NON-DISPERSIVE HIGH PRESSURE HIGH TEMPERATURE X-RAY DIFFRACTION ANALYSIS

P. J. Freud and P. N. LaMori

Battelle Memorial Institute, Columbus Laboratories
Columbus, Ohio

INTRODUCTION

All current high pressure X-ray diffraction apparatus uses dispersive techniques. These techniques are characterized by use of monochromatic radiation and measurements of Bragg angles, and, in general, they can measure lattice parameters to only 0.1% and require exposures of 1/4 to many days. Accurate intensity measurements are obtainable in only a few systems.

Recently several semiconductor device manufacturers have reported a remarkable improvement in solid state detector systems for measurements of X-ray energies. Giessen and Gordon[1] reported use of a Li drifted silicon detector to analyze X-ray energy spectra. This technique is somewhat analogous to time of flight neutron diffraction. For X-rays the crystal analyzer is at a constant angle and analyzes the continuous energy spectrum with a multichannel analyzer. This technique can be used to accurately measure intensities and gather data at a faster rate than dispersive techniques on the same apparatus. In addition, lattice parameters can be determined with improved accuracy by simple curve fitting techniques.

The purpose of this paper is to describe the use of the energy analysis technique, especially with a particular high pressure apparatus. This apparatus has only recently been described in detail.[2] Design of this apparatus and its use for dispersive analysis will therefore be briefly described.

APPARATUS

Dispersive Technique

The high pressure cell is based on the high compression belt developed by Bundy.[3] In the application used here the belt die is split in half on a plane perpendicular to the die axis. A series of splits and fan shaped grooves are ground into the mating surfaces of the die halves to permit entrance and collimation of the X-ray beam, exit of the undiffracted beam and exit of

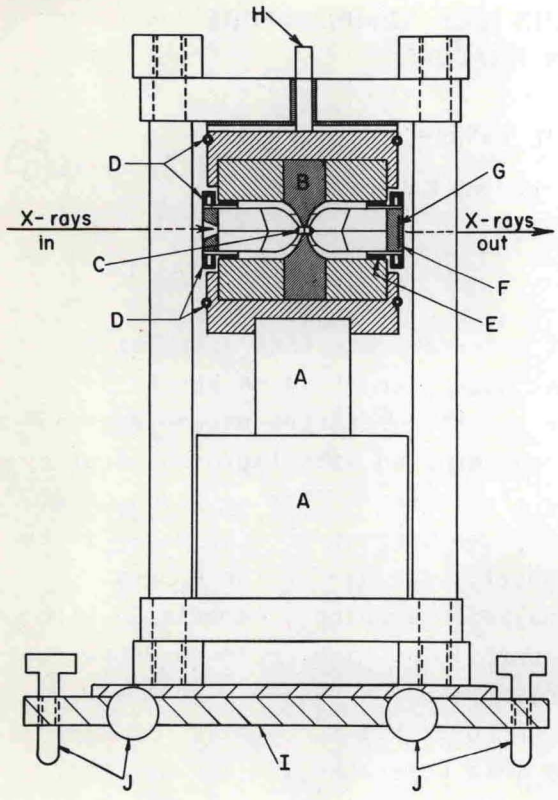

Fig. 1. Schematic drawing of the high-pressure apparatus. A--hydraulic 50-ton ram; B--WC pistons; C--die assembly; D--water cooling tubes; E--rubber shim to position die water-cooling tube; F--film cassette; G--X-ray film; H--insulated current lead; I--pressure positioning table; J--adjusting screws for vertical and horizontal positioning.

the diffracted beam. This apparatus is described fully in (2).

Figure 1 is a schematic of the high pressure assembly and shows the split die halves in place between the pistons. A fifty ton ram provides for force between the pistons and this force will produce over 100 kilobars pressure using 0.150 inch pistons and a 0.200 inch die bore. Since the assembly weights less than 100 lbs it can be placed on the top of a conventional microfocus X-ray source. Alignment is obtained by means of a positioning table on which it sits. This table provides lateral and vertical motion and rotation about the front of the entrance groove.

The unique feature of the design is the split die shown in cut-away in Figure 2. The inner piece is hardened tool steel (Carpenter Hampton RC 60), while the outer binding ring is high strength steel (Vasojet 1000, RC 52). After the two pieces are assembled and the mating surface is ground flat, the grooves and fans are ground into this surface. The entrance-exit groove is accurately placed on a diameter line of the die. Therefore, when the X-ray beam is detected emerging from the exit groove and its intensity maximized, the system is aligned. The sample is located on the axis of the die and since it is rigidly fixed to the die and the die geometry, misalignment will be caused only by lateral sample movement within the high pressure region. This type of movement is small because of the axial symmetry of the high pressure geometry.

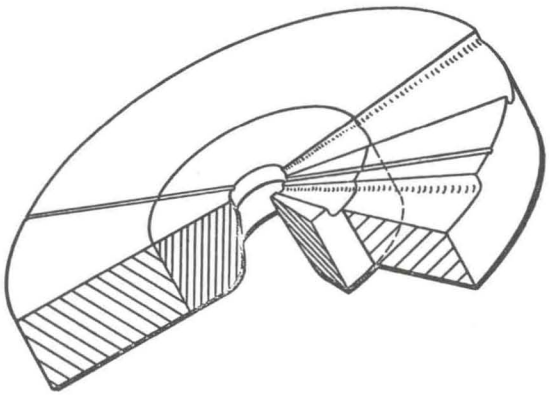

Fig. 2. One-half of the split-die assembly showing mating surface with groove for entrance for X-ray beam and exit of undeviated beam and fan-shaped slots for exit of diffracted rays.

The fan shaped slots allow diffracted X-rays to emerge from the high pressure regions. They cover the 2θ diffraction angles of 5 to 30° and 20 to 45° when using dispersive analysis. With MoKα radiation one measures a d-value range of 8 to 0.9 Å. For the dispersive analysis technique a film cassette is positioned around the outside diameter of the die; this provides an accurate and stable reference of sample to film distance of 114.8 mm.

Two methods are used to prevent extrusion of the high pressure medium into the grooves and fans. Epoxy loaded with amorphous boron is placed into the fans and grooves for a distance of 0.5 cm from the die bore. Alternately, a beryllium ring of wedge shaped cross section is placed in a similarly shaped taper ground into the bore edge. Both methods contain the pressure medium to sample pressures of 100 kilobars.

The details of the high pressure cell are shown in Figure 3. The relatively large high pressure volume makes possible internal heating, and temperatures greater than 1000°C are attainable. Carbon rods sheathed in boron nitride tubes provide resistive heating when current is passed through them from piston to piston. A thermocouple monitors the sample temperature and is brought out through a split lavite gasket. The pressure medium is a pressed amorphous boron disc with the sample packed in a 10 mil hole at the center. A beryllium ring is shown here providing the pressure seal. The X-ray beam would pass through the sample in a direction perpendicular to the plane of the figure and between the carbon heater rods.

Non-Dispersive Technique

For non-dispersive analysis, the sample is irradiated with white radiation and an energy-intensity analysis is made of the X-rays diffracted at a fixed angle from the incident beam. From Bragg's equations written in terms of energy instead of wavelength, the angular and energy range requirements can

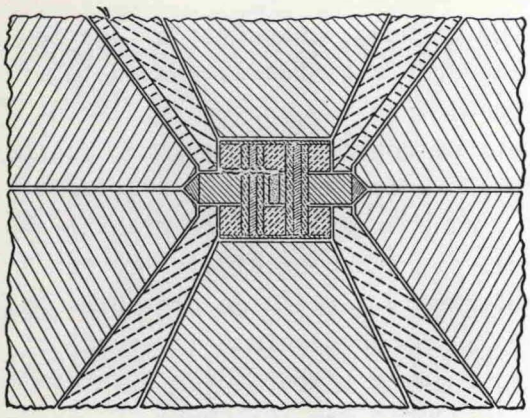

Fig. 3. Schematic diagram of assembled internal components filling the high-pressure volume of the apparatus.

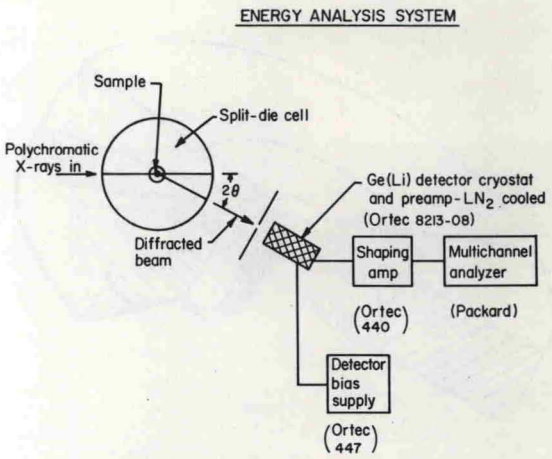

Fig. 4. Energy analysis system.

be calculated for a given range of d-values of interest.

$$\lambda = 2d \sin \theta = \frac{12.40}{\text{Energy}} \text{ (kilovolts)}$$

For example at an angle of 15° = 2θ and with a useful energy range of 15-50 Kev the d-value range of 3.2 to 0.9 Å will be observed. By using different angles different d-value ranges may be obtained for a fixed energy range of white radiation.

The split die system was modified by placing a narrow slit along the outside diameter of the die opposite one of the diffraction fans and at a fixed angle from the entrance exit groove, Figure 4. White X-radiation was produced in the microfocus unit with the use of a tungsten target run at 55-60 kv and 6 ma. The diffracted radiation was analyzed with an Ortec lithium drifted germanium detector placed behind the slit. The associated equipment consists of a dewar to cool the detector, preamplifier located in the detector housing, shaping amplifier, detector bias supply, and multichannel pulse height analyzer. The natural line width of the detector system is about 500 eV, FWHM at 50 keV. The angular spread of the diffraction geometry produces a $\Delta 2\theta$ of 1/2° and thus 1000 eV line width.

To monitor the intensity-energy distribution of the white radiation, the detector is rotated behind the exit-groove of the split die system. This will provide a

normalization of the diffraction peaks to obtain relative intensities.

The energy analysis system is calibrated with radioactive γ and X-ray sources of precisely known energies. Calibrations to better than 0.1% are possible.

RESULTS

Iron

The energy analysis data are obtained in digital form as counts versus channel number in the multichannel analyzer. The data are also displayed on an oscilloscope trace; this allows constant monitoring of the received signal. Figure 5 shows a computer plot of the digital output for an iron sample at about 25 kb. The first six lines are labeled. When the peaks are analyzed on an expanded scale, the energy position of a peak maximum can be determined to within ± 0.1%. With these positionings, it was found that the pattern can be indexed to that degree of accuracy, therefore it will be possible to calculate lattice parameters to better than one part per thousand.

The background is seen to be a fairly smooth function of energy with some structure apparent around the (200) peak. This is probably due to scattering from the amorphous boron pressure medium.

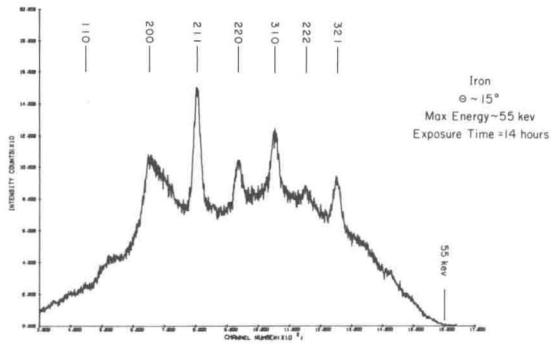

Fig. 5. Computer plot of iron pattern. Energy is linear with channel number (33.3 eV/ch).

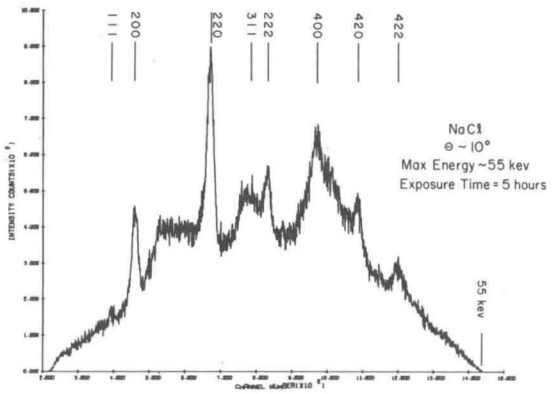

Fig. 6. Computer plot of NaCl pattern. Energy is linear with channel number (37.3 eV/ch).

NaCl

Figure 6 is a pattern for NaCl also taken under a pressure of about 25 kb but at a slightly smaller diffraction angle. Here six lines can be indexed. Indications of the weak (111) and (311) lines can be seen. The same accuracy of 0.1% per line was also found for this pattern. The broad band appearing

between (200) and (220) corresponds to an amorphous boron band observed on films.

DISCUSSION

We believe that the X-ray energy analysis system offers many advantages over the usual dispersive analysis for high pressure systems. First, we believe the method will be more accurate for determining lattice parameters than dispersive techniques. The energy calibration of the analysis system can be made easily with nuclear X-ray and γ-ray sources and can be made before and after each run. Without the use of any peak fitting formula we have been able to position and index peaks to within 0.1%. It is possible that an even higher degree of accuracy could be obtained with more sophisticated analysis techniques. By averaging lattice parameters calculated from a number of lines of one pattern, lattice parameter measurement could be made to an accuracy of a few parts per 10,000. This is at least 5 times better than we have been able to do with measurements of film powder patterns in the split die system.

The speed of making measurements is increased over dispersive techniques for a number of reasons. Because of the higher energies of the X-rays used, absorption in the pressure medium and sample is lower. Neither a monochromator nor filter are needed; there is no attenuation from these sources. The Li drifted Ge detector counter efficiency is essentially 100% over this energy range. The tungsten target can be run at a much higher power level than molybdenum increasing the relative intensity of white versus monochromatic radiation for high pressure work. Finally, the system eliminates wasted time as a continuous display of the data is available on a scope readout. (See Figure 7). If no significant change develops in the pattern (this can be determined in a few minutes) the pressure-temperature conditions can be changed.

With the proper choice of geometry, the signal to noise ratio can be enhanced. If the fan shaped slot is replaced with a collimating groove then the counter will see a greatly reduced portion of irradiated pressure medium and scattering into the counter will be greatly reduced from this source.

A blowup of the die bore, Figure 8, illustrates this point. With a 250 μ entrance groove and a 120 μ diffraction groove both extending the 2" of die radius the amount of irradiated pressure medium that is seen by the detector is very small compared with the sample volume

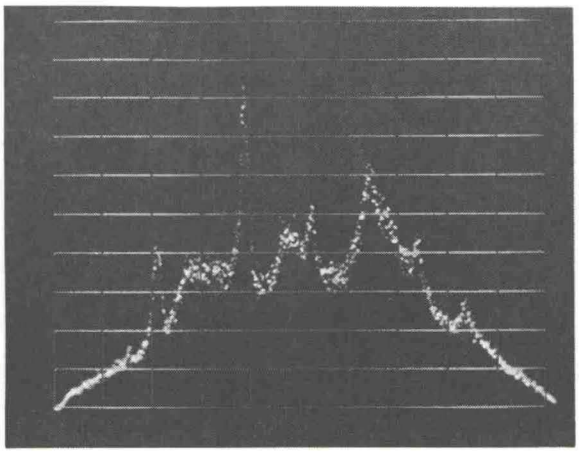

Fig. 7. Oscilloscope output of NaCl pattern, same data as Figure 6.

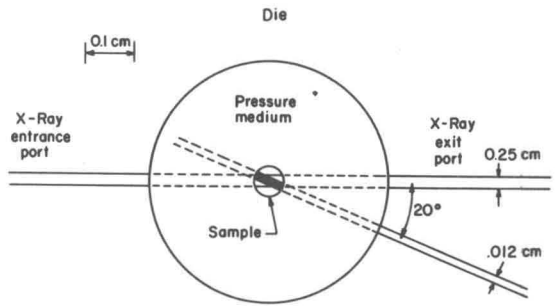

Fig. 8. Enlarged view of die bore showing the effect of double collimation.

seen. Thus, the scattered background resulting from the pressure medium can be reduced to nearly zero, enhancing the signal to noise ratio.

The Fe and NaCl patterns shown above did not use this system but just had a narrow slit at the end of the fan slot. So, for those examples, the counter saw almost all of the irradiated pressure medium which most likely made the major contribution to the background intensity.

Another advantage that could accrue from this double collimation would be the removal of the restriction on the non-crystallinity of the pressure medium. Since the counter doesn't see the medium, no interferring patterns will result. The use of boron nitride as a pressure medium would enhance the pressure transmittance to the sample over amorphous boron and would also be advantageous because of its high temperature stability and ease of fabrication.

Finally the fabrication of the die for non-dispersive use is much simpler since only single collimating grooves are needed instead of entire fan slots. Because less material has to be removed from a groove as opposed to a fan, the die strength will be enhanced and the high pressure limit increased.

Non-dispersive analysis used in conjunction with the geometrically stable split-die high pressure system offers unique capabilities for high pressure, high temperature diffraction studies. The capabilities should be applicable to other high pressure X-ray diffraction systems.

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