LATTICE CONSTANTS OF THE CUPROUS AND SILVER HALIDES

BY

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A n essential idea, established by W. L. BRAGG, is that it should be possible to attribute to every chemical atom, considered as a sphere, a constant radius. This hypothesis of "constant atomic radii" has shown itself to be of great importance in the investigations of new types of structures.

The atomic radii are calculated from the known simple structures, by using an arbitrary chosen starting-point, as has actually been done by different authors.

It should be noticed, however, that the radii calculated in this way for heteropolar compounds give the value of the radius of the *ion* and hence it will differ from that of the *atom*.

In comparing the different atomic radii it should only be permitted to compare the atoms under identical conditions, reached by comparisons between "the true atomic radii" defined as the radii of the atoms when being outside the influence of an exterior field of force, a condition approximately reached in the gaseous state.[1]

Further it should be noticed that the atoms frequently occur with different valencies and therefore with different radii of the ions, which is especially salient in compounds like the metals of the sixth and seventh groups of the periodic system, these metals also being able to form negative ions.

On account of these facts there exists in several compounds an apparently great disagreement from the hypothesis of constant atomic radii.

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[1] Cfr. Norsk Geol. Tidsskr. *8*, 267 (1925).

Moreover there occur less salient discrepancies, on account of a greater or lesser deformation of the ions. As shown by FAJANS the anions may be arranged in a series of increasing deformability of the ions:

$$F^-\langle NO_3 \ \langle SO_4^{--}\langle CO_3 \ ^-\langle Cl \ \langle Br^-\langle I^-\langle CN^-\langle O \ \ \langle S \ \ \langle Se \ \ .$$
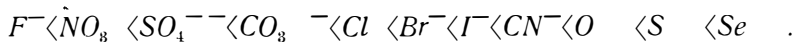
He has also shown that the metals with the peripheric electron orbits arranged according to the type of the cuprous ion (eighteen peripheric electrons) affect a greater deformation of the anions than the metals with noble gas orbits.

This difference in the deformation is so great that it may often be observed in the lattice spacings (e. g. of the monohalides).

Thus the differences between the radii of the chloride, bromide and iodide ions of the alkali halides are greater than the corresponding differences between the cuprous, thallous and silver halides.

The data from the X-ray analyses hitherto carried out on the monohalides of the heavy metals are meagre; thus many of the reflections demanded by the zinc sulfide grouping have never been observed on photographs of the cuprous halides. Moreover, the determinations of the lattice spacings are partly inconsistent.

It would therefore be of great importance to determine the lattice spacings of these compounds with a higher degree of accuracy.

For this purpose the method of WYCKOFF[1] was used. The principles of this method are briefly the following: A Debye-Scherrer photograph is made of a sample containing an intimately mixed powder composed of the substance to be determined and sodium chloride, the latter thus serving as a standard. In this way there occur lines from sodium chloride side by side with lines from the other substance. The lattice spacing of sodium chloride $a = 5{,}628 \ \mathring{A}$ serves as an accurate standard for X-ray measurements. From this figure it is possible to compute the theoretical reflection angles of the different planes of the sodium chloride lattice for different radiations. For $Cu \ K_\alpha = 1{,}539 \ \mathring{A}$, the figures quoted in the tables are obtained.

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[1] Zeitschr. f. Krist. 59, 55 (1923).

By measuring the differences between the outer edges of the reflection lines from the substance and the nearest sodium chloride lines, it is easy to get an accurate determination of the reflecting angles, from the planes of the substance. When using a camera with a diameter $D = 58$ mm., the reflection angle φ may in this way be determined with a maximum error of $\pm\ 0{,}03°$, provided the concerning reflection line from the substance has approximately the same intensity as the sodium chloride line referred to. Working in this way the usual sources of error are omitted (errors depending on divergence of the X ray beam, absorbtion, excentricity of the samples, etc.). In the films of the pure substances the reflection angle φ of each line was found from the formula

$$\varphi = \frac{90\ (2\ d \quad s)}{2\ \pi\ r} \quad K$$

where $2\,d$ is the distance between two corresponding lines, s the diameter of the sample, r the radius of the camera and K a correction term, empirically determined for each film.[1] Apparatus, procedure and calculation of the films are described in a previous paper.[2] A copper target was used.

In the last column of the tables, $sin^2\ \varphi$ is quoted as a product of the common factor, X, and the sum of the square of the indices, $\Sigma h^2 = q$. By the calculation of the length of the edge of the unit cube, the different figures for X were attributed a value proportional to q. (Concerning the reason for this procedure we may refer to our previous paper[2])

The intensities quoted in the tables were computed from the usual formula

$$I = \frac{(A^2 + B^2)\,j}{\Sigma h^2} \cdot \frac{1 + \cos^2 2\ \varphi}{2\ \cos \varphi}$$

$(A^2 + B^2)$ being the structure factor, j the frequency of the reflecting planes of the form.

The salts used for the following determinations were made by precipitation of pure, water-soluble salts.

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[1] Cfr. V. M. GOLDSCHMIDT, L. THOMASSEN; Vid. Selsk. Skr. I, 1923, nr. 2.
[2] Zeitschr. f. physikal. Chemie *117*, 478 (1925).

Table 1. Cuprous Chloride.

Indices	φ in degrees	$\sin^2\varphi = \Sigma h^2 \cdot X$	Intensities	
			obs.	calc
β 111	12,83			
111	14,26	3 · 0,02020	10	10
200	16,56	4 · 0,02030	1	0,5
β 220	21,19			
220	23,77	8 · 0,02030	10	9
β 311	25,11			
311	28,23	11 · 0,02035	8	7
222			—	0,2
β 400	30,85			
400	34,66	16 · 0,02021	3	2
331	38,33	19 · 0,02025	4	4
β 422	38,77			
420			—	0,2
422	44,22	24 · 0,02028	6	6
511 } 333	47,69	27 · 0,02026	4	4
440	53,63	32 · 0,02026	2	2
531	57,30	35 · 0,02022	6	6

$\sin^2\varphi = \Sigma h^2 \cdot 0{,}02026 \quad a_0 = 5{,}406$ Å

Table 2. Cuprous Chloride + Sodium Chloride.

Indices		φ in degrees		$\sin^2\varphi = \Sigma h^2 \cdot X$
NaCl	CuCl	NaCl theor.	CuCl obs.	
	β 111		12,88	3 · 0,01656
	111		14,28	3 · 0,02025
200		15,87		
β 220	β 220		21,36	8 · 0,01688
220	220	22,75	23,75	8 · 0,02027
β 222	β 311	28,27		co nc dence
222	311	33,16		co nc dence
400	400	37,70	34,65	16 · 0,02020
420	331	42,06	38,30	19 · 0,02022
422	422		44,25	24 · 0,02029
	511		47,69	27 · 0,02025
440	440	50,67	53,63	32 · 0,02026
600 } 442	531	55,12	57,41	35 · 0,02028
620		59,85		

$\sin^2\varphi = \Sigma h^2 \cdot 0{,}020250 \quad \mathbf{e_0 = 5{,}407}$ Å

β rad at on: $\sin^2\varphi = \Sigma h^2 \cdot 0{,}01657 \quad a_0 = 5{,}40$ Å

Table 3. Cuprous Bromide.

Indices	φ in degrees	sin²φ = Σh²·X	Intensities obs.	Intensities calc.
β 111	12,42	3·0,01830	10	10
111	13,66		—	0,2
200				
β 220	20,27	8·0,01831	9	9
220	22,49		7	6
β 311	23,90	11·0,01828	2	2
311	26,64		4	3
222				
400	32,68	16·0,01822	—	0,1
331	36,10	19·0,01828	5	7
420				
422	41,53	24·0,01831	4	3
511 } 333 }	44,70	27·0,01833	2	2
440	49,85	32·0,01828	5	7
531	53,21	35·0,01832	—	0,1
442 } 600 }				
620	58,80	40·0,01829	4	6

sin²φ = Σh²·0,01831 a_0 = 5,686 Å

Table 4. Cuprous Bromide + Sodium Chloride.

Indices NaCl	Indices CuBr	φ NaCl theor.	φ CuBr obs.	sin²φ = Σh²·X
β 111	β 111			coincidence
111	111			coincidence
β 200		15,87		
200		22,75		
β 220	β 220			coincidence
220	220			coincidence
	β 311		23,84	11·0,01485
	311		26,69	11·0,01834
222		28,27		
	β 331		32,23	19·0,01496
400	400	33,16	32,73	16·0,01827
	331		36,21	19·0,01836
	β 422		36,75	24·0,01492
420		37,70		
422	422	42,06	41,60	24·0,01837
	511		44,76	27·0,01836
440		50,67		
	531		53,32	35·0,01838
600 } 442 }		55,12		
620	620	59,85	58,90	40·0,01833

sin²φ = Σh²·0,018346 a_0 = 5,681 Å

β radiation: sin²φ = Σh²·0,01836   sin²φ = Σh²·0,01492 a_0 = 5,69 Å

Table 5. Cuprous Iodide

Indices	γ in degrees	Intensities obs.	Intensities calc.	sin²γ = Σh² · X
β 111	11,34	5	10	$3 \cdot 0{,}01618$
111	12,73	1	1	$4 \cdot 0{,}01620$
200	14,71			
β 220	18,87	10	9	$8 \cdot 0{,}01608$
220	21,02			
β 311	22,33			
311	25,01	9	8	$11 \cdot 0{,}01625$
222	26,16	1	0,5	$12 \cdot 0{,}01612$
β 400	27,34			
β 331	30,01			
400	30,60	3	2	$16 \cdot 0{,}01620$
331	33,67	5	4	$19 \cdot 0{,}01618$
β 422	34,17			
420	34,69	3	1	$20 \cdot 0{,}01620$
β 333 } β 511	36,65			
422	38,63	10	5	$24 \cdot 0{,}01623$
β 440	40,51			
333 } 511	41,45	8	4	$27 \cdot 0{,}01623$
β 531	42,84			
440	46,10	5	2	$32 \cdot 0{,}01622$
β 620	46,50			
531	48,93	10	5	$35 \cdot 0{,}01623$
600 } 442	49,77	4	0,5	$36 \cdot 0{,}01619$
620	53,63	8	4	$40 \cdot 0{,}01623$
533	56,55	6	5	$43 \cdot 0{,}01619$
622	57 59	3	0,5	$44 \cdot 0{,}01619$

$\sin^2 \gamma = \Sigma h^2 \cdot 0{,}016196 \quad a_0 = 6{,}046 \text{ Å}$

Table 6. Cuprous Iodide + Sodium Chloride.

Indices NaCl	Indices CuJ	γ NaCl theor.	γ CuJ obs.	sin²γ = Σh² · X
	β 111		11,50	$3 \cdot 0{,}01325$
	111		12,69	$3 \cdot 0{,}01609$
200		15,87		
	β 220		19,00	$8 \cdot 0{,}01325$
	220		21,11	$8 \cdot 0{,}01621$
	β 311		22,50	$11 \cdot 0{,}01331$
220		22,75		
	311		24,94	$11 \cdot 0{,}01616$
222		28,27		
	400		30,66	$16 \cdot 0{,}01625$
400		33,16		
	331		33,66	$19 \cdot 0{,}01616$
420		37,70		
	422		38,60	$24 \cdot 0{,}01622$
	511 } 333		41,43	$27 \cdot 0{,}01622$
422		42,06		
	440		46,09	$32 \cdot 0{,}01622$
	531		48,91	$35 \cdot 0{,}01622$
	600 } 442		49,77	$36 \cdot 0{,}01619$
440		50,67		
	620		53,62	$40 \cdot 0{,}01617$
600 } 442		55,12		
	533		56,56	$43 \cdot 0{,}01619$
	622		57,61	$44 \cdot 0{,}01621$

$\sin^2 \gamma = \Sigma h^2 \cdot 0{,}016193 \quad a_0 = 6{,}047 \text{ Å}$

β radiation: $\sin^2 \gamma = \Sigma h^2 \cdot 0{,}01328 \quad a_0 = 6{,}03 \text{ Å}$

Table 7. Silver Chloride.

Indices	γ in degrees	$\sin^2\gamma = \Sigma h^2 \cdot X$	Intensities obs.	Intensities calc.
111	13,83	$3 \cdot 0,01902$	2	3
β 200	14,25			
200	16,07	$4 \cdot 0,01918$	10	10
β 220	20,64			
220	23,14	$8 \cdot 0,01931$	8	9
β 311	24,50			
β 222	25,65			
311	27,45	$11 \cdot 0,01934$	6	3
222	28,77	$12 \cdot 0,01930$	6	4
β 420, 400	33,89		6	3
331	37,36	$19 \cdot 0,01936$	2	1
β 422, 420	38,58		8	7
β 333} β 511}	41,05			
422	43,03	$24 \cdot 0,01942$	7	6
333} 511}	46,32	$27 \cdot 0,01936$	4	1
440	51,78	$32 \cdot 0,01925$	4	2
531	55,22	$35 \cdot 0,01927$	4	2
600} 422}	56,41	$36 \cdot 0,01927$	10	8

$\sin^2\gamma = \Sigma h^2 \cdot 0,01930 \quad a_0 = 5,539$ Å

Table 8. Silver Chloride + Sodium Chloride.

Indices NaCl	Indices AgCl	γ NaCl theor.	γ AgCl obs.	$\sin^2\gamma = \Sigma h^2 \cdot X$
111	111			coincidence
β 200	β 200			coincidence
200	200	15,87		coincidence
β 220			20,75	$8 \cdot 0,01569$
220	β 220	22,75		
	220		23,15	$8 \cdot 0,01932$
	β 311		24,52	$11 \cdot 0,01566$
	β 222		25,74	$12 \cdot 0,01572$
	311		27,47	$11 \cdot 0,01934$
222	222	28,27	28,74	$12 \cdot 0,01927$
400	400	33,16	33,68	$16 \cdot 0,01922$
	β 420		34,16	$20 \cdot 0,01576$
	331		37,25	coincidence
β 422 420	420	37,70	38,32	$20 \cdot 0,01922$
422	422	42,06	42,86	$24 \cdot 0,01928$
511	333} 511}	45,27	46,21	$27 \cdot 0,01930$
	β 600} β 442}		48,87	$36 \cdot 0,01576$
440	440	50,67	51,72	$32 \cdot 0,01926$
600} 442}	600} 442}	55,12	56,32	$36 \cdot 0,01924$
620	620	59,85	61,35	$40 \cdot 0,01925$

$\sin^2\gamma = \Sigma h^2 \cdot 0,019260 \quad a_0 = 5,515$ Å

β radiation: $\sin^2\gamma = \Sigma h^2 \cdot 0,01574 \quad a_0 = 5,54$ Å

Table 9. Silver Bromide.

Indices	φ in degrees	$\sin^2\varphi = \Sigma h^2 \cdot X$	Intensities obs.	Intensities calc.
111			—	0,2
β 200	13,97			
200	15,47	4·0,01779	10	10
β 220	19,95			
220	22,21	8·0,01787	10	9
β 222	24,82			
311			<1	0,1
222	27,65	12·0,01795	5	4
β 400	28,85			
400	32,39	16·0,01793	3	2
β 420	32,78			
331			—	0,1
β 422	36,17			
420	36,73	20·0,01789	7	6
422	40,92	24·0,01787	6	5,5
β 440	43,14			
511 } 333 }			—	0,1
β 442 } β 600 }	45,61			
440	49,16	32·0,01787	2	3
531			—	0,1
442 } 600 }	53,40	36·0,01790	6	6
620	57,74	40·0,01787	5	5

$\sin^2\varphi = \Sigma h^2 \cdot 0,01788 \quad a_0 = 5,755$ Å

Table 10. Silver Bromide + Sodium Chloride.

Indices NaCl	Indices AgBr	φ in degrees NaCl theor.	φ in degrees AgBr obs.	$\sin^2\varphi = \Sigma h^2 \cdot X$
β 200	β 200			coincidence
200	200	15,87	15,55	4·0,01796
	β 220		19,96	8·0,01457
220	220	22,75	22 20	8·0,01785
β 222	β 222		24,64	12·0,01449
222	222	28,27	27,65	12·0,01795
400	400	33,16	32,36	16·0,01791
420	420	37,70	36,70	20·0,01786
422	422	42,06	40,95	24·0,01789
440	440	50,67	49,18	32·0,01789
600 } 442 }	600 } 442 }	55,12	53,38	36·0,01789
620	620	59,85	57,71	40·0,01787
	622		62,44	44·0,01786

$\sin^2\varphi = \Sigma h^2 \cdot 0,017879 \quad a_0 = 5,755$ Å

β radiation: $\sin^2\varphi = \Sigma h^2 \cdot 0,01452 \quad a_0 = 5,77$ Å

Table 12. Silver Iodide + Sodium Chloride.

Indices		φ in degrees		$\sin^2\varphi = \Sigma h^2 \cdot X$
NaCl	AgJ	NaCl theor.	AgJ obs.	
	111		11,88	$3 \cdot 0{,}01413$
200		15,87		
	β 220		17 64	$8 \cdot 0{,}01147$
	220		19 56	$8 \cdot 0{,}01401$
220	311	22,75	23,15	$11 \cdot 0{,}01405$
222	400	28,27		coincidence
	331		31,06	$19 \cdot 0{,}01401$
400		33 16		
420	422	37,70	35,46	$24 \cdot 0{,}01399$
	511		38 00	$27 \cdot 0{,}01404$
422	440	42,06		coincidence
	531		44 56	$35 \cdot 0{,}01407$
		50,67		

$\sin^2\varphi = \Sigma h^2 \cdot 0{,}014056$ **$a_0 = 6{,}491$ Å**

β radiation: $\sin^2\varphi = \Sigma h^2 \cdot 0{,}01147$ $a_0 = 6{,}49$ Å

Table 11. Silver Iodide.

Indices	φ in degrees	$\sin^2\varphi = \Sigma h^2 \cdot X$	Intensities obs.	Intensities calc.
111	11,79	$3 \cdot 0{,}01392$	6	10
200			—	$< 0{,}1$
β 220	17,55			
220	19,57	$8 \cdot 0{,}01402$	10	10
311	23,07	$11 \cdot 0{,}01394$	9	7
222			—	$< 0{,}1$
400	28,17	$16 \cdot 0{,}01394$	1	2
331	31,06	$19 \cdot 0{,}01401$	3	4
420			—	$< 0{,}1$
422	35,57	$24 \cdot 0{,}01403$	4	6
333 } 511	37,88	$27 \cdot 0{,}01396$	3	3
440	41,92	$32 \cdot 0{,}01395$	2	2
531	44,54	$35 \cdot 0{,}01401$	5	4
600 } 422			—	$< 0{,}1$
620	48,72	$40 \cdot 0{,}01411$	2	3
533	51,15	$43 \cdot 0{,}01411$	2	2
622			—	$< 0{,}1$
444	54,80	$48 \cdot 0{,}01412$	1	1
711	57, 8	$51 \cdot 0{,}01402$	3	2

$\sin^2\varphi = \Sigma h^2 \cdot 0{,}014035$ $a_0 = 6{,}495$ Å

Cuprous Chloride, CuCl. X-ray investigations on this salt have been carried out by R. W. G. WYCKOFF[1] and E. W. POSNJAC and by W. P. DAVEY.[2] The zinc sulfide grouping was stated. The length of the edge of the unit cube was given to $a = 5,49\ \mathring{A}$, and $a = 5,36\ \mathring{A}$ respectively.

The new measurements gave a $5,407\ \mathring{A}$.

Cuprous Bromide, CuBr. This compound has been investigated by the same authors. The zinc sulfide arrangement was stated, and the lattice constant found to be $a = 5,82\ \mathring{A}$ and $5,75\ \mathring{A}$ respectively.

The new measurements gave $a = 5,681\ \mathring{A}$.

Cuprous Iodide, CuI. Three investigations have been made of this crystal. The two said authors give $a = 6,10\ \mathring{A}$ and $6,07\ \mathring{A}$ resp. The third investigation was made upon the mineral *marshite* by G. AMINOFF.[3] He states a $6,02\ \mathring{A}$. The observed intensities agree with the zinc sulfide grouping.

The new measurements gave $a = 6,047\ \mathring{A}$.

For the three said cuprous halides the observed intensities of the reflection lines are in good agreement with those calculated for the zinc sulfide grouping (cfr. table 1, 3, 5).

Silver Chloride, AgCl. The following values have been published for the length of the edge of the unit cube of this salt, crystalizing in the sodium chloride arrangement; W. P. DAVEY (loc. cit.) states $a = 5,52\ \mathring{A}$, and R. B. WILSEY[4] gives a $5,540\ \mathring{A}$.

The new measurements gave $a = 5,545\ \mathring{A}$ in close agreement with WILSEY'S value.

Silver Bromide, AgBr. This salt has also been investigated by W. P. DAVEY (loc. cit.) and by R. B. WILSEY (loc. cit.). The values for the lattice constant given by these authors are $a = 5,78\ \mathring{A}$ and $5,768\ \mathring{A}$ resp.

The new measurements lead to $a = 5,755\ \mathring{A}$ in good agreement with WILSEY'S data.

The observed intensities for the two said silver halides agree well with those calculated for the sodium chloride grouping (cfr. table 7, 9).

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[1] Journ. Am. Chem. Soc. *44, 30,* (1922).
[2] Phys. Rev. *19,* 248, (1922).
[3] Geol. För. Förh. *44,* 444, (1922).
[4] Phil. Mag., *46,* 487, (1923).

Silver Iodide, AgI. It has been shown that artificial silver iodide at an ordinary temperature is mostly met with as a mixture of hexagonal and cubic crystals, assigned to the zinc oxide and zinc sulfide grouping respectively.

According to R. B. WILSEY (loc. cit.) the lattice constant of the cubic crystal is given to $a = 6,493$ Å.

The new measurements gave a $6,491$ Å, in close agreement with the result obtained by WILSEY. No additional lines from the hexagonal modification were observed on the films used for these measurements. As seen from table 11 the intensities are in good accordance with the zinc sulfide grouping.

Summary.

The lattice spacings of the cuprous and silver halides were redetermined. The values obtained for the three silver halides are in close agreement with those published by R. B. WILSEY (loc. cit.).   There is good agreement between observed and calculated intensities.

	Structure[1]		Lattice Constant
$CuCl$	zinc sulfide [4 b, 4 d]	a_0	5,407 Å
$CuBr$	zinc sulfide [4 b, 4 d]	a_0	5,681 Å
CuI	zinc sulfide [4 b, 4 d]	a_0	6,047 Å
$AgCl$	sodium chloride [4 b, 4 c]	a_0	5,545 Å
$AgBr$	sodium chloride [4 b, 4 c]	a_0	5,755 Å
AgI	zinc sulfide [4 b, 4 d]	a_0	6,491 Å

Shortest Atomic Distances.

	Cl'		Br'		J'
Cu·	2,341	0,119	2,460	0,158	2,618
	0,432		0,418		0,193
Ag·	2,773	0,105	2,878	÷ 0,067	2,811

In the preceeding table the shortest atomic distances and their differences are calculated. The shortest atomic distance for $Ag\,J$ is not comparable with those of the two other silver halides, on account of different structures.

Mineralogical Institute of the University
                              Oslo, Febr. 26th, 1926.

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[1] The symboles correspond to WYCKOFF'S tables (The Analytical Expression of the Results of the Theory of Space-Groups, Washington, 1922.)