 2, 175–182, February 1964
Printed in U. S. A.

High Pressure–High Temperature, X-Ray Diffraction Apparatus*

J. Dean Barnett and H. Tracy Hall†
Brigham Young University, Provo, Utah
(Received 29 August 1963)

A tetrahedral-anvil press has been developed that permits x-ray diffraction powder measurements at pressures to 75 kb and temperatures to 1000°C. A counting technique, rather than photographic film, is used for x-ray detection. Sample tetrahedra of compressed LiH, boron, and boron-filled plastic are used in place of the pyrophyllite customarily used for this purpose. Two possible entrance pupils are used for the x-ray beam; (1) through an anvil face, and (2) through one of the compressible gaskets. Examples of the use of this versatile apparatus for determining crystal structures (KCl, Ba, and Sn), volume compressibility (Ba), lattice-parameter changes (BN), and phase diagrams (Sn) are given.

I. INTRODUCTION

A SURVEY of procedures currently being utilized to study materials under high pressure, high temperature conditions indicates a need for developing improved techniques for obtaining more fundamental information. The relative ease with which the electrical resistance of semiconductors and metals can be measured as a function of pressure has made this the dominant procedure used to explore polymorphism, melting, etc. Such measurements, however, yield little fundamental information concerning the new phases discovered.

The use of x-ray diffraction analysis to obtain basic data is rather obvious, and attempts to use this method were discussed in the literature as early as 1933. The prime contribution of x-ray diffraction data to the field of high pressure research is in structure analysis. Since any microscopic theory of the solid-state properties of a material is structure dependent—in fact, usually structure dominated—the theoretical interpretation of most observed phenomena is ambiguous without structure data. Such data also give the most meaningful information concerning chemical bonding. In addition to the usefulness of x-ray diffraction data in structure determination, x-ray analysis must also be considered as a valuable and versatile tool for observing other solid-state phenomena. The pressure independence inherent in the diffraction process eliminates some of the most troublesome problems encountered in pressure-dependent systems. For example, the emf of thermocouples is influenced by pressure and causes uncertainties in temperature measurements. In piston-displacement procedures for measuring volume, high pressures distort pistons and cylinders, thus causing uncertainties in determining volume changes.

At the time this work was initiated in 1959, several techniques had been developed to obtain x-ray diffraction data at moderate pressures. A review of these earlier techniques has already been given by Jamieson and Lawson.[1] Since 1960 Piermarini and Weir,[2] using two diamond pistons in a Bridgman anvil arrangement, have obtained x-ray photographs to 60 kb by passing the x-ray beam directly through the two anvils. Jamieson[3] has obtained x-ray data at pressures in excess of 100 kb by using amorphous boron as a pressure gasket between Bridgman anvils made of cemented tungsten carbide. In this arrangement the x-ray beam passes through the gasket perpendicular to the axis of the pressure system.

Although flat-anvil techniques have several advantages, especially with respect to cost and simplicity, they suffer from three basic limitations: (1) A large pressure gradient exists over the sample region. This makes measurements in

* This work was supported by the U. S. Army Research Office, Durham, North Carolina.
† Alfred P. Sloan Research Fellow.

[1] J. C. Jamieson and A. W. Lawson, in *Modern Very High Pressure Techniques*, edited by R. H. Wentorf, Jr. (Butterworths Scientific Publications Ltd., London, 1962), pp. 70–92.
[2] G. J. Piermarini and C. E. Wier, J. Res. Natl. Bur. Std. **A66**, 325 (1962).
[3] J. C. Jamieson, J. Appl. Phys. **33**, 776 (1962).

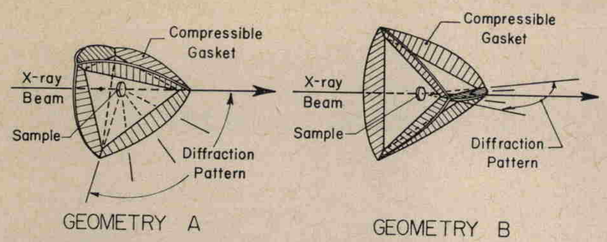

FIG. 1. Tetrahedral sample chamber showing the two possible x-ray geometries using the compressible gasket as the exit pupil.

which the pressure must be specified within a small interval difficult. (2) The uniaxial pressure produces preferred orientation among the crystallites as the sample spreads out into the thin wafer. This preferred orientation makes relative intensity measurements somewhat unreliable and hampers the interpretation of the pattern for crystal-structure determination. (3) The pressure, for a given anvil load, developed within the sample depends upon the nature of the sample since the compressibility and gasket-forming properties of each sample are different. Consequently, the apparatus calibration will be different for different sample materials. The above limitations are a consequence of the "two-dimensional" sample chamber provided by Bridgman anvils and would not be present in a system with a three-dimensional "finite" volume. A three-dimensional sample chamber with a finite volume is also the distinguishing feature of those high pressure systems possessing high temperature capabilities.

II. DESIGN CONSIDERATIONS

There are presently three types of apparatus capable of maintaining high temperature simultaneously with pressures approaching 100 kb: (1) piston-cylinder type systems variously modified for double staging or other support, (2) belt-type apparatus with its ramifications, and (3) multi-anvil devices. Of these systems, multi-anvil devices are most readily adapted to diffraction work since their compressible gaskets form in planes rather than cylinders, cones, or other such shapes. The possible arrangements of sample, electrical leads and contacts, heating elements, etc. are much greater in multi-anvil presses than in the other devices mentioned, and component assembly is usually much simpler. These features are very desirable in order to provide proper entry for the primary x-ray beam and proper exit for the diffracted rays.

During the past several years, we have developed a tetrahedral-anvil press for x-ray diffraction use. It is inherently capable of making diffraction measurements at pressures to 100 kb simultaneously with temperatures to 1000°C. In matching the x-ray geometry of the standard Debye-Scherrer powder method to the geometry of the tetrahedral-anvil press, two possibilities exist for placement of the x-ray entrance and exit pupils. These possibilities are illustrated in Fig. 1. In geometry A the x-ray beam enters the chamber through a hole in the anvil face. In geometry B the x-ray beam enters through one of the gaskets. Both arrangements have been used in the present apparatus, and a discussion of their relative merits is given below.

In either of the above x-ray geometries (with 1-in. tetrahedrons), the x-ray beam must pass through from $\frac{3}{4}$ to 1 in. of the tetrahedron chamber material, including the compressible gaskets. Since x rays are being scattered by the chamber material all along the path of the direct x-ray beam, the x-ray background is abnormally high. Furthermore, the x-ray line intensities are low due to absorption and to the relatively small solid angle available for the emergence of the diffracted beam. Therefore, some method of background discrimination is necessary. The use of a counting technique as opposed to photographic film for detection of the diffracted x rays allows this discrimination in two ways: (1) A directed slit system can be used to restrict the region from which x rays enter the counter. This reduces background scattering from the chamber material. (2) The use of a pulse-height selector and a counter with proportional characteristics allows an electronic discrimination against the white radiation emanating from the x-ray tube. A counting system provides additional advantages over a film technique in that it provides for continuous observation, individual line scanning, and direct intensity measurement.

III. APPARATUS

A photograph of the apparatus is shown in Fig. 2. The tetrahedral press is of the tie-bar design, similar to the original tetrahedral press.[4] The 600-ton capacity hydraulic rams were specially designed for this system. All parts of the press are machined to a precision consistent with an x-ray diffractometer. The position of each ram is monitored to 0.001 in. by a dial indicator, which is mechanically attached to each piston, and the four rams are maintained at equal travel for all pressures. This precaution is taken to minimize movement of the sample relative to the x-ray system. The x-ray counters are mounted on motor-driven carriages, which move on high precision geared tracks. The tracks are mounted on the tie-bars of the press to give stability. The drive motors are equipped with gear boxes to allow angular scanning rates from $\frac{1}{25}$ to 2°/min.

The important features of the apparatus, including the relationship of the two x-ray geometries as they relate to the press geometry, are shown in Fig. 3. The plane of this drawing is the plane containing the axes of two rams and the axis of the tie-bar between these rams, and is also the plane perpendicular to the opposite tie-bar. The other two rams and four tie-bars do not pass through this plane. This

[4] H. T. Hall, Rev. Sci. Instr. **29**, 267 (1958).