THE ATOMIC PARAMETERS OF γ-SILVER-CADMIUM

BY

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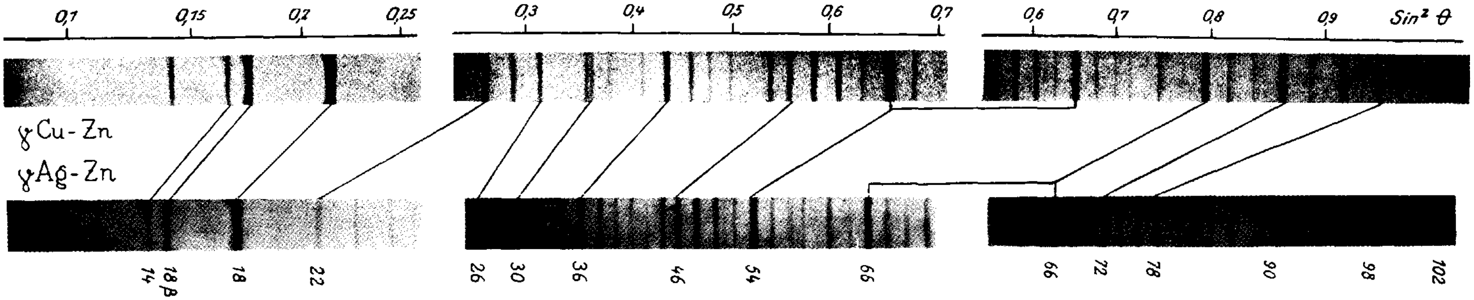
TARTU 1939

K. Mattieseni trükikoda o./ü., Tartu, 1939.



The figure shows the close resemblance between powder photographs of γ-brass (upper triple) and γ Ag-Cd (lower triple). The photographs of γ-brass are by A. Westgren and G. Phragmén, and those of γ Ag-Cd by H. Ålstrand and A. Westgren. Approximate scale $^2/_3$ natural size.

Contents: — (1) Introduction. (2) Intensities of reflections. (3) The first approximation. (4) Equations of re-adjustments and the first re-adjustments. (5) Second and third re-adjustments and final parameters. (6) Interatomic distances and distribution of atoms. (7) Summary of results.

1. Introduction. Using the X-ray powder method, G. Natta and M. Freri[1]), and H. Ålstrand and A. Westgren[2]) assigned to γ Ag-Cd the body-centred structure of γ-brass with 52 atoms to the unit cube. A determination of atomic positions in the unit cube was, however, not attempted by them. It is the purpose of the present paper to give the results of an attempt to determine these positions from the data and powder photographs of Ålstrand and Westgren made available to us by Professor A. Westgren.

2. Intensities of reflections. The close resemblance between the powder photographs of γ Ag-Cd and γ-brass reproduced on Plate I, suggests that the distribution of silver and cadmium atoms in the unit cube of γ Ag-Cd is similar to that of copper and zinc atoms in the unit cube of γ-brass. On this assumption and on the fact that the atomic scattering factors for silver and cadmium are nearly equal, as are those for copper and zinc, the structure amplitude of γ Ag-Cd assumes the same form as the structure amplitude of γ-brass, *i. e.*,

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1) Rend. Acad. Lincei (6) 6. 1927. 506—509.
2) Z. anorg. allg. Ch. 175. 1928. 91.

F (*hkl*)

$$
\begin{aligned}
F(hkl) = {} & 2\cos 2\pi ha \,.\, \cos 2\pi ka \,.\, \cos 2\pi la \\
& + 2\cos 2\pi hb \,.\, \cos 2\pi kb \,.\, \cos 2\pi lb + \cos 2\pi hc \\
& + \cos 2\pi kc + \cos 2\pi lc \\
& + 2\,(\cos 2\pi hd \,.\, \cos 2\pi kd \,.\, \cos 2\pi le \\
& + \cos 2\pi hd \,.\, \cos 2\pi ke \,.\, \cos 2\pi ld \\
& + \cos 2\pi he \,.\, \cos 2\pi kd \,.\, \cos 2\pi ld) \\
& + 2i\{-\sin 2\pi ha \,.\, \sin 2\pi ka \,.\, \sin 2\pi la \\
& + \sin 2\pi hb \,.\, \sin 2\pi kb \,.\, \sin 2\pi lb \\
& - \sin 2\pi hd \,.\, \sin 2\pi kd \,.\, \sin 2\pi le \\
& - \sin 2\pi hd \,.\, \sin 2\pi ke \,.\, \sin 2\pi ld \\
& - \sin 2\pi he \,.\, \sin 2\pi kd \,.\, \sin 2\pi ld\}
\end{aligned}
$$

[3]),

a, b, c, d, e — *a*, *b*, *c*, *d* and *e* being the atomic parameters of four sets of structurally equivalent positions, "A", "B", "C", and "D" containing respectively 8, 8, 12, and 24 atoms. The present task is to utilize the observed intensities in order to deduce such values for atomic parameters that would give the best agreement of the calculated intensities of reflections with the estimated intensities. These values were sought for by a method of successive approximations, the relative intensities being calculated from the formula

I, Θ, *p*

$$
I(hkl) = \frac{1+\cos^2\Theta}{\sin^2\Theta \,.\, \cos\Theta} \cdot p \,.\, F^2(hkl), \qquad (1)
$$

where Θ is the glancing angle and p the number of co-operating planes.

3. The first approximation. As a first approximation it was assumed that tbe atomic parameters of the silver and the cadmium atoms in γ Ag-Cd are equal to those of the copper and the zinc atoms in γ-brass, namely,

$$
a = 0.110, \ b = 0.172, \ c = 0.355, \ d = 0.313, \ e = 0.036 \qquad (2)
$$

if expressed as fractional co-ordinates of the unit cube[4]). The intensities of the reflections of the highest orders calculated for these numerical values of atomic parameters from

[3]) A. J. Bradley and J. Thewlis, Proc. Roy. Soc. London, (A) 112. 1926. 684.
[4]) A. J. Bradley and C. H. Gregory, Phil. Mag. 12. 1931. 154.

formula (1) are listed in column I of Table 1. This table contains the data of all the α_1-reflections obtained by that precision camera of the focussing type which covers the range of the

Table 1.

Comparison of the calculated and visually estimated intensities of the widest deviated reflections of a powder photograph of γAg-Cd of the composition $Ag_{37.8}\,Cd_{62.2}$.

λ	$\sin^2\Theta$	Q^2	*hkl*	I		I*		$I_{est.}$
α	0.5450	58	730	20		42		v. w.
α_1	0.5821	62	732 + 651	79		85		w.
β*	0.6037*	78*	752	18	24	19	30	v. w.
α_1	0.6041	64	800	6		11		
β*	0.6195*	80*	840	3	433	2	405	st.
α_1	0.6203	66	811 + 741 + 554	430		403		
α_1	0.6391	68	820 + 644	60		101		w.
α_1	0.6583	70	653	41		34		w.
α_1	0.6767	72	822 + 660	188		172		m.
α_1	0.6960	74	831 + 750 + 743	40	85	66	105	w.
β*	0.6966*	90*	930 + 851 + 754	45		39		
α_1	0.7149	76	662	105		100		w.
α_1	0.7334	78	752	85		88		w.
α_1	0.7525	80	840	15		8		v. w.
β*	0.7585*	98*	941 + 853 + 770	102		129		w.*
α_1	0.7712	82	901 + 833	79		86		w.
β	0.7895	102	1011 + 772	56	68	47	72	w.
α_1	0.7898	84	842	12		25		
α_2	0.7936	84	842	6		13		v. w.
α_1	0.8093	86	921 + 761 + 655	65		44		w.
α_2	0.8124	86	921 + 761 + 655	33		22		w.
α_1*	0.8281*	88*	664	19		24		v. w.*
α_2*	0.8312*	88*	664	9		12		v. w.*
β	0.8358	108	1022 + 666	71		67		v. w.
α_1	0.8467	90	930 + 851 + 754	266		227		m.
β	0.8824*	114	871 + 855 + 774	260	338	263	309	w.
α_1	0.8835	94	932 + 763	78		46		
α_2	0.8880	94	932 + 763	40		24		v. w.
α_1*	0.9030*	96*	844	3		17		abs.*

Continued at the bottom of the next page.

widest deviated reflections, and besides the only α-reflection of this range, and some significant α_2- and β-reflections. The correspondence of these calculated intensities to the visual estimations listed in the last column, is unsatisfactory. Notable discrepancies of the calculated and estimated intensity ratios are listed in Table 2. These are: —

(1) in case of α_1-reflections the ratios

$$I(\alpha_1 68):I(\alpha_1 62),\ I(\alpha_1 68):I(\alpha_1 76),\ I(\alpha_1 68):I(\alpha_1 78),\ I(\alpha_1 68):I(\alpha_1 82),\ \text{and}\ I(\alpha_1 70):I(\alpha_1 86); \tag{3}$$

(2) in case of α_2-reflections the ratios

$$I(\alpha_2 84):I(\alpha_2 88)\ \text{and}\ I(\alpha_2 86):I(\alpha_2 94); \tag{4}$$

(3) and in case of β-reflections the ratios

$$I(\beta\,98):I(\beta\,120)\ \text{and}\ I(\beta\,118):I(\beta\,108). \tag{5}$$

Continued from the bottom of the preceding page.

β	0.9136	118	1033 + 961	55	60	v. w.
α_1	0.9222	98	941 + 853 + 770	780	990	v. st.
β	0.9295	120	1042	125	112	v. w.
α_1	0.9410	100	1000 + 860	153	189	w.
α_1	0.9599	102	1011 + 772	590	495	st.

λ spectral line of Fe-K radiation;
$\sin^2\Theta$ for observed glancing angles Θ;
Q^2 sum of squares of indices of the reflections;
hkl indices of reflections;
I intensities calculated with unadjusted parameters;
I* intensities calculated with thrice re-adjusted parameters;
$I_{est.}$ estimated intensities: — v. st. = very strong, st. = strong, m. = medium, w. = weak, v. w. = very weak., abs. = absent.

In computing the intensities of reflections from formula (1), the results obtained for α- and β-reflections were multiplied by 1.5 and 0.25 respectively to account for the intensity ratios $I_\alpha : I_{\alpha_1} : I_\beta = 150:100:25$.

For the data in the first three, and in the last column, except those marked by asterisks (*), we are obliged to a private communication by Professor A. Westgren of Stockholm. The data marked by asterisks are our additions, verified where necessary by inspection of a powder photograph kindly sent us by Professor A. Westgren.

Table 2.

Comparison of estimated intensity ratios with intensity ratios calculated with unadjusted and succesively re-adjusted atomic parameters.

$I_i : I_j$	k	k'	k''	k'''	k_{ij}
$I(\alpha_1\ 68) : I(\alpha_1\ 62) =$ w.: w.	0.76	1.15	1.16	1.19	1.1
$I(\alpha_1\ 68) : I(\alpha_1\ 76) =$ w.: w.	0.57	1.05	0.98	1.01	1.0
$I(\alpha_1\ 68) : I(\alpha_1\ 78) =$ w.: w.	0.71	1.14	1.09	1.15	1.1
$I(\alpha_1\ 68) : I(\alpha_1\ 82) =$ w.: w.	0.76	1.25	1.18	1.18	1.1
$I(\alpha_1\ 70) : I(\alpha_1\ 86) =$ w.: w.	0.63	0.67	0.77	0.78	1.0
$I(\alpha_2\ 84) : I(\alpha_2\ 88) =$ vw.: vw.	0.65	0.85	1.02	1.04	1.1
$I(\alpha_2\ 86) : I(\alpha_2\ 94) =$ w.: vw.	0.83	1.23	0.93	0.95	1.1
$I(\beta\ 98) : I(\beta\ 120) =$ w.: vw.	0.84	1.24	1.12	1.16	1.2
$I(\beta\ 118) : I(\beta\ 108) =$ vw.: vw.	0.78	0.86	0.93	0.90	1.1

k, k', k'', and k''' intensity ratios calculated with unadjusted, once, twice, and thrice re-adjusted atomic parameters respectively; k_{ij} estimated intensity ratios.

On the evidence of the visual estimations from Table 1 all these ratios should be equal to or greater than one, whilst according to the calculated data listed in column k of Table 2 these ratios range from 0.57 to 0.84. Therefore it is obvious that the atomic parameters of γ Ag-Cd differ from those of γ-brass, and that re-adjustments in the parameter values stated in (2) must be made.

4. Equations of re-adjustments and the first re-adjustments. To calculate the re-adjustments of the atomic parameters, the expression of intensity as given by formula (1) was expanded into the series

$$I = I_0 + \frac{\partial I_0}{\partial a} \cdot \alpha + \frac{\partial I_0}{\partial b} \cdot \beta + \frac{\partial I_0}{\partial c} \cdot \gamma + \frac{\partial I_0}{\partial d} \cdot \delta + \frac{\partial I_0}{\partial e} \cdot \varepsilon$$

where α, β, γ, δ, and ε are the sought for variations of the atomic parameters a, b, c, d, and e respectively. Next the values of the partial differentials in this series were calculated from the squares of the corresponding structure amplitudes as increments of intensities due to parameter increments $2\pi . \Delta a = 2\pi . \Delta b = 2\pi . \Delta c = 2\pi . \Delta d = 2\pi . \Delta e = +0^{\circ}.2$, and that for $\alpha, \beta, \gamma, \delta, \varepsilon$

all the fifteen reflections entering into the nine ratios (3) to (5). Thus nine equations of the type

$$\frac{I_{io}+\frac{\partial I_{io}}{\partial a}\cdot\alpha+\frac{\partial I_{io}}{\partial b}\cdot\beta+\frac{\partial I_{io}}{\partial c}\cdot\gamma+\frac{\partial I_{io}}{\partial d}\cdot\delta+\frac{\partial I_{io}}{\partial e}\cdot\varepsilon}{I_{jo}+\frac{\partial I_{jo}}{\partial a}\cdot\alpha+\frac{\partial I_{jo}}{\partial b}\cdot\beta+\frac{\partial I_{jo}}{\partial c}\cdot\gamma+\frac{\partial I_{jo}}{\partial d}\cdot\delta+\frac{\partial I_{jo}}{\partial c}\cdot\varepsilon}=k_{ij}$$

k_{ij} were arrived at, where k_{ij} is the estimated ratio of intensities. Finally, by a careful comparison of the intensities of the corresponding pairs of reflections from a powder photograph kindly sent us by professor A. Westgren, the numerical values listed in the last column of Table 2 were assigned to the intensity ratios k_{ij}. The nine numerical equations thus established were converted into Gauss's normal equations and solved for the five variations α, β, γ, δ, and ε.

The result, the first re-adjustments,

$$2\pi\alpha_1=-2^0.2,\quad 2\pi\beta_1=+0^0.8,\quad 2\pi\gamma_1=+1^0.4,\quad 2\pi\delta_1=-1^0.5,$$

and $$2\pi\varepsilon_1=+1^0.5,$$

however, turned out to be too great to be related linearly with the square of the structure amplitude.

5. **Second and third re-adjustments and final parameters.** Therefore, the entire calculation was repeated once over substituting for the parameters of γ-brass, the rejusted values: —

$$2\pi a_1=37^0.4,\quad 2\pi b_1=62^0.7,\quad 2\pi c_1=129^0.2,\quad 2\pi d_1=112^0.2,$$

and $$2\pi e_1=14^0.5. \tag{6}$$

This yielded the second set of re-adjustments: —

$$2\pi\alpha_2=+0^0.5,\quad 2\pi\beta_2=+0^0.2,\quad 2\pi\gamma_2=-0^0.2,\quad 2\pi\delta_2=+0^0.2,$$

and $$2\pi\varepsilon_2=-0^0.7; \tag{7}$$

whilst a check-up with the eight last equations leads to the third set: —

$$2\pi\alpha_3=-0^0.1,\quad 2\pi\beta_3=+0^0.1,\quad 2\pi\gamma_3=0^0.0,\quad 2\pi\delta_3=0^0.0,$$

and $$2\pi\varepsilon_3=+0^0.2. \tag{8}$$

These once, twice, and thrice re-adjusted parameter values were tested by calculating all the intensity ratios referred to and by comparing the calculated intensity ratios, k', k'', and k''' respectively, with the visually estimated ratios k_{i}. Table 2, comparing and summarizing the effect of all the consecutive re-adjustments, shows that the correspondence of the consecutively calculated intensity ratios with the visually estimated ratios increases from column to column, *i. e.* with each consecutive re-adjustment. Since the agreement between the observed values in the last column and the calculated values in the last but one column is already sufficiently good, and since an improvement of the agreement is not to be expected by a continuation of the process of consecutive approximations, the thrice re-adjusted parameter values are adopted as the correct atomic parameters of γ Ag-Cd. By the three sets of re-adjustments (6) to (8) the tentatively adopted parameter values (2) are changed into: — k', k'', k'''

$$2\pi a_3 = 37^0.0, \quad 2\pi b_3 = 63^0.0, \quad 2\pi c_3 = 129^0.0, \quad 2\pi d_3 = 111^0.4,$$
$$2\pi e_3 = 14^0.0$$

or

$$a_3 = 0.105, \quad b_3 = 0.175, \quad c_3 = 0.358, \quad d_3 = 0.309, \quad e_3 = 0.039 \qquad (9)$$

respectively. These values inserted into equation (1) yield the calculated intensities listed in column I* of Table 1, which agree sufficiently well with the estimated values of the last column to afford consistent confirmation of the correctness of the parameter values adopted. This is corroborated by Table 3 which compares the intensities of the calculated and visually estimated intensities obtained by those two precision cameras of the focussing type which cover the ranges of the least and the moderately deviated reflections. Table 3 and Table 1 are summ ed up by Figure 1.

6. Interatomic distances and distribution of atoms. The atomic scattering factors of silver and cadmium are so nearly equal that there are difficulties in distinguishing the positions of silver atoms from those of cadmium by intensity considerations. But some hints on the atomic distribution, nevertheless, may be obtained by considering interatomic distances in, and between the four sets of structurally equivalent positions "A", "B", "C", and "D". The corresponding distances of the closest approach of atoms calculated from the thrice re-adjusted atomic parameters (9) are listed in Table 4, the accu-

Table 3.

Comparison of calculated and visually estimated intensities of the least and the moderately deviated reflections of a powder photograph of γ Ag-Cd of the composition $Ag_{37.8}\,Cd_{62.2}$.

λ	Q^2	*hkl*	I		$I^*_{est.}$
α	12	222	138		w.
α	14	321	102		w.
α^*	16*	400	0		abs.*
α	18	411 + 330	2430	2466	v. st.
β^*	22*	332	36		
α	20	420	29		v. w.
α	22	332	173		w.
α	24	422	100		w.
α	26	510 + 431	79		v. w.
α	30	521	33		w.
α	32	440	10		v. w.
α	34	530 + 433	34		v. w.
α	36	600 + 442	253		m.
β^*	46*	631	31	120	w.
α	38	611 + 532	89		
α^*	40*	620	0		abs.*
α^*	42*	541	1		abs.*
α^*	44*	622	7		abs.*
α	46	631	153	161	w.
β^*	56*	642	8		
α	48	444	234		m.
α	50	710 + 550 + 543	173		m.
α	52	640	45		w.
α	54	721 + 633 + 552	843	944	v. st.
β^*	66*	811 + 741 + 554	101		
β^*	68*	820 + 644	25	66	w.
α	56	642	41		
α	58	730	28		v. w.

λ spectral line of Fe-K radiation;
Q^2 sum of squares of indices of the reflections;
hkl indices of reflections;
I* intensities calculated with thrice re-adjusted parameters;

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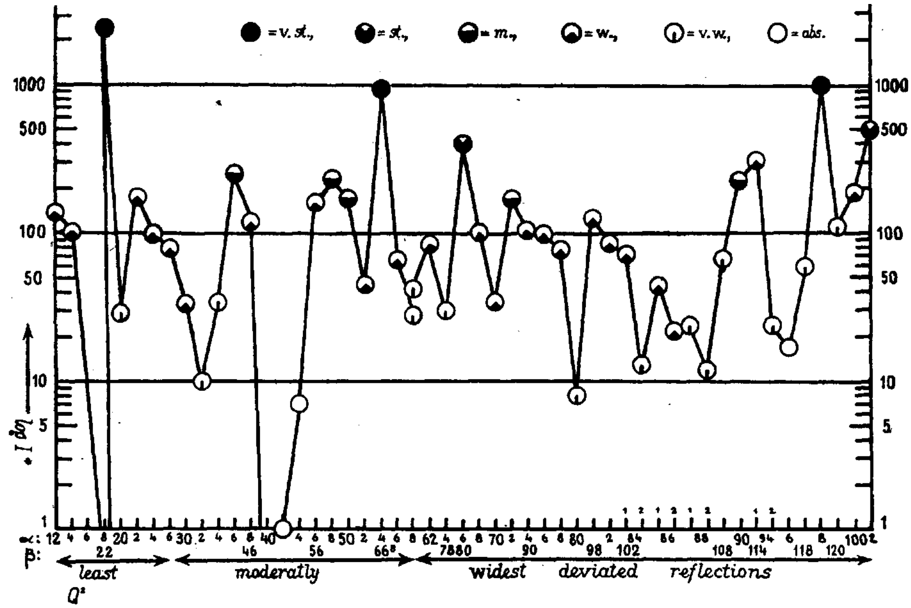

Figure 1.
Comparison of calculated and visually estimated intensities of reflections of a powder photograph of γ Ag-Cd of the composition $Ag_{37.8}$ $Cd_{62.2}$.
Logarithms of intensities calculated with thrice re-adjusted parameter values, log I*, are plotted against sums of squares of indices of reflections, Q^2, visual estimations being marked by appropriately shadowed circles located at the tops of corresponding ordinates. The figure shows that the calculated values are in agreement with visual estimations

racy of the data being about 0.1 Å. The closest approaches of neighbouring atoms in the position "A", and "D", namely A — A = 2.96 Å, A — D = 2.95 Å, and D — D = 2.99 Å, differ only

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$I_{est.}$ estimated intensities: — v. st. = very strong, m = medium, w. = weak, v.w. = very weak, abs. = absent.

In computing the intensities of reflections from formula (1), the results obtained for β-reflections were multiplied by $^1/_6$ to account for the intensity ratio $I_\alpha : I_\beta = 150:25$.

For the data in the first two, and in the last column, except those marked by asterisks (*), we are obliged to a private communication by Professor A. Westgren. The data marked with asterisks are our additions, checked where necessary with powder photographs kindly sent to us for inspection by Professor A. Westgren.

Table 4.

Closest approaches of different kinds of neighbouring atoms calculated from the finally adopted atomic parameters.

Neighbouring atoms	Distances in Å	Neighbouring atoms	Distances in Å
A — A	2.96	B — D	2.86
A — B	2.96	C — C	2.83
A — C	2.92	C — D	2.88
A — D	2.95	C — D	3.14
B — B	4.93	C — D	3.24
B — C	3.07	D — D	2.99
B — D	2.85		

Closest approach in pure cadmium 2.973 Å;
Closest approach in pure silver 2.882 Å.

slightly from the closest approach of the nearest neighbours in pure cadmium, 2.973 Å; and the closest approach of neighbouring atoms in the position "C", namely C — C = 2.83 Å, differs only slightly from the interatomic distance of the nearest neighbours in pure silver, 2.882 Å. There are altogether $8 + 24 = 32$ atoms in the sets "A" and "D", which is the number of cadmium atoms of Ag_5Cd_8 per unit cube; and there are altogether $8 + 12 = 20$ atoms in the sets "B" and "C", which is the number of the silver atoms of Ag_5Cd_8 per unit cube. This suggests that all the silver atoms occupy positions "B" and "C", and all the cadmium atoms positions "A" and "D", resulting in a distribution of atoms homologous to that of the silver and the zinc atoms in Ag_5Zn_8 [5]).

7. Summary of results. By the re-adjustments of the atomic parameters of γ-brass three successive sets of atomic parameters for γ Ag-Cd are derived. These sets are tested by comparing the intensities calculated for them with the observed intensities of reflections of γ Ag-Cd. For the thrice re-adjusted atomic parameters $a = 0.105$, $b = 0.175$, $c = 0.358$, $d = 0.310$, and $e = 0.038$ the agreement between the observed and calculated intensities is sufficiently good to afford confirmation of the correctness of these values. Interatomic distances calculated

[5]) A. J. Bradley and J. Thewlis, Proc. Roy. Soc. London (A) 112. 690. 1926.

from the adopted atomic parameters suggest a regular distribution of the silver and the cadmium atoms, the silver atoms occupying positions of "B" atoms and "C" atoms, the cadmium atoms those of "A" atoms and "D" atoms.

The authors express their thanks to Professor A. Westgren for his kindness in making available his and Mr. H. Ålstrand's powder photographs and the data of γ Ag-Cd.

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July 1939.