tus. The absolute accuracy is approximately one half this value, due to uncertainty in the sample position.

B. Temperature Capabilities

The inherent temperature capabilities of the x-ray apparatus are the same as the tetrahedral anvil press. Present work has been generally limited to temperatures below 500°C, although some exploratory work has been carried out to 1000°C. Extension to higher temperatures appears feasible for at least some studies, and work in this direction will be carried out when the need arises.

The limiting factors in temperature attainment are the properties of the x-ray transparent sample-chamber material. The active nature of LiH at high temperatures and its low melting temperature (682°C at one bar) restrict its use. Boron-filled plastic tetrahedra have been used in all temperature work to date. Our limited experience at the higher temperatures indicates that 1000°C represents a practical limit for the plastic used. Mixtures of boron and BN powders formed into tetrahedra show promise for use at higher temperatures. Structure-determination studies at high temperature and high pressure are carried out in precisely the same manner as discussed above. Care is taken in sample preparation to avoid obstruction of the x-ray beam by the thermocouple, heaters, or electrical connections. The temperature is maintained and monitored throughout the x-ray scan that may last several hours. The structure of tin II at 39 kb and 314°C has been determined using the apparatus. The structure consists of single atoms placed at each point of a body-centered tetragonal lattice with $a=3.81$ Å and $c=3.48$ Å.

In addition to structure analysis, the x-ray apparatus is a powerful tool for detecting and studying phase changes. As an example of such a study, the melting curve of tin first reported by Dudley and Hall[6] was investigated to 45 kb, and the tin I-II phase line was followed from the 34 kb cusp in the melting curve to 75 kb. A comparison of this work with previous workers is shown in Fig. 8. Melting was detected by the disappearance of the (200) and (101) lines of tin I (ordinary white tin) below 34 kb and by the disappearance of the (110) and (101) lines of tin II above 34 kb. Detection of melting by this technique is defined to within a few degrees Centigrade depending upon the intensity of the peak being observed. Errors greater than this can result from improper location of the thermocouple bead and from temperature gradients within the tetrahedron chamber. The tin I-II phase change was observed by the disappearance of the (200) and (101) lines of tin I and the appearance of (110) and (101) lines of tin II. This transformation takes place in a few seconds, and the phase change is reversible within a range of less than 2°C.

[6] J. D. Dudley and H. T. Hall, Phys. Rev. **118**, 1211 (1960).

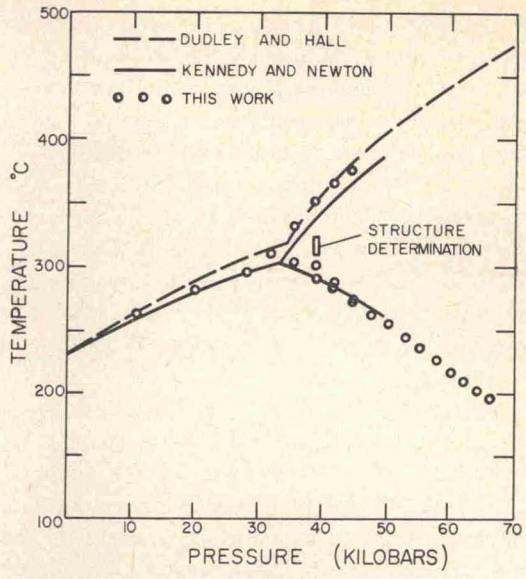

FIG. 8. Phase diagram of tin as measured by x-ray diffraction techniques.

Again the versatility of a counting technique is evident in the above mentioned phase studies. If adequate x-ray intensities are available, as was the case in some of the tin studies, several points on a phase line or melting curve can be measured in an hour. The addition of the time variable to the observation of polymorphism gives information not otherwise attainable. Furthermore, the short time interval between occurrence, observation, and evaluation of the phenomena allows one to direct the progress of a study in a more effective manner and to obtain a conceptual "feel" for the kinetics of the phenomena not afforded when the time element is not present.

Due to the relatively long scanning time required for a structure determination, the temperature attainable is lower than that for phase diagram studies. Excursions to high temperatures for 2–5 min may well be adequate to determine phase lines and melting curves; however, high temperatures must be maintained for several hours to make a structure analysis.

C. Thermodynamic Data

The x-ray attachment to the tetrahedral anvil apparatus makes available, for the first time, an instrument capable of making volume measurements simultaneous with the attainment of pressures up to 100 kb and temperatures to 1000°C. A relatively large new thermodynamic region now becomes available for such studies, and the possibility of confirming theoretical equations of state for solids or of obtaining empirical relationships becomes evident. Preliminary studies have been made to confirm the capabilities of the apparatus, but adequate time has not been available to undertake a measurement over the complete range of pressure and temperature for any sample.

Compressibility and thermal expansion measurements by x-ray techniques require a relatively high degree of accuracy since the analysis yields a volume rather than a change in volume. Furthermore, relative accuracy is lost in computing volume from linear dimensions. As an illustration of the apparatus capabilities, the compressibility of barium was measured to 60 kb and compared with Bridgman's data (see Fig. 9). The problem of pressure calibration at elevated temperatures became evident during preliminary studies of thermal expansion at high pressures, and further investigation was felt necessary before reporting any data.

For low symmetry crystal systems, x rays detect, in addition to the microscopic PVT data, changes in unit cell dimensions which shed light on the single-crystal elastic constants at high pressures. We have observed, for example, the different compressibilities along the a and c axes of hexagonal $NaNO_3$ and hexagonal BN. For BN the percentage change in the lattice parameters, the c/a ratio, and the resulting compressibility curve as shown in Fig. 10. The work by Kabalkina and Vereshchagin[7] to 17 kb is shown for comparison.

D. Miscellaneous Techniques

The fundamental nature of the x-ray diffraction process and its lack of dependence on external influences provide a technique for investigating several high pressure phenomena in a manner not previously available The simultaneous observation of two phases of one material as indicated for KCl in Fig. 6 is one illustration. Similarly one can simultaneously observe two different substances in intimate contact, thus assuring equal pressures. Such a technique should be useful in pressure and temperature calibration studies.

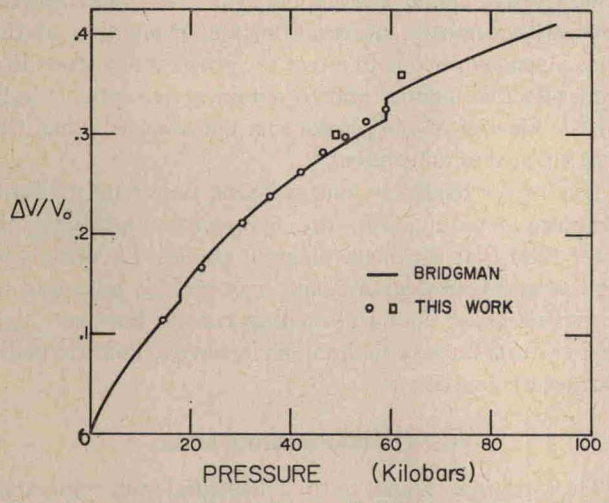

FIG. 9. Compressibility of Ba to 60 kb. ○: determined using geometry A. □: determined using geometry B yielding greater accuracy.

[7] S. S. Kabalkina and L. F. Vereshchagin, Doklady Akad. Nauk SSSR **134**, 330 (1960) [English transl.: Soviet Phys.—Doklady **5**, 1065 (1961)].

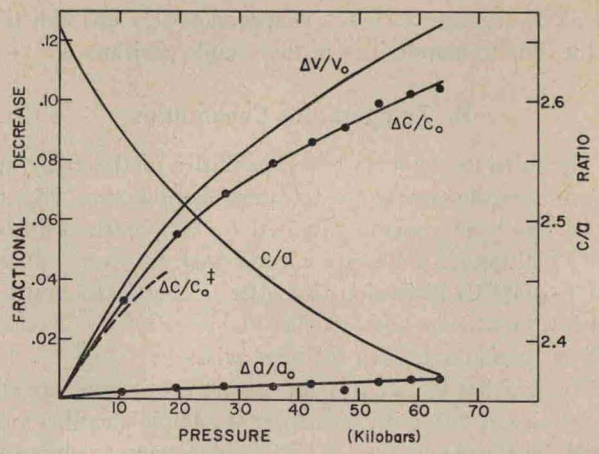

FIG. 10. Lattice parameters of hexagonal BN as a function of pressure to 70 kb. The dashed curve is data reported by Kabalkina and Vereshchagin (See Ref. 7).

Since a one-to-one correspondence must be assumed between the atomic separation and pressure in a given phase, x-ray diffraction measurements also provide a method of separating the true sample hysteresis from apparatus hysteresis during decrease of pressure. Furthermore, if a calibrating substance of known compressibility is mixed with the sample, the pressure is known at any time after numerous applications and reversals of pressure and temperature. Such studies may be useful in learning more about the operation of the tetrahedral press itself. Limited observations of this nature have been made.

The possibility of observing the onset of a chemical reaction as well as measuring reaction rates is evident. The use of two independent counters in such a study would have great advantages. Experiments of this nature have not yet been conducted.

VI. ACKNOWLEDGMENTS

The authors express their thanks to the following graduate students for their assistance in carrying out various phases of the work: Gordon Bethers, Leo Merrill, Roy Bennion, Vern Bean, and Rondo Jeffery.