

Unit Cell Determination of Silver Azide

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Introduction

Studies of silver azide have been made by Bassiere,¹ West,² and Hughes,³ and unit cell dimensions have been determined by them.

Investigations by:

	a_o (Kx)	b_o (Kx)	c_o (Kx)
Bassiere	5.58	5.93	6.04
West	5.58	5.90	5.96
Hughes	5.59	5.88	6.00

Space group: Ibam D_{2h}^{26}

Ibam restrictions: $hk\bar{l}$: $h + k + l = 2n$

$Ok\bar{l}$: $k = 2n$

$h0\bar{l}$: $h = 2n$

This experiment was intended as a more accurate determination of the unit cell dimensions. A Debye-Scherrer X-ray diffraction photograph of silver azide powder was taken, using potassium chloride as a standardization of the camera. In order to establish the proper indices which correlate with the angles of reflection, an average of the above unit cell dimensions was taken. The established indices were then fitted with the experimental observations and an averaging

¹M. Bassiere. Compt Rendeu, 201, 735-737 (1935).

²C. D. West. Zeit. fur Krist, 95, 421 (1935).

³E. W. Hughes. Cornell Ph.D. thesis.

process was done on a computer to determine the unit cell dimensions.

Experimental

1. Preparation of silver azide.

Mix silver nitrate solution 0.0507 formal and sodium azide solution 0.0503 formal, heat and allow to crystallize overnight.

2. Run X-ray diffractions of silver azide powder, expose for 22-1/2 hours.

Camera 7161

Knife edges

Back stop 20.153 degrees
Collimater 20.124 degrees

Camera radius 9.9662 centimeters

Copper targets:

$$K\alpha_1 = 1.54050$$

$$K\alpha_2 = 1.54434$$

$$\text{unresolved } 1.5418$$

Measured values

$4 \sin^2 \theta / \lambda^2$	Best correlation	$4 \sin^2 \theta / \lambda^2$	Best correlation
.0621	110	.4046	132
.0625	110	.4046	132
.1122	002	.4310	321
.1122	002	.4310	321
.1174	020	.4478	004
.1174	020	.4493	004
.1302	200	.4623	040
.1305	200	.5105	400
.1749	112	.5507	330
.1752	112	.5612	024
.2289	022	.5762	204
.2289	022	.5914	240
.2436	220	.6284	420
.2444	220	.6605	332
.2939	130	.6899	224
.2935	130	.7389	422
.3199	310	.9419	521
.3576	222	.9575	404
.3570	222	.9938	334

From the above data $1/c_0^2$ was calculated by the following steps.

$$\text{Since: } (4 \sin^2 \theta / \lambda^2) = \frac{h^2}{a_0^2} + \frac{k^2}{b_0^2} + \frac{l^2}{c_0^2}$$

$$\text{then: } (1/c_0^2) = \left[(4 \sin^2 \theta / \lambda^2) - (h^2/a_0^2) - (k^2/b_0^2) \right] (1/l^2)$$

h^2/a_0^2 and k^2/b_0^2 were calculated from previous values, calculated by Dr. Hughes.

$$\frac{1}{\bar{c}_0^2} = \frac{1}{n} \sum_1^n 1/c_0^2$$

The values of $1/\bar{b}_0^2$ and $1/\bar{a}_0^2$ were then calculated using the new value of $1/\bar{c}_0^2$. $1/\bar{c}_0^2$ was recalculated using the new values of $1/\bar{b}_0^2$ and $1/\bar{a}_0^2$. The whole process was repeated (on a computer) until a convergence was noted.

The data obtained using the first 32 values of the above data is:

$$\begin{array}{ll} 1/\bar{a}_0^2 = .03222 & \bar{a}_0 = 5.571 \text{ \AA} \\ 1/\bar{b}_0^2 = .02906 & \bar{b}_0 = 5.866 \text{ \AA} \\ 1/\bar{c}_0^2 = .02785 & \bar{c}_0 = 5.992 \text{ \AA} \end{array}$$

Equal weight was assigned to all values, which led to inaccuracy due to the greater inaccuracy in the lowest reflections. There was too much doubt of the proper hkl values in the higher reflections.

From this data, selected values were taken to determine the final results, with greater weight given to higher index values, in the manner indicated below.

Calculation of $1/c_0^{-2}$ using selected values

Index	$4 \sin^2 \theta / \lambda^2$	$(1/\lambda^2)(4 \sin^2 \theta / \lambda^2 - h^2 / a_0^2 - k^2 / b_0^2)$
222	.3576	.02810
222	.3570	.02795
132	.4046	.02773
132	.4046	.02773
332	.6605	.02725
422	.7389	.02680
352	1.1279	.02785
002	.1122	.02805
002	.1122	.02805
022	.2289	.02818
022	.2289	.02818
112	.1749	.02840
112	.1750	.02840
		$\Sigma = .36447 \Rightarrow .02804$ (average)
343	1.0072	.02802 $\Rightarrow .02802$ (average)
004	.4478	.02799
004	.4493	.02808
024	.5612	.02781
204	.5762	.02796
404	.9575	.02763
334	.9938	.02764
244	1.0337	.02749
		$\Sigma = .19460 \Rightarrow .02780$ (average)
145	1.1935	.02785 $\Rightarrow .02785$ (average)
026	1.1145	.02773
226	1.2425	.02771
316	1.3154	.02767
		$\Sigma = .08311 \Rightarrow .02770$ (average)

weight according to the square of the indices:

$$1/c_0^{-2} = .027816$$

$$1/c_0^{-2} = \frac{\sum_1^n l^2 / c_0^2}{\sum l^2}$$

Calculation of $1/b_0^2$ using selected values

Index	$4 \sin^2 \theta / \lambda^2$	$(1/k^2)(4 \sin^2 \theta / \lambda^2 - h^2/a_0^2 - l^2/c_0^2)$
020	.1174	.02935
020	.1174	.02935
022	.2289	.02953
022	.2289	.02953
220	.2436	.02867
220	.2444	.02888
222	.3576	.02938
222	.3570	.02933
321	.4310	.02833
321	.4310	.02833
024	.5612	.02950
420	.6284	.02822
224	.6899	.02945
422	.7389	.02815
521	.9419	.02718
026	1.1145	.02933
226	1.2428	.02918
		$\Sigma = .49179 \Rightarrow .02893$ (average)
130	.2939	.02908
130	.2935	.02403
132	.4046	.02907
132	.4046	.02907
330	.5507	.02897
332	.6605	.02886
334	.9938	.02896
		$\Rightarrow .02901$ (average)
040	.4623	.02889
240	.5913	.02891
440	.9742	.02867
244	1.0337	.02885
145	1.1925	.02924
		$\Rightarrow .02891$ (average)
062	1.1495	.02886 $\Rightarrow .02886$

weighted average = $.02893 = 1/b_0^2$

Calculation of $1/a_0^{-2}$

Index	$4 \sin^2 \theta / \lambda^2$	$(\frac{1}{h^2})(4 \sin^2 \theta / \lambda^2 - k^2 / b_0^2 - l^2 / c_0^2)$	
200	.1302	.03255	
200	.1305	.03262	
220	.2436	.03200	
220	.2444	.03220	
222	.3576	.03280	
222	.3570	.03265	
204	.5762	.03325	
240	.5914	.03225	
244	1.0337	.03203	
260	1.1653	.03122	
226	1.2428	.03250	
			$\Rightarrow .03237$ (average)
310	.3199	.03233	
321	.4310	.03197	
321	.4310	.03197	
330	.5507	.03229	
332	.6605	.03218	
334	.9938	.03228	
352	1.1240	.03230	
316	1.3154	.03214	
			$\Rightarrow .03218$ (average)
400	.5105	.03191	
420	.6284	.03205	
422	.7389	.03205	
404	.9575	.03214	
440	.9742	.03199	
			$\Rightarrow .03202$ (average)
521	.9419		$\Rightarrow .03194$

weighted average = $.03213 = 1/a_0^{-2}$

Results:

$$1/a_0^{-2} = .03213 \pm .00014$$

$$\overline{a_0} = 5.583 \pm 0.008 \text{ \AA}$$

$$1/b_0^{-2} = .02893 \pm .00002$$

$$\overline{b_0} = 5.880 \pm 0.002$$

$$1/\bar{c}_0^2 = .02782 \pm .0012$$

$$\bar{c}_0 = 5.996 \pm 0.013$$

The calculations on the previous pages seemed to be tending toward certain values. The unit cell dimensions of these values are:

$$a_0 = 5.590 \overset{\circ}{\text{A}}$$

$$b_0 = 5.882 \overset{\circ}{\text{A}}$$

$$c_0 = 6.009 \overset{\circ}{\text{A}}$$

All are within the above limits.

Discussion:

Silver azide is an explosive compound which detonates with application of heat. There is some evidence that the unit cell dimensions are distorted when subjected to intense radiation. In order to properly determine the cell dimensions, a series of photographs should be run, with varied length of exposure, then extrapolated to zero.

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