

## Linear Compressibility Quadric of Hexagonal Silver Iodide

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The linear compressibilities of hexagonal silver iodide have been measured for eight different crystallographic directions. Samples inside a supported beryllium cylinder were subjected to hydrostatic pressure, and X-ray diffraction patterns were observed. Pressures within the vessel were determined by prior calibration against the known elastic constants of potassium iodide. The elliptic compressibility quadric was fitted by least squares to the linear compressibility data, yielding  $\beta_a = 1.46 \pm 0.42 \times 10^{-9}$ /bar and  $\beta_c = 1.09 \pm 0.32 \times 10^{-6}$ /bar. The large uncertainties attached to these values result from both the linear regression fits about the initial compression data (maximum of  $\pm 17\%$ ) and least-squares fit of the quadric surface (maximum of  $\pm 30\%$ ) to the linear compressibilities.

### INTRODUCTION

The determination of the linear compressibilities of hexagonal AgI is part of a study of the elastic constants of this material presently in progress in this laboratory. Much effort has already been expended to obtain the complete elastic compliances, but experimental difficulties (including preparation of good single crystals) are presently insurmountable. The data presented by *Davis and Blair* [1968] in a recent abstract contain very large uncertainties in all but  $S_{33}$  and  $S_{13}$  and therefore should be ignored, or at most used as crude approximations. In spite of the large uncertainties involved, the following data on linear compressibilities are probably the best that can be obtained in any laboratory until a method for growing larger perfect single crystals can be developed.

### EXPERIMENTAL METHOD

The apparatus for measuring the linear compressibilities of hexagonal AgI consists of a supported beryllium cylinder fitted with an O-ringed piston. The casing of the cylinder is slotted for the X-ray beam. The sample, in the form of a fine powder, is placed at the bottom of the blind hole in the beryllium and a pressure fluid such as pentane placed in the bore of the cylinder. The vessel is then mounted in a small press which fits into the sample holder of a standard diffractometer. Details of this device and its capability are being described

elsewhere [*Davis and Walawender*, 1968]. The limitations of the technique include use of short-wavelength radiation (molybdenum) and restricted range of Bragg angle. Such limitations would make it impossible to obtain absolute accuracy in measurement of spacing. However, the same sample is used throughout all of the pressure runs, and, inasmuch as one is measuring differences in lattice spacings, most of the systematic errors inherent in measuring absolute spacings become inconsequential. Such errors include absorption and sample-height errors due to different sample preparations, absorption variations with Bragg angle, and most errors of diffractometer misalignment. The major source of error involved with the technique is a sample-height error resulting from dilatation of press and piston parts during changes in pressure. Several runs were discarded because of the large errors introduced by pressure changes. The present data were collected by use of a sensitive externally mounted dial indicator gage whose indicator pin rested on the top of the steel cylinder. Sample height changes were controlled to within  $10 \mu$  and usually to less than  $5 \mu$ . Although the O-rings on the piston created very little friction in the vessel, a calibration of the internal pressure was made using KI (compressibility data from *Slater* [1924]), and the results are illustrated in Figure 1.

Many experimental problems were encountered in measuring the compressibilities. The



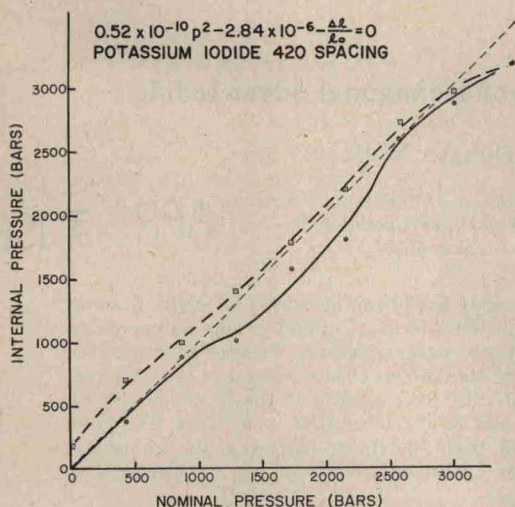


Fig. 1. Calibration of beryllium pressure vessel. Piston diameter = 0.187 in., kerosene pressure fluid. Increasing pressure data given by circles, decreasing pressure data given by squares. Estimated maximum uncertainty about the mean is  $\pm 150$  bars.

AgI could not be ground because shear stress destroys the hexagonal stacking sequence and creates a cubic stacking sequence. A finely precipitated hexagonal AgI was therefore used which created broad peaks in the patterns. This led to some uncertainty in the reproducibility of the measurements, and three complete runs with both increasing pressure and decreasing pressure were completed and averaged to obtain the final results.

Material for the linear compressibility studies was prepared by adding 5 grams of commercial AgI to 200 ml of water and then adding KI to the mixture until the solution became clear. The solution was filtered and the filtrate added to 1500 ml of boiling water. AgI was precipitated in a solution with excess I and was shown by X-ray analysis to be nearly 100% of the hexagonal phase. The final precipitate was then filtered and washed.

### RESULTS

The linear compressibilities for the 110, 211, 213, 112, 203, 103, 105, and 002 diffraction spacings, for hexagonal AgI were determined. The hydrostatic pressures which varied from 0 to 3500 bars were determined from Figure 1. Three runs were completed for each diffraction spacing and data collected for both increasing

pressure and decreasing pressure. The increasing and decreasing pressure values for each run were averaged and then the values for all three runs were averaged, yielding the final values for  $\Delta 2\theta/2\theta_0$ . For the small increments with which we are dealing in this study,  $\Delta 2\theta/2\theta_0$  is equal to  $\Delta l/l_0 = \epsilon$ , and these values were plotted against the internal pressure. The data for the individual spacings are tabulated in Figure 2A to 2G and in Table 1. The slope of the line thus gives the value

$$\partial(\Delta l/l_0)/\partial P = -C \quad (1)$$

Because the data distribution is linear at these low pressures, the integral of this relationship shows that  $C$  is also equal to  $\beta_{hkl}$ , the linear compressibility. Integration of equation 1 yields  $\beta_{hkl} = \epsilon/(P - P_0) = (\epsilon - \epsilon_0)/P$ , where  $P_0$  is the mean stress and  $\epsilon_0$  the mean strain stored in the sample. The maximum strain stored is  $2\epsilon_0$ . Equation 1 was fitted to the data by least squares.

With one exception (211), the strain intercept  $\epsilon_0$  lies below the pressure axis, yielding a positive value for  $\epsilon_0$ . The negative value for 211 is not considered significant in view of the considerable variation in  $\epsilon_0$  for the other directions.

The observed residual strains (including surface tension strains) are partially released by the compression cycle. This strain was displayed as a combination of an initially smaller average  $d$  spacing for that particular diffraction plane than was present after the pressure cycle and by a region of 'indifference' to pressure changes at low strains. These data do indicate that the maximum stress that can be stored in fine aggregates of AgI is approximately 750 bars ( $2\epsilon_0 = 0.0012$ ), and it represents an aggregate yield strength considerably larger than that observed for strained single crystals. A similar relationship has been observed with this method on substances such as  $KNO_3$  and KI.<sup>1</sup>

Figure 3 presents the data plotted on polar coordinates, with the quadric equation

$$\beta' = \beta_a(1 - l^2) + \beta_c l^2 \quad (2)$$

where  $l$  is the direction cosine of  $\beta'$  with respect to  $\beta_a$ , fitted to the data by means of least

<sup>1</sup> The data of Figure 1 are a composite of three runs, one of which showed slight residual strain; the effect is lost in the averaging.