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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 $\beta_a = 1.46 \pm 0.42 \times 10^{-6}$/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 ±17%) and least-squares fit of the quadric surface (maximum of ±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 μ and usually to less than 5 μ. 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

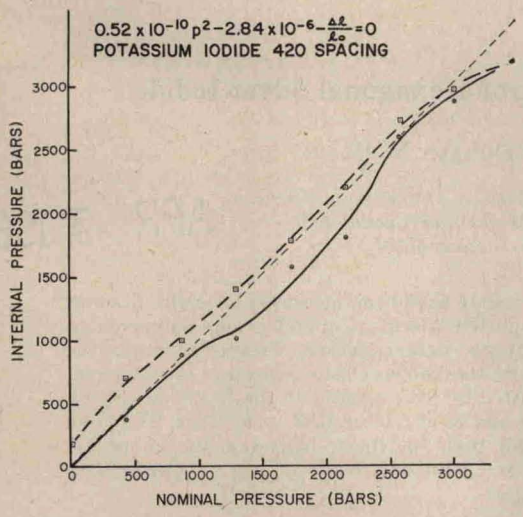

Fig. 1. Calibration of beryllium pressure vessel. Piston diameter = 0.187 in., kerosense pressure fluid. Increasing pressure data given by circles, decreasing pressure data given by squares. Estimated maximum uncertainty about the mean is ±150 bars.

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 2*A* to 2*G* and in Table 1. The slope of the line thus gives the value

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

Because the data distribution is linear at these low pressures, the integral of this relationship shows that C is also equal to β_{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 ϵ_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 ϵ_0 lies below the pressure axis, yielding a positive value for ϵ_0. The negative value for 211 is not considered significant in view of the considerable variation in ϵ_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.[1]

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

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

where l is the direction cosine of β' with respect to β_c, fitted to the data by means of least

[1] 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.

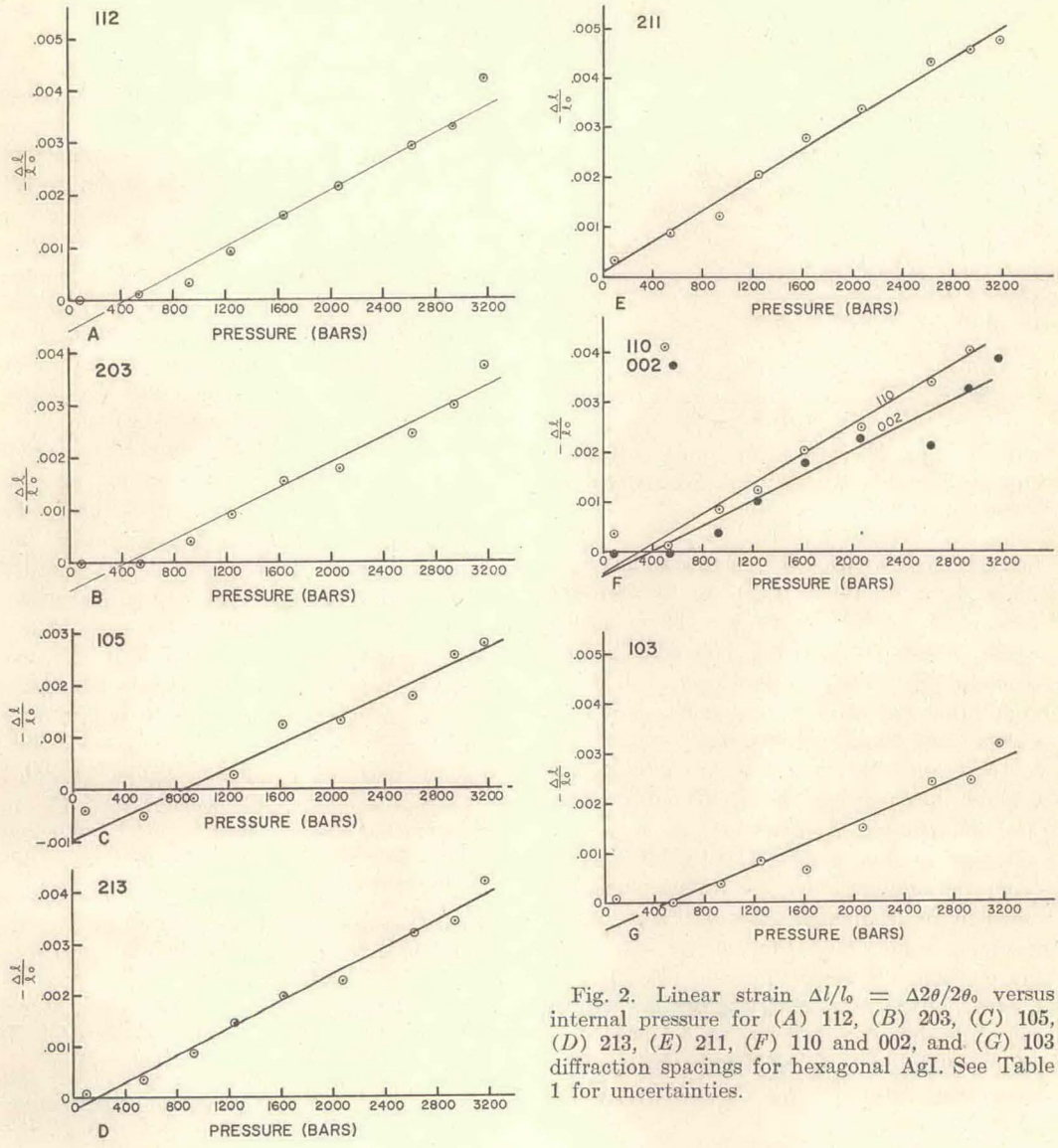

Fig. 2. Linear strain $\Delta l/l_0 = \Delta 2\theta/2\theta_0$ versus internal pressure for (*A*) 112, (*B*) 203, (*C*) 105, (*D*) 213, (*E*) 211, (*F*) 110 and 002, and (*G*) 103 diffraction spacings for hexagonal AgI. See Table 1 for uncertainties.

TABLE 1. Experimental Linear Compressibilities and Error Analysis

hkl	β_{hkl} 10^{-6}/bar	s_{ep} 10^{-4}	$\pm\Delta\beta$ 10^{-6}/bar	e 10^{-6}/bar	$\pm(\Delta\beta + e)$ 10^{-6}/bar
002	1.258	3.9	0.18	0.17	0.35
105	1.126	3.5	0.16	0.01	0.17
103	1.050	3.7	0.17	0.15	0.32
203	1.217	2.9	0.13	0.10	0.23
112	1.344	2.8	0.13	0.02	0.15
213	1.312	3.0	0.14	0.05	0.19
211	1.560	2.8	0.13	0.12	0.25
110	1.495	5.4	0.25	0.04	0.29

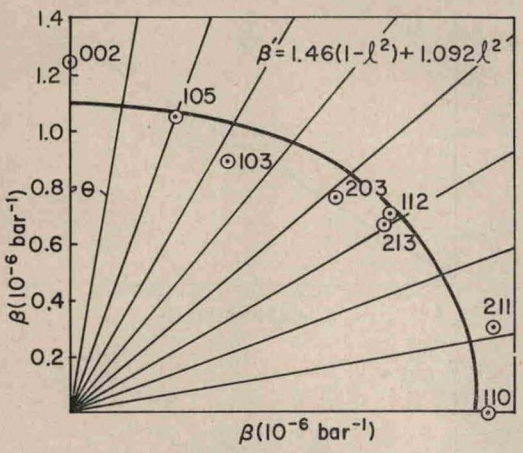

Fig. 3. One quadrant of the linear compressibility surface for hexagonal AgI. See Table 1 for fitting uncertainty.

squares. This fit yields the compressibility constants $\beta_a = (1.46 \pm 0.42) \times 10^{-6}$/bar and $\beta_c = (1.09 \pm 0.32) \times 10^{-6}$/bar. There is some scatter to the plot, and the data actually fit a parabolic relationship much better. The rather large errors attendant to β_a and β_c result from both scatter about the original plots of $\Delta l/l_0$ versus P and the scatter about the quadric. Table 1 also includes the calculated *standard error of estimate* $s_{\epsilon p}$ obtained from the linear regression analysis of the β_{hkl} values. If one considers the initial unaveraged data which resulted in the composite plots of Figure 2, the maximum value of $s_{\epsilon p}$ obtained was 5.4×10^{-4} and was that for the 103 spacing.

Errors observed in scattering of the compression plots, however, are not valid measures of the uncertainties in β_{hkl} for each spacing. This is adequately given by *Dixon and Massey* [1957, p. 194].

$$\Delta\beta_{hkl} = \frac{t_{0.90} s_{\epsilon p}}{s_p (N-1)^{1/2}}$$

at the 90% confidence level of the assumed t distribution, with two degrees of freedom. The uncertainties $\Delta\beta_{hkl}$ for each spacing are given in Table 1.

Calculation of β_a and β_c by least-squares fit of the compressibility quadric (equation 1) to the β_{hkl} values of Table 1 results in a fitting error e given by

$$e = \beta_a(1 - l^2) + \beta_c l^2 - \beta_{hkl}'$$

which is also additive to $s_{\epsilon p}$ in terms of the uncertainty in β_{hkl}' calculated from the compressibility quadric.

Table 1 shows that the uncertainties stemming from the direct measurements lie between 8 and 17%, but those ($\Delta\beta_{hkl} + e$) associated with β' calculated from the quadric parameters run as high as 30%. The source of the uncertainties is obviously experimental and lies in (1) slight variations in sample height and (2) random errors, including chart-reading limitations imposed by low Bragg-angle measurements.

The only published data for the elasticity of hexagonal AgI is a volume compressibility of 4.11×10^{-6}/bar given by *Richards and Jones* [1909] for iodyrite (naturally occurring hexagonal AgI). J. Wachtman, quoted in *Burley* [1964], gives a value of 10.1×10^{-6}/bar for polycrystalline material. No statement as to phase composition is given, but in view of the sample preparation it was most likely a mixture of cubic and hexagonal forms. The present linear compressibility data yield a volume compressibility of 4.01×10^{-6}/bar, which is in good agreement with the data of Richards and Jones. However, the poor agreement with Wachtman's value should be better, in view of the close similarity of structures of the two AgI polymorphs.

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