

A refinement of the crystal structure of gallium

By **BRAHAMA D. SHARMA** * and **JERRY DONOHUE**

Department of Chemistry, University of Southern California
Los Angeles, California

With 2 figures

(Received March 18, 1962)

Auszug

Von Weissenberg-Aufnahmen erhaltene neue Intensitätswerte wurden durch Projektionen und verallgemeinerte Projektionen der Elektronendichte auf (100) verbessert. Die erhaltenen verbesserten Positionsparameter sind $y = 0,1549 \pm 0,0008$ und $z = 0,0810 \pm 0,0006$. Die nächsten Nachbarn eines Galliumatoms sind eines in 2,484 Å und je zwei in 2,691 Å, 2,730 Å und 2,788 Å Entfernung. Diese Abstände werden auf Grund von PAULINGS Theorien über die metallische Bindung diskutiert. Die Schlußfolgerung ist, daß im metallischen Gallium jedes Atom eine Einfachbindung und sechs zusätzliche Bindungen der Größenordnung 0,3 bis 0,5 ausbildet.

Abstract

New data obtained from Weissenberg photographs of single crystals of metallic gallium have been refined by projections and generalized projections of the electron density on (100). The revised positional parameters thus obtained are $y = 0.1549 \pm 0.0008$ and $z = 0.0810 \pm 0.0006$. The closest neighbors of a gallium atom are one at 2.484 Å, and two each at 2.691 Å, 2.730 Å, and 2.788 Å. These distances are discussed in terms of the metallic bond theories of PAULING. It is concluded that in gallium metal each atom forms one single bond and six additional bonds of order between 0.3 and 0.5.

Introduction

The structure of gallium was first correctly determined by LAVES¹ who found that the crystals were orthorhombic, with $a = 4.515$ Å, $b = 4.515$ Å, $c = 7.657$ Å (from kX), temperature not stated, eight atoms in positions $8f$ of space group $Abma$ (D_{2h}^{18}), with $x = 0.080$

* Present address: Gates and Crellin Laboratory, California Institute of Technology.

¹ F. LAVES, Kristallstruktur und Morphologie des Galliums. Z. Kristallogr. 84 (1933) 256–298.

± 0.001 and $z = 0.159 \pm 0.002$ or 0.153 ± 0.002 . The crystal system and space group were determined from single-crystal data recorded on oscillation, rotation, and Weissenberg photographs. (An earlier study², which had assigned gallium to the tetragonal system, was shown by LAVES to be erroneous). The values for the two positional parameters were based on trial and error considerations of visually estimated intensities, and their limits of error were apparently fixed subjectively.

In a subsequent study, BRADLEY³ confirmed the space group, and found slightly different values for the lattice constants, *viz.*, $a = 4.5259 \text{ \AA}$, $b = 4.5199 \text{ \AA}$, $c = 7.6603 \text{ \AA}$ (from kX), temperature not stated, BRADLEY also determined new values for the positional parameters by use of the following procedures: Photometer measurements of three regions of powder photographs ($\text{NiK}\alpha$) were compared with artificial curves constructed with selected values of the parameters. Since each region covered a very small range of ϑ , the effects of absorptions, temperature factor, and f curve were stated to have no influence on the comparisons. In the theoretical curves, moreover, a certain width and shape was assumed for each reflection, said quantities having been determined from the actual measurements. The precise details of the above methods were not given. In the case of the first region, from curves constructed with $z = 0.153$ and $x = 0.078$ or 0.080 , it was concluded that the value $x = 0.080$ was slightly high. In the case of the second region, from curves constructed with $x = 0.078$ and $z = 0.152$, 0.153 , or 0.159 it was concluded that $z = 0.159$ was impossible and that $z = 0.152$ was to be slightly preferred over $z = 0.153$. In the case of the third region, curves for $x = 0.078$ and $z = 0.153$ or 0.159 also showed that $z = 0.159$ was impossible. The effect of simultaneous variation of the two parameters was not tested. The values finally chosen by BRADLEY were $x = 0.0785 \pm 0.0005$ and $z = 0.1525 \pm 0.0005$, the limits again being apparently assigned subjectively.

The lattice constants have also been determined recently by SWANSON and FUYAT⁴, who gave 25°C as the temperature of their experiment. Their results will be compared with the others later.

² F. M. JAEGER, P. TERPSTRA und H. G. K. WESTENBRINK, Die Kristallstruktur des metallischen Galliums. *Z. Kristallogr.* **66** (1928) 195–216.

³ A. J. BRADLEY, The crystal structure of gallium. *Z. Kristallogr.* **91** (1935) 302–316.

⁴ H. E. SWANSON and R. K. FUYAT, Standard X-ray Diffraction Powder Patterns. U. S. Dept. of Commerce **2** (1953) 9.

In view of the discrepancies between the results described by LAVES and BRADLEY, and because only a limited amount of diffraction data was used in both of those determinations, we decided to reinvestigate the structure of gallium by the use of more extensive data in order to obtain revised values for the positional parameters, the interatomic distances, and the respective standard errors as given by more objective methods.

Experimental

Fine droplets of liquid gallium were attached to glass fibers, cooled in the freezing compartment of a refrigerator, and examined by x-ray diffraction. As expected, extensive supercooling was observed, but eventually one spherical droplet of radius 0.1 mm was found to be crystalline, and, even better, a single crystal. This specimen was then used to record, in a Weissenberg camera, the zero, first, and second layers about the two shorter axes. At this stage, the axes were relabeled so that the space-group symbol would be the conventional one, *Cmca*. This means that, in addition to the obvious axial transformations, the x of LAVES and BRADLEY becomes z , and that their z becomes y .

The intensities on the six different Weissenberg layers were estimated visually with the aid of the multiple-film technique. The values of the F^2 thus obtained were placed on the same relative scale by the usual correlation methods. Since for this crystal absorption effects are far from negligible, a second set of relative F^2 , corrected for absorption ($\mu r = 3.74$), were calculated from the first set. The multiplicative absorption correction used on the intensities was that given for a powder rod in the Internationale Tabellen⁵, and varied from 13.7 at $\vartheta = 0^\circ$ to 1.2 at $\vartheta = 90^\circ$.

Refinement of parameters

The $(0kl)$, $(1kl)$, and $(2kl)$ reflections were used to calculate projections and generalized projections of the electron density on (100) . The signs of the F 's were assigned on the basis of the LAVES and BRADLEY parameters, both of which agreed in this respect. Both the uncorrected and corrected values of the F 's were used. Projections made with the calculated values of the F 's were used to determine the series-termination errors. A resumé of these calculations is presented in Table 1. It

⁵ Internationale Tabellen zur Bestimmung von Kristallstrukturen, vol. 2, p. 584. Verlag Bornträger, Berlin, 1935.

Table 1. *Positional parameters as obtained by the Fourier method*

	No absorption correction		With absorption correction	
	<i>y</i>	<i>z</i>	<i>y</i>	<i>z</i>
Projections made with F_{obs}				
<i>0kl</i>	0.1547	0.0796	0.1545	0.0796
<i>1kl</i>	.1554	.0831	.1551	.0826
<i>2kl</i>	.1537	.0846	.1546	.0853
Projections made with F_{calc}				
<i>0kl</i>	0.1553	0.0771	0.1553	0.0781
<i>1kl</i>	.1548	.0852	.1546	.0844
<i>2kl</i>	.1528	.0893	.1541	.0892
Final Fourier parameters				
<i>0kl</i>	0.1541	0.0821	0.1537	0.0811
<i>1kl</i>	.1560	.0810	.1556	.0808
<i>2kl</i>	.1546	.0799	.1551	.0814
Average	.1549	.0810	.1548	.0811

is interesting that correction of the intensities for absorption had virtually no effect on the resulting parameters. We accept the average values and their standard errors as the best values for the positional parameters, *viz.*, $y = 0.1549 \pm 0.0008$ and $z = 0.0810 \pm 0.0006$.

(A least squares treatment of the corrected data gave the values $y = 0.1549 \pm 0.0005$ and $z = 0.0803 \pm 0.0011$, both of which are in excellent agreement with the Fourier values, but we feel that the Fourier data are to be considered more reliable because of the difficulty in assigning the appropriate weights in the least-squares calculations. The absorption corrections also make the correlation among the six layers a not entirely straightforward procedure. The Fourier method as applied here does not suffer from this defect).

The comparison among the positional parameters and lattice constants as obtained in the several studies is given in Table 2. It may be

Table 2. *Lattice constants and positional parameters*

	LAVES	BRADLEY	SWANSON and FUYAT	This work
<i>a</i>	4.515 Å	4.5199 Å	4.523 Å	—
<i>b</i>	7.657	7.6603	7.661	—
<i>c</i>	4.515	4.5259	4.524	—
<i>y</i>	0.153 or 0.159	0.1525	—	0.1549
<i>z</i>	0.080	0.0785	—	0.0810

noted that our values for the parameters differ from those of BRADLEY by more than his stated limits of error, but do not differ significantly from the earlier values of LAVES.

The observed structure factors (corrected for absorption), are compared with those calculated with the values $y = 0.1548$ and $z = 0.0808$ and the f curve of the Internationale Tabellen including an isotropic temperature factor of $B = 0.48 \text{ \AA}^2$, in Table 3. Because

Table 3. *Observed and calculated structure factors*

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
000	-	248	063	41	40	153	< 9	1	242	56	- 46	400	90	114
002	93	91	064	34	- 35	154	89	81	243	79	73	402	58	55
004	46	- 51	080	8	7	171	86	80	244	39	30	420	51	- 40
020	74	- 77	081	49	- 47	172	52	- 42	260	95	101	421	52	- 49
021	83	- 88	082	< 5	3	173	< 5	3	261	30	21	422	32	- 19
022	39	- 31	083	60	- 83	191	60	- 58	262	56	49	440	76	- 73
023	112	-123	111	84	95	192	36	- 43	263	42	37	441	39	33
024	17	18	112	98	-114	200	147	174	264	31	- 33	442	41	- 35
025	47	- 46	113	< 10	3	202	73	75	280	9	7	460	74	78
040	112	-117	114	78	- 81	204	49	- 47	281	50	- 44	461	23	17
041	66	51	115	50	- 42	220	73	- 59	311	73	65	462	35	38
042	57	- 52	131	118	-140	221	71	- 70	312	70	- 85	511	46	45
043	64	80	132	42	- 27	222	39	- 26	331	88	-105	512	51	- 60
044	36	33	133	13	- 5	223	72	-110	332	30	- 21	531	59	- 73
045	31	31	134	28	- 21	224	26	17	331	21	14	532	16	- 15
060	92	112	135	69	70	225	46	- 42	352	66	84			
061	30	23	151	36	17	240	102	-100	371	67	68			
062	50	53	152	94	101	241	59	44	372	42	- 36			

of the large absorption corrections, no particular significance should be attached to the value of B . The absolute and relative inter-layer scale factors were determined by comparison of the F_{obs} and F_{calc} . The R value, omitting accidentally absent reflections, is 14.3%.

Discussion

If the recently determined lattice constants of SWANSON and FUYAT are used, together with the revised positional parameters given above, each gallium atom is found to have the following nearest neighbors:

- (a) 1 at $2.484 \pm 0.012 \text{ \AA}$
- (b) 2 at $2.691 \pm 0.007 \text{ \AA}$
- (c) 2 at $2.730 \pm 0.003 \text{ \AA}$
- (d) 2 at $2.788 \pm 0.007 \text{ \AA}$.

The stated uncertainties are the standard errors, and do not include any contribution due to errors in the lattice constants. The next closest neighbors are at 3.753 \AA . The coordination number of gallium is thus one or seven, depending on the point of view. LAVES¹ and

PAULING⁶ both considered that Ga_2 units existed in the crystal, and in a more detailed discussion, PAULING, making use of the interatomic distances given by BRADLEY (in kX), assigned bond numbers of 1.21, 0.43, 0.38, and 0.31 to the four respective kinds of shortest distances. These results were obtained by the use of the well-known equation

$$R(1) - R(n) = 0.300 \log n$$

where $R(1)$ is the single bond radius and n the bond number for radius $R(n)$. This treatment gave $R(1) = 1.245$.

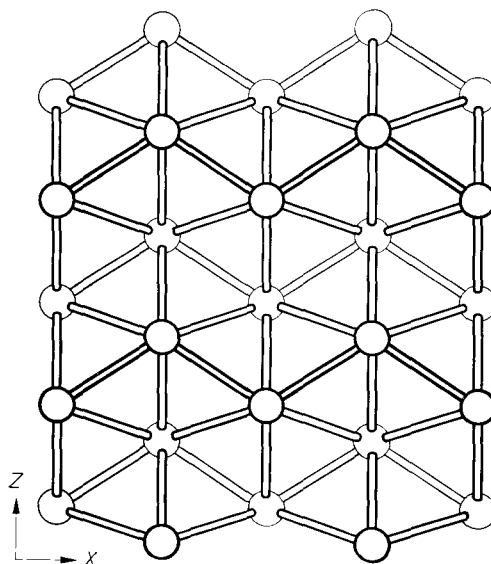


Fig. 1. A portion of four unit cells of the gallium structure projected on (010). The bonds between the layers, *i. e.*, down from the lower atoms and up from the upper atoms, are not shown

The structure itself may be described as consisting of a stacking of somewhat distorted and puckered hexagonal close packed layers, with the bonds between the layers being the strongest, *i. e.*, approximately single bonds, and the bonds within the layers rather weaker, *i. e.*, somewhat less than half bonds. A view perpendicular to one of the layers is shown in Fig. 1, and a view showing the bonding between the layers is shown in Fig. 2.

⁶ L. PAULING, Atomic radii and interatomic distances in metals. *J. Amer. Chem. Soc.* **69** (1947) 542–553.

A quantitative treatment of the nature of the bonding in this metal is difficult, and depends on just which values are assumed for both the valence and single-bond radius for the gallium atom. If, following the first discussion of PAULING⁶, valence of 3.44 is assumed then a value of 1.247 Å for the single-bond radius is obtained, and the bond numbers are 1.04, 0.47, 0.40, and 0.32 for the four different short distances. Except in the case of the shortest distance, which is now virtually a single bond, these values are not too different from those obtained by PAULING from the results of BRADLEY.

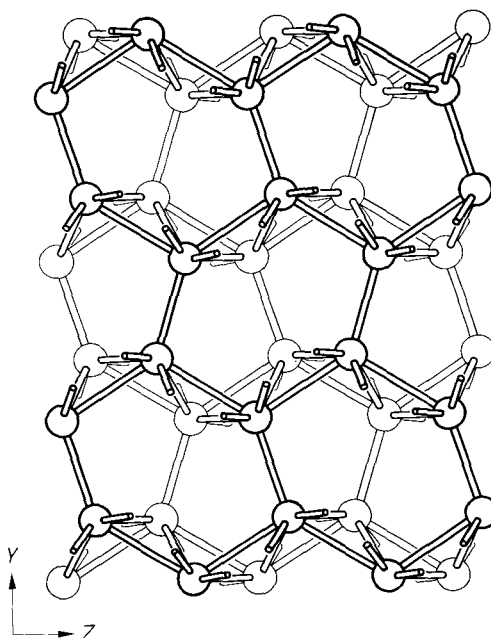


Fig. 2. Four unit cells of the gallium structure projected on (100)

In a later treatment, PAULING⁷, on the basis of his valence-bond theory, considered that in gallium metal there is resonance between two kinds of gallium atoms, *A* and *B*, with valences of 5 and 3, respectively, in the ratio of one to three. The electron configurations are $3d^9 4s 4p^3$ for *A* and $3d^{10} 4s 4p^2$ for *B*. The resulting valence is thus 3.50. The equations of PAULING for first long period,

$$R(1)_{\delta, z} = 1.825 - 0.043z - \delta(1.600 - 0.100z)$$

$$R(1)_{sp^2} = 1.825 - 0.043z$$

⁷ L. PAULING, A resonating-valence-bond theory of metals and interatomic compounds. Proc. Roy. Soc. [London] A **196** (1949) 343–362.

where z = number of electrons outside the argon shell and δ the amount of d character in the bond, then give the values 1.206 Å and 1.266 Å for the radii of Ga-*A* and Ga-*B*, and a single-bond radius of 1.251 Å on the basis of 25% Ga-*A* and 75% Ga-*B*. It is seen that this second method gives a single-bond radius which now differs by an insignificant amount, namely 0.004 Å, from that obtained by the first method, and, unless some future adjustments are made in the constants of the equations used in either or both methods, that it is not possible to decide which interpretation is to be preferred.

Acknowledgments

This work was supported by a grant from the National Science Foundation. The figures were prepared by Mrs. MARYELLIN REINECKE. The metallic gallium was a loan from Prof. JAMES C. WARF. We wish to express our thanks to all three of the foregoing.