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The Study of the Elastic Constants of White Tin by Diffuse X-ray Reflexion

By S. C. Prasad and W. A. Wooster

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

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Tin crystals were grown by lowering a tube containing the melt through a vertical furnace, at a rate of 5 mm.hr.$^{-1}$. Crystals obtained were spherical or cylindrical of diameter about 2 cm. Faces parallel to (100), (110) and (103) were cut with a chisel or microtome. The surface imperfections were removed by electrolytic polishing. The diffuse reflexions from regions of reciprocal space surrounding the reciprocal points 400, 440 and 103 were investigated using a Geiger-counter spectrometer. The results were: $c_{11} = 8{\cdot}6$, $c_{33} = 13{\cdot}3$, $c_{44} = 4{\cdot}9$, $c_{66} = 5{\cdot}3$, $c_{12} = 3{\cdot}5$, $c_{13} = 3{\cdot}0 \times 10^{11}$ dyne. cm.$^{-2}$, the estimated accuracy being 7%. The values for c_{33}, c_{44}, c_{66} and c_{12} differ considerably from previous values given by Bridgman.

A noteworthy feature of the diffuse reflexion was the background intensity. Although this did not interfere with the measurement of the elastic constants, it indicates the presence of diffuse reflexion due to some other cause than that which is associated with the long acoustic waves.

Introduction

The elastic constants of tetragonal white tin were first studied by Bridgman (1925) using static compressional and torsional measurements. Bridgman himself pointed out the low accuracy with which certain of the elastic moduli were necessarily determined. This arose because the moduli in question could not be measured directly, but only derived from expressions involving several moduli. Another fundamental difficulty arose from the great ease with which tin deforms plastically on being subjected to stresses of magnitude appreciable by Bridgman's method of measurement. Several measurements of the bulk compressibility have been made (Richards, 1907; Adams, Williamson & Johnston, 1919; Bridgman, 1925, 1949). The measurements are mutually consistent and are, in the present work, accepted as the basis of final deductions of the elastic constants.

Diffuse X-ray reflexions from tin have been studied in Holland. Arlman & Kronig (1943) took Laue photographs which showed a square net of diffuse streaks when X-rays travelled along the axis [001] (which was perpendicular to the film). These were attributed to lattice defects. An alternative interpretation was given later by Bouman, Arlman & Reijen (1946), who attempted to explain the streaks in terms of thermal vibrations of the atoms. In this calculation they used the elastic constants of Bridgman. The present work suggests that some of Bridgman's values are seriously in error, but even if the correct values had been used it would have been very difficult to explain the streaks in terms of thermal vibrations. Thermal effects, generally speaking, give rise to circular or oval diffuse spots which are quite different from the streaks joining reciprocal-lattice points found by Arlman & Kronig (1943).

Preparation and orientation of the crystals

The tin used was supplied by Messrs Johnson Matthey and Co. and was stated to contain not more than 0·005% of impurities. About 14 cm.^{3} of tin were melted in a Pyrex vessel filled with argon at a pressure of about 10^{-2} mm. Hg and allowed to solidify into a cylinder having a lower end which tapered and was curved. When the glass vessel was sealed off from the pump the space above the tin was filled with argon at about the same pressure as mentioned above. The vessel was suspended on a tungsten wire and lowered through a vertical furnace at a uniform rate of approximately 5 mm. hr.$^{-1}$. The melting point of tin is 232° C. and it was found best to maintain the temperature at the centre of the furnace at 300° C. The temperature variation at the centre of the furnace was $\pm 2°$ C. The internal diameter of the furnace was 3·6 cm. and its length 26 cm. The diameter of the glass vessel was such that it would drop easily through the furnace tube. From the beginning to the end of a run occupied about 40 hr. The crystals were etched in a mixture of concentrated ferric chloride and hydrochloric acid. Usually the whole specimen was shown by the etching to be a single crystal, though occasionally regions near the top of the specimen were of a different orientation from the main bulk.

The orientation of the crystals was determined by X-rays, using the combined oscillation-and-Laue photograph method. The cylindrical or spherical tin block, just as it came from the furnace, was set upon the goniometer so that, after one or more photographs, a symmetry plane was perpendicular to the vertical axis of rotation of the Unicam oscillation goniometer. Using the microscope on the instrument, an ink line was described by marking the intersection of the axis of the microscope with the surface of the specimen as the latter was rotated about the vertical axis. Using a fine saw, the block was cut parallel to the plane defined by the ink line. Great care had to be taken during the cutting operations in order to avoid causing plastic deformation of the crystal. The sawn surface was cut with a chisel or microtome so that the final surface was not less than 1 mm. from the sawn surface. Finally, the disturbances caused by the chisel or microtome were removed by electrolytic polishing, using a mixture of perchloric acid (60%, specific gravity 1·58) and acetic anhydride. One volume of the former was used with four volumes of the latter liquid, and due care was taken to avoid an explosion. The cathode was of tin; the voltage maintained across the polishing cell was 45–50, and the current density was 0·15–0·20 A.cm.$^{-2}$. The polishing could not be carried on for more than 5 min. at a time (maximum permissible temperature 30° C.) and after each polishing period the liquid was cooled by its surrounding ice bath. The polishing was repeated several times until X-ray photographs gave sharp spots and no powder rings. Finally the surface was very lightly etched to show its single crystalline character.

The choice of diffuse reflexions

The intensity of diffuse scattering due to the contribution from a small volume element in reciprocal space has been given by Ramachandran & Wooster (1951*a*). This intensity is proportional to a factor $K[ABC]_{hkl}$, which corresponds to a volume element lying on a line (rekha) passing through the nearest reciprocal-lattice point (relp). A, B, C are numbers proportional to the direction cosines u_1, u_2, u_3 of the rekha, and hkl are the indices of the relp. Using the conventional tensor notation,

$$K[ABC]_{hkl} = P_i P_k (A^{-1})_{ik} ,$$

where P_i are the direction cosines of the line (rel-vector) joining the relp to the origin and $(A^{-1})_{ik}$ are terms of the symmetrical matrix reciprocal to the matrix A_{ik}, where

$$A_{ik} = c_{ilkm} u_l u_m .$$

When the appropriate non-zero values of the elastic constants, c_{ilkm}, are inserted in the above equations the following values are obtained;

$$K[100]_{h00}=1/c_{11},\quad K[010]_{h00}=1/c_{66},\quad K[001]_{h00}=1/c_{44} ,$$
$$K[1/\sqrt{2},\, 1/\sqrt{2},\, 0]_{h00}=1/(c_{11}-c_{12})+1/(c_{11}+c_{12}+2c_{66}) .$$

Thus from observations on the diffuse reflexions close to the relp 400 (which has a convenient θ-value of 32°) the constants c_{11}, c_{44}, c_{66}, and c_{12} can be found. (For β-tin the crystallographic constants relating to cell dimensions etc. are $a = 5{\cdot}819$, $c = 3{\cdot}175$ Å; space group $I4/amd$; structure type $A5$.) Usually absolute measurements are not made but only relative measurements. In this case the following K-ratio,

$$K[100]_{h00}/K[010]_{h00} = c_{66}/c_{11} = \chi_{66} ,$$

gives the ratio of two elastic constants. (The symbol χ_{ik} is used to represent the ratio c_{ik}/c_{11}.) The K-ratio

$$K[1/\sqrt{2},\, 1/\sqrt{2},\, 0]_{h00}/K[100]_{h00} = 1/(1-\chi_{12})+1/(1+\chi_{12}+2\chi_{66})$$

enables a value of χ_{12} to be obtained. It is usually found best not to solve such quadratic equations in a direct manner but rather to substitute approximate values of χ_{12} and find which gives best agreement with the observed K-ratio. This procedure readily shows the influence on the calculated K-ratio of a given change in one of the χ_{ik} values.

Confirmation of the values obtained from the relp $h00$ can be obtained from the relp $hh0$. Thus the important rekhas perpendicular to [001] give the following relations:

$$K(1/\sqrt{2},\, 1/\sqrt{2},\, 0)_{hh0} = 2/(c_{11}+c_{12}+2c_{66}) ,$$
$$K(\bar{1}/\sqrt{2},\, 1/\sqrt{2},\, 0)_{hh0} = 2/(c_{11}-c_{12}) ,$$
$$K[100]_{hh0} = \tfrac{1}{2}(1/c_{11}+1/c_{66}) .$$

The rekhas perpendicular to [$\bar{1}$10] give

$$K(1/\sqrt{2},\, 1/\sqrt{2},\, 0)_{hh0} = 2/(c_{11}+c_{12}+2c_{66}) ,$$
$$K[001]_{hh0} = 1/c_{44} .$$

The second K-value giving $(c_{11}-c_{12})$ is especially sensitive to a change in the value of c_{12}, and is the best means of determining this elastic constant.

To determine the remaining c_{ik}'s it would be simplest to use a relp $00l$. However, using Cu $K\alpha$ radiation, no reflexion of suitable θ-value is available. The rel-vector 103 makes an angle of 10° with [001] and this reflexion is moderately strong and has a convenient θ-value. The relations between the K-values and the c_{ik}'s may be expressed in terms of the direction cosines P, Q, R of the normal to the plane (103) as follows:

$$K[001]_{103} = P^2/c_{44}+R^2/c_{33} ,$$
$$K[100]_{103} = P^2/c_{11}+R^2/c_{44} .$$

From these relations c_{33} is obtained. Further,

$$K[1/\sqrt{2},\, 0,\, 1/\sqrt{2}]_{103} = \frac{2[P^2(c_{44}+c_{33})-2PR(c_{13}+c_{44})+R^2(c_{11}+c_{44})]}{(c_{11}+c_{44})(c_{44}+c_{33})-(c_{13}+c_{44})^2} ,$$

$$K[\bar{1}/\sqrt{2},\, 0,\, 1/\sqrt{2}]_{103} = \frac{2[P^2(c_{44}+c_{33})+2PR(c_{13}+c_{44})+R^2(c_{11}+c_{44})]}{(c_{11}+c_{44})(c_{44}+c_{33})-(c_{13}+c_{44})^2} .$$

The mean value, $\bar{K}$, of these two K-values is given by

$$\bar{K} = \frac{2[P^2(c_{44}+c_{33})+R^2(c_{11}+c_{44})]}{(c_{11}+c_{44})(c_{44}+c_{33})-(c_{13}+c_{44})^2} ,$$

and in this expression only c_{13} is unknown. The value of c_{13} can therefore be found from the observations on the relp 103. Thus all six c_{ik}'s can be found by these measurements on selected rekhas and relps.

Experimental details and results

The apparatus and method used was the same as that described by Ramachandran & Wooster (1951*a*, *b*). Cu $K\alpha$ radiation was used throughout. Three faces cut on separate crystals were used; these faces were parallel respectively to planes (100), (110) and (103). The indices of the reflexions were 400, 440, and 103. The usual correction for absorption was modified to allow for the inclinations, of about 1°, of the cut faces to the atomic planes; the χ-divergence correction and the second-order diffuse-reflexion correction were made. Corrections for χ-divergence amounted to about 10% for points close to the relp and fell to zero for the points further away from the relp, because a constant size of slit was used in front of the counter. Corrections for the divergences i and φ were found to be unnecessary. There was no appreciable mosaic spread but along certain rekhas there was a general increase in the background, which will be discussed later. Tables 1–5 and Fig. 1 (which is plotted from Table 5) give the results obtained. The last row of the table shows the extent of the abnormally high general background for certain rekhas.

From the data obtained from relp 400 the following K-ratios and χ-values of the elastic ratios were derived:

$$K[001]/K[100] = 1{\cdot}736, \qquad \chi_{44} = 0{\cdot}576;$$
$$K[010]/K[100] = 1{\cdot}632, \qquad \chi_{66} = 0{\cdot}613;$$
$$K[1/\sqrt{2}, 1/\sqrt{2}, 0]/K[100] = 2{\cdot}08, \qquad \chi_{12} = 0{\cdot}412.$$

From the data obtained from the relp 440, the following K-ratios were obtained:

$$K[\bar{1}/\sqrt{2}, 1/\sqrt{2}, 0]/K[1/\sqrt{2}, 1/\sqrt{2}, 0] = 4{\cdot}50,$$
$$K[001]/K[1/\sqrt{2}, 1/\sqrt{2}, 0] = 2{\cdot}37\,.$$

Table 1. *Relp* 400: *section perpendicular to* [001]*

		Counts in 5 min. for rekha parallel to								
		[100]			[010]			[110]		
R (cm.)	$1/R^2$ (cm.$^{-2}$)	Total	I_2	I_1+ background	Total	I_2	I_1+ background	Total	I_2	I_1+ background
4·5	0·049	—	—	—	189·1	2·0	187·1	108·9	3·5	105·4
3·0	0·111	104·5	1·2	103·3	275·5	3·3	272·2	216·1	5·5	210·6
2·0	0·25	198·9	1·7	197·2	478·7	5·3	473·4	474·2	8·5	465·7
1·5	0·444	378·5	2·6	375·9	714·6	6·7	707·9	773·9	10·9	763·0
1·25	0·64	551·7	3·2	548·5	931·7	7·6	924·1	1073·2	12·7	1060·5
Mean slope				809			1320			1683
Intercept on the axis of ordinates				20			120			20

* In Tables 1–5 I_1, I_2 correspond to the number of counts in 5 min. due respectively to the first- and second-order thermal diffuse scattering.

Table 2. *Relp* 400: *section perpendicular to* [010]

		Counts in 5 min. for rekha parallel to					
		[100]			[001]		
R (cm.)	$1/R^2$ (cm.$^{-2}$)	Total	I_2	I_1+ background	Total	I_2	I_1+ background
4·5	0·049	64·5	1·0	63·5	196	3·2	192·8
3	0·111	127·2	1·5	125·7	295	4·6	290·4
2	0·25	258·7	2·3	256·4	527·6	6·9	520·7
Mean slope				952			1653
Intercept on the axis of ordinates				20			110

Table 3. *Relp* 440: *section perpendicular to* [001]

		Counts in 5 min. for rekha parallel to								
		[110]			[$\bar{1}$10]			[100]		
R (cm.)	$1/R^2$ (cm.$^{-2}$)	Total	I_2	I_1+ background	Total	I_2	I_1+ background	Total	I_2	I_1+ background
4·5	0·049	46·9	0·9	46·0	160·3	18·9	141·4	113·3	1·3	112·0
3	0·111	76·0	1·2	74·8	307·0	26·8	280·2	153·5	1·6	151·9
2	0·25	162·6	2·0	160·2	704·2	43·4	660·8	304·5	3·0	301·5
1·5	0·444	258·9	2·6	256·3	1133·4	53·3	1080·1	449·6	3·7	445·9
1·25	0·64	382·0	3·2	378·8	—	—	—	—	—	—
Mean slope				558			2506			951
Intercept on axis of ordinates				20			20			60

Table 4. *Relp* 440: *section perpendicular to* [$\bar{1}$10]

		Counts in 5 min. for rekha parallel to					
		[110]			[001]		
R (cm.)	$1/R^2$ (cm.$^{-2}$)	Total	I_2	I_1+ background	Total	I_2	I_1+ background
4·5	0·049	63·7	1·4	62·3	186·5	2·7	183·8
3	0·111	86·6	1·4	85·2	291·5	4·4	287·1
2	0·25	168·6	2·1	166·5	461·3	5·7	455·6
1·5	0·444	289·5	2·9	286·6	752·3	7·9	744·4
1·25	0·64	404·8	3·4	401·4	—	—	—
Mean slope				598			1414
Intercept on axis of ordinates				20			118

Table 5. *Relp* 103: *section perpendicular to* [010]

		Counts in 5 min. for rekha parallel to								
		[001]			[100]			Mean of $(1/\sqrt{2}, 0, 1/\sqrt{2})$ and $(\bar{1}/\sqrt{2}, 0, 1/\sqrt{2})$		
R (cm.)	$1/R^2$ (cm.$^{-2}$)	Total	I_2	I_1+ background	Total	I_2	I_1+ background	Total	I_2	I_1+ background
4·5	0·049	52·8	0·2	52·6	150	2·3	147·7	69·3	1·2	68·1
3	0·111	74·5	0·5	74·0	195·6	3·7	191·9	101·2	1·8	99·4
2	0·25	108·6	0·7	107·9	290·5	5·5	285·0	169·9	2·6	167·3
1·5	0·444	165·8	0·9	164·9	399·2	6·7	392·5	252·8	3·2	249·6
Mean slope				268			684			502
Intercept on the axis of ordinates				42			114			42

When the ratios obtained from relp 400 were used to calculate these ratios the values 4·49 and 2·29 were obtained. The differences were within the experimental error.

Using the value of χ_{66} obtained from 400, the first K-ratio gives $\chi_{12} = 0{\cdot}414$. The mean of this and the value from 400 gives a final value of

$$\chi_{12} = 0{\cdot}413\ .$$

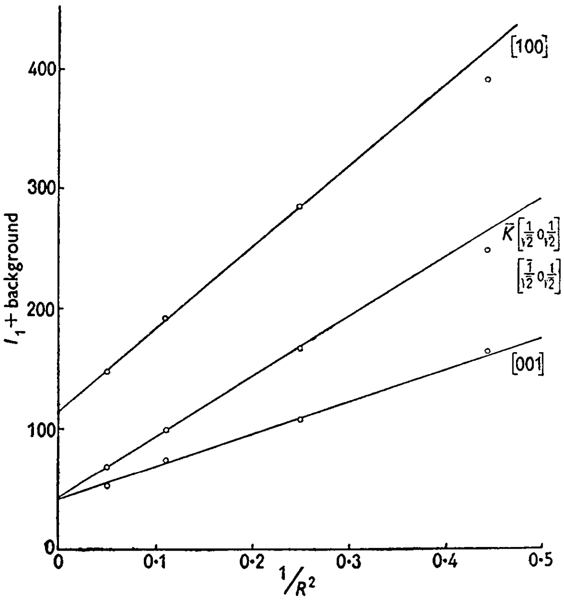

Fig. 1. Plot of diffuse intensity (I_1+background scattering) against $1/R^2$ for the 103 relp and rekhas perpendicular to [010].

The value of χ_{44} obtained from the second K-ratio of 440 is 0·558 and the mean of this and the previous value from 400 gives the final result

$$\chi_{44} = 0{\cdot}567\ .$$

The relp 103 gave the K-ratios

$$K[100]/K[001] = 2{\cdot}55,\quad \bar{K}[111]/K[001] = 1{\cdot}87\ .$$

The values calculated from these results and the value of χ_{44} given above, are:

$$\chi_{33} = 1{\cdot}55,\quad \chi_{13} = 0{\cdot}346\ .$$

The summary of the χ-values is therefore:

$$\chi_{33} = 1{\cdot}55,\quad \chi_{44} = 0{\cdot}576,\quad \chi_{66} = 0{\cdot}613;$$
$$\chi_{12} = 0{\cdot}412,\quad \chi_{13} = 0{\cdot}346\ .$$

Derivation of absolute values of the elastic constants

The coefficient of cubic compressibility β is related to the s_{ik}'s by the equation

$$\beta = 2s_{11}+s_{33}+4s_{13}+2s_{12}\ .$$

The values of β obtained previously are:

19×10^{-13} cm.^{2} dyne^{-1}	(Richards, 1907),
18·7	(Adams *et al.*, 1919),
19·1	(Bridgman, 1925),
18·7*	(Bridgman, 1949),

* Value obtained by extrapolation of results to zero pressure.

Table 6. *Values of c_{ik} and s_{ik}*

c_{ik}	Present authors (dyne cm.$^{-2}$)	Bridgman (dyne cm.$^{-2}$)	s_{ik}	Present authors (cm.^{2} dyne^{-1})	Bridgman (cm.^{2} dyne^{-1})
c_{11}	$8{\cdot}6\times10^{11}$	$8{\cdot}40\times10^{11}$	s_{11}	$14{\cdot}6\times10^{-13}$	$18{\cdot}5\times10^{-13}$
c_{33}	13·3	9·67	s_{33}	8·5	11·8
c_{44}	4·9	1·75	s_{44}	20·6	57·0
c_{66}	5·3	0·74	s_{66}	19·0	135
c_{12}	3·5	4·87	s_{12}	−5·3	−9·9
c_{13}	3·0	2·81	s_{13}	−2·07	−2·5

and the last Bridgman value has been accepted here.

From the χ-values the s_{ik} values were calculated in terms of c_{11} and when these were used in the equation for β, the value of c_{11} was obtained:

$$c_{11} = 8{\cdot}58\times10^{11} \text{ dyne cm.}^{-2}.$$

Using this value of c_{11}, all the c_{ik}'s can be obtained from the χ-values. The final set of c_{ik}'s and s_{ik}'s is given in Table 6 together with Bridgman's values. An absolute measurement was made using $K[100]_{400}$ and this gave a value about 6% lower than the value given above for c_{11}. The accuracy of this X-ray measurement was not higher than 15% and so the values quoted above are taken as the final values.

Diffuse reflexion of non-elastic origin

It will be seen from Tables 1–5 and Fig. 1 that the straight lines through the observed points for a given relp cut the axis of ordinates at different heights above the base line. In using the mean slope of each line to determine the K-value of a given rekha it has been assumed that the background over the whole range of $1/R^2$ is equal to the intercept on the axis of ordinates. When the background is due only to Compton scattering there is no possibility that it will vary significantly over the small angular ranges used here. However, the enhanced background found for certain rekhas might vary with distance from the relp. To test this possibility a thorough investigation has been made of the variation of the background for a large number of rekhas and for considerable distances from the relp. This work will be published later, but for the present purpose it is sufficient to notice that the background for every rekha remains constant beyond the range of the thermal scattering. This is true of the large as well as of the small background intensities. The determination of the mean slope has not, therefore, been affected by the high background intensities for certain rekhas.

Discussion

Bridgman (1925) determined the elastic moduli, s_{ik}, of tin by a method involving static compression and torsion. The values so obtained, together with the elastic constants, c_{ik}, calculated from the s_{ik}, are given in Table 6.

Bridgman determined s_{11} as the mean of four values, of which the extreme values differed by 30%; s_{33} was obtained independently. The moduli s_{13} and s_{12} were obtained from two equations involving s_{11} and s_{33}. The accuracy of these four moduli does not appear to be greater than 30%. Bridgman's values for s_{44} and s_{66} are unexpectedly high. Since the values of several other moduli were involved in the determination of s_{44} and s_{66} their accuracy was less than that applicable to the other moduli.

The present investigation shows that c_{33} is appreciably greater than Bridgman's value, and c_{12} is somewhat smaller. The main differences between the two sets of values of c_{ik} lies in the values of c_{44} and c_{66}: the present values are several times greater than the former values. The accuracy of the constants determined here depends on the measurement of cubic compressibility as well as on that of diffuse reflexion. The total accuracy is probably about ±7% and is the same for all the constants.

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