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# Ternary Lamellar Compounds of Graphite with Aluminum Bromide and Bromine

Tadashi SASA, Yoichi TAKAHASHI, and Takashi MUKAIBO
*Department of Nuclear Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo*

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Graphite was allowed to react with binary reactants of aluminum bromide and bromine. The formation of ternary lamellar compounds was observed. A change in the activity of the reactants in the system gave three compounds I, II, and III with different contents of aluminum bromide and bromine. Compound I, obtained as the reaction product of graphite with the solution of bromine saturated with aluminum bromide, has a composition of $C_9AlBr_3 \cdot Br_2$, and a lamellar structure of the first stage with $I_c$ of 10.24 Å. Compound II, which has the lowest bromine content, has a composition of $C_{24}AlBr_3 \cdot Br_{0.3}$ and a lamellar structure of the second stage with $I_c$ of 13.35 Å. Compound III, obtained at a bromine activity higher than that for compound I, has a non-stoichiometric composition of about $C_{5-6}Br(AlBr_3)_{0.2}$, and a structure of the second stage with $I_c$ from 13.58 to 13.72 Å. The phase diagram of the ternary system was derived. Compounds I and III have higher bromine contents than $C_8Br$, which is the saturation compound of graphite-bromine system. This is supposed to be due to the stabilization of bromine by the coexistence of aluminum bromide.

There are a large number of chemical substances which react with graphite to form lamellar compounds. In some cases, two different chemical species are intercalated together in the graphite crystal. They are called ternary lamellar compounds. Halogens and alkali metals form a type such as $C_8Br_xCl_{1-x}$[1] or

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[1] G. Furdin, B. Bach, and A. Herold, *C. R. Acad. Sci. Paris, Ser. C*, **271**, 683 (1970).

$C_8Cs_xRb_{1-x}$.[2] These compounds are considered to be a solid solution of two kinds of binary lamellar compounds. Most ternary lamellar compounds known, such as $C_nCl(AlCl_3)_3$,[3] are defined to be compounds containing three components. It is peculiar that the mole ratio of the two reactants takes a fixed value in the ternary lamellar compound of this type. In many cases, the reactant does not react with graphite by itself and requires another component for the lamellar reaction to occur. Hennig[3] studied the lamellar compounds of this type extensively, especially on the ternary system of graphite–metal chloride–chlorine.[3,4] Alkali or alkaline-earth metals[5] are also known to form this type of graphite compound with ammonia. Other graphite compounds of the ternary system containing alkali metals have recently come to be known.[6,7] However, most of them are studied under limited conditions and what the phases with respect to the compositions and structures in each ternary system are not known.

The authors[8] reported that aluminum bromide ($AlBr_3$) forms a ternary compound of graphite in the presence of bromine. In the present study, the compositions and structures of the ternary lamellar compounds of graphite–$AlBr_3$–$Br_2$ were investigated in detail under the conditions of various activities of bromine and aluminum bromide.

## Experimental

*Materials.* The following two types of graphite were used.

(1) Natural graphite with pitch-binder, heat-treated at 3000°C, $c_0=6.708\pm0.002$ Å.

(2) Pyrolytic graphite deposited at 1700°C and heat-treated at 3000°C, $c_0=6.712\pm0.002$ Å.

GR-grade bromine was distilled and passed through concentrated sulfuric acid before use. Aluminum bromide was prepared by the reaction between aluminum chips of high purity and bromine vapor and the following distillation to remove excess free bromine and aluminum.

*Formation of the Ternary Compounds and X-ray Structural Analysis.* The ternary compounds of graphite–$AlBr_3$–$Br_2$ were prepared by the direct reaction of graphite and a liquid mixture of $AlBr_3$ and $Br_2$. Pyrolytic graphite, about 0.5 mm in thickness, was placed in an evacuated glass bulb, which was connected by a constriction to another bulb containing the mixture of the reactants. In some cases bromine was doped directly to the graphite sample into the form of a residue compound. The graphite sample was exposed to the reactant liquid at 120°C for 24 hr. The whole system was then cooled gradually for 24 hr to attain equilibrium at room temperature (25°C). The excess reactant condensed on the surface of the sample was removed carefully by evaporation during the course of cooling.

The changes in weight and macroscopic thickness of the sample were measured after the reaction. The sample was taken out of the glass tube in an atmosphere of dry argon and mounted on a sample holder for X-ray diffraction. The front surface of the sample was then covered with a Teflon sheet 0.05 mm thick to prevent decomposition in the air. X-ray diffraction measurements were carried out by means of a G. M. counter with a strip-chart recorder.

*Chemical Analyses of the Compounds.* The sample of the ternary compound prepared from natural graphite was heated in vacuum at 500°C for the decomposition. The released $AlBr_3$ and $Br_2$ were collected separately, and their amounts were determined by both weight measurements and chemical analyses. After decomposition, a few per cent of the reactants was found to remain persistently in the graphite sample. The residue compound was burnt at 1200°C in a stream of air for the determination of Al in the form of $Al_2O_3$, from which the amounts of $AlBr_3$ and $Br_2$ contained in the compound were estimated. The total content of each reactant was determined as the sum of the amounts of released and residual reactants. The original weight of the graphite sample was used as the amount of carbon in the ternary compound.

The samples prepared from pyrolytic graphite were found to be inadequate for chemical analyses, as their decomposition was much more difficult than that of the samples prepared from natural graphite. It was confirmed that the samples prepared from the two different types of graphite had nearly the same contents of reactants under the same conditions of reaction.

## Results

*(1) Formation of Ternary Compounds.* The change of composition of the ternary compound with the increase of activity of bromine with activity of $AlBr_3$ fixed at unity is shown in Fig. 1. As the solubility of $AlBr_3$ in $Br_2$ liquid is known to be about 40 mol% at 25°C,[9] the activity of $AlBr_3$ remains at unity until $Br_2$ content exceeds 60 mol% in the binary reactant.

We investigated the relation between the content of $AlBr_3$ and that of Br in the ternary compound over relatively low range in bromine content, where the

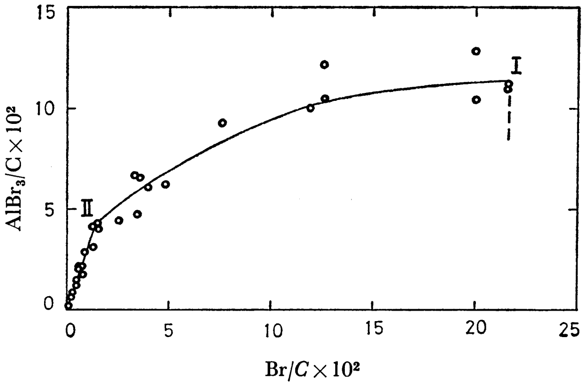

Fig. 1. Compositions of ternary lamellar compounds of graphite with $AlBr_3$ and bromine, while the activity of $AlBr_3$ is unity.

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[2] D. Billaud and A. Herold, *ibid.*, **269**, 490 (1969).

[3] M. L. Dzurus and G. R. Hennig, *J. Amer. Chem. Soc.*, **79**, 1051 (1957).

[4] W. Rüdorff, E. Stumpp, W. Spriessler, and F. W. Siecke, *Angew. Chem.*, **75**, 130 (1963).

[5] W. Rüdorff, S. Schulze, and O. Rubisch, *Z. Anorg. Allgem. Chem.*, **282**, 232 (1955).

[6] M. Nomine and L. Bonnetain, *J. Chim. Phys.*,**66**, 1731 (1969).

[7] D. Ginderow and R. Setton, *Carbon*, **6**, 81 (1968).

[8] T. Sasa, Y. Takahashi, and T. Mukaibo, This Bulletin, **45**, 937 (1972).

[9] J. J. Burbage and A. B. Garrett, *J. Phys. Chem.*, **56**, 730 (1952).

ratio of $AlBr_3$ to Br was found to be nearly three up to the bromine content of Br/C=0.14[8] (Fig. 1). Beyond this bromine content, the ratio of $AlBr_3$ to Br decreased so that a distinct break of the curve was observed. This break point (II, Fig. 1) corresponds to an approximate atomic composition of $C_{24}AlBr_3 \cdot Br_{0.3}$. Beyond point II, the composition changes along a line extending to point I. The compound corresponding to I was obtained when the sample was kept in equilibrium with the solution of bromine saturated with $AlBr_3$ at room temperature. The contents of the reactants in compound I were determined by chemical analysis to be $AlBr_3/C=0.11\pm0.02$ and $Br/C=0.22\pm0.02$ in mole ratio, which lead to an approximate composition of $C_9AlBr_3 \cdot Br_2$.

*(2) Compounds I and II.* It is remarkable that compound I ($C_9AlBr_3 \cdot Br_2$) had a bromine content far higher than $C_8Br$, which is the saturation compound of the binary system of graphite–bromine. The formation of compound I was accompanied by a considerable dimensional change and a distinct color change of the graphite. The samples prepared from the pyrolytic graphite gave a thickness about three times as large as the original samples and a dark green color with metallic luster. Compound I was hygroscopic and unstable in the air, and easily released bromine vapor. It decomposed to compound II in a vacuum at room temperature.

Compound II had the same black color as that of the original pyrolytic graphite, and its macroscopic thickness was about twice as large as that of the original one. Although compound II was comparatively stable, a gradual decomposition was observed in moist air.

The results of X-ray study of compounds I and II prepared from pyrolytic graphite sample are shown in Tables 1 and 2. The lattice constant $I_c$ indicates the distance from one reactant layer to the next along the direction of $c$-axis, neglecting the AB stacking of carbon layers or reactant layers. The results shown in Table 1, together with the observations of the macroscopic dimensional change of the sample along the direction of $c$-axis, lead to the conclusion that compound I has a structure of the first stage, where every layer spacing of graphite is intercalated by reactants and expands from 3.35 Å to 10.24 Å. It is concluded also, from the results shown in Table 2, that compound II has a structure of the second stage with an expansion of every other carbon layer spacing from 3.35 Å to 10.00 Å.

Table 1. X-ray diffraction patterns of compound I $C_9AlBr_3 \cdot Br_2$, $I_c$=10.24Å, Cu$K\alpha$

| 0 0 $l$ | $2\theta^\circ_{obs}$ | $2\theta^\circ_{calc}$ | Intensity (obs) |
|---|---|---|---|
| 0 0 1 | 8.7 | 8.6 | 59 |
| 0 0 2 | 17.3 | 17.3 | 50 |
| 0 0 3 | 26.2 | 26.1 | 1000 |
| 0 0 4 | 34.9 | 35.0 | 66 |
| 0 0 5 | 44.2 | 44.2 | 8 |
| 0 0 6 | 53.6 | 53.7 | 385 |
| 0 0 7 | 63.5 | 63.6 | 22 |
| 0 0 8 | — | 74.0 | — |
| 0 0 9 | 85.3 | 85.3 | 88 |
| 0 0 10 | 97.6 | 97.6 | 9 |
| 0 0 11 | — | 111.7 | — |
| 0 0 12 | 128.9 | 128.9 | 34 |

Table 2. X-ray diffraction patterns of compound II $C_{24}AlBr_3 \cdot Br_{0.3}$, $I_c$=13.35Å, Cu$K\alpha$

| 0 0 $l$ | $2\theta^\circ_{obs}$ | $2\theta^\circ_{calc}$ | Intensity (obs) |
|---|---|---|---|
| 0 0 1 | 6.7 | 6.6 | 6 |
| 0 0 2 | 13.3 | 13.3 | 29 |
| 0 0 3 | 20.0 | 19.9 | 45 |
| 0 0 4 | 26.7 | 26.7 | 1000 |
| 0 0 5 | 33.6 | 33.6 | 24 |
| 0 0 6 | 40.5 | 40.5 | 19 |
| 0 0 7 | 47.8 | 47.7 | 9 |
| 0 0 8 | 55.0 | 55.0 | 297 |
| 0 0 9 | 62.6 | 62.6 | 9 |
| 0 0 10 | 70.6 | 70.5 | 4 |
| 0 0 11 | — | 78.8 | — |
| 0 0 12 | 87.7 | 87.7 | 79 |
| 0 0 13 | 97.5 | 97.3 | 6 |
| 0 0 14 | — | 107.8 | — |
| 0 0 15 | — | 119.9 | — |
| 0 0 16 | 134.7 | 134.7 | 30 |

The X-ray study on the sample with an intermediate composition between the compounds I and II showed the coexistence of these two phases, no other intermediate phase being observed. The X-ray diffraction pattern of the sample with the reactant contents below that of compound II showed a mixture of patterns of original graphite and compound II.

*(3) Intermediate Phase between Compound I and $C_8Br$.* The reaction of graphite with the binary solution of $AlBr_3$ and $Br_2$ was carried out, in which the activity of $AlBr_3$ was changed from zero to unity. The change of the composition of the compound with the change of activity of $AlBr_3$ is shown in Fig. 2. The diversity of the results of chemical analyses might be attributed to the possible errors caused by the condensation of excess reactants or decomposition of the compounds during the course of removing excess reactants. The curve in Fig. 2, which extends from $C_8Br$ to compound

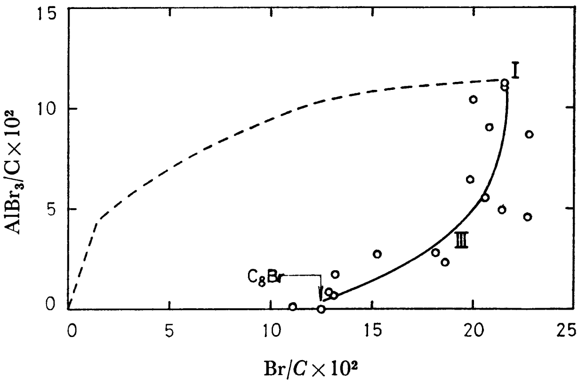

Fig. 2. Compositions of the ternary compounds with the change of the activity of $AlBr_3$.
Dashed line, from Fig. 1.

Table 3. X-ray diffraction patterns of compound III $C_6Br(AlBr_3)_{0.2}$, $I_c$=13.59Å, Cu$K\alpha$

| 0 0 $l$ | $2\theta^\circ_{obs}$ | $2\theta^\circ_{calc}$ | Intensity (obs) |
|---|---|---|---|
| 0 0 1 | — | 6.5 | — |
| 0 0 2 | — | 13.0 | — |
| 0 0 3 | 19.5 | 19.6 | 41 |
| 0 0 4 | 26.0 | 26.2 | 1000 |
| 0 0 5 | 32.7 | 33.0 | 123 |
| 0 0 6 | 39.6 | 39.8 | 106 |
| 0 0 7 | 46.4 | 46.8 | 48 |
| 0 0 8 | 53.8 | 54.0 | 747 |
| 0 0 9 | 61.2 | 61.4 | 62 |
| 0 0 10 | 69.0 | 69.1 | 41 |
| 0 0 11 | — | 77.2 | — |
| 0 0 12 | 85.7 | 85.8 | 232 |
| 0 0 13 | 94.9 | 95.0 | 21 |
| 0 0 14 | — | 105.2 | — |
| 0 0 15 | — | 116.6 | — |
| 0 0 16 | 130.4 | 130.4 | 186 |

I, shows a bend in its midst (III in Fig. 2). X-ray diffraction confirmed the existence of the third new phase around point III. The results of structural analysis of compound III (Table 3) and the macroscopic dimensional change of the sample lead to the conclusion that compound III has a structure of the second stage similar to compound II. Its composition was observed to change from $C_{6.2}Br(AlBr_3)_{0.2}$ to $C_{5.1}Br(AlBr_3)_{0.2}$, and its lattice constant $I_c$ varied also from 13.72 to 13.58 Å. It is considered that compound III is non-stoichiometric. It was black like the original graphite or compound II, not being so stable in the air. Decomposition of compound III was observed in a vacuum to produce compound II finally. No new phase other than compound III was found in the composition range from $C_8Br$ to compound I.

The composition, stage and spacing of carbon layers which contain a reactant layer between them are summarized in Table 4 for each compound together with the data for $C_8Br$.

Table 4. Ternary lamellar compounds of graphite with aluminum bromide and bromine

| Compound | Composition | Stage | Carbon layer spacing (Å) |
|---|---|---|---|
| **I** | $C_9AlBr_3 \cdot Br_2$ | 1 | 10.24 |
| **II** | $C_{24}AlBr_3 \cdot Br_{0.3}$ | 2 | 10.00 |
| **III** | $C_{5-6}Br(AlBr_3)_{0.2}$ | 2 | 10.22<br>≀<br>10.37 |
| C-Br | $C_8Br$ | 2 | 7.03 |

## Discussion

*(1) Ternary System, Graphite–AlBr$_3$–Br$_2$.* The phase diagram of the present ternary system at 25°C is derived from Figs. 1 and 2, and illustrated in Fig. 3. The region surrounded by the dashed curve represents the extent of the composition of the graphite lamellar compounds. Points I, II, and III in Fig. 3 correspond to compounds I, II, and III. The non-stoichiometric compound III is not represented by a single point, but has a certain range of composition. Along line O–A, the existence of several graphite bromine lamellar compounds having the structures of 5th stage to 2nd stage are known.[10] On line O–II, no phase other than compound II and original graphite was observed. Along line I–II, the coexistence of I and II with a varying ratio was observed. The situations are similar on lines I—III and A-III.

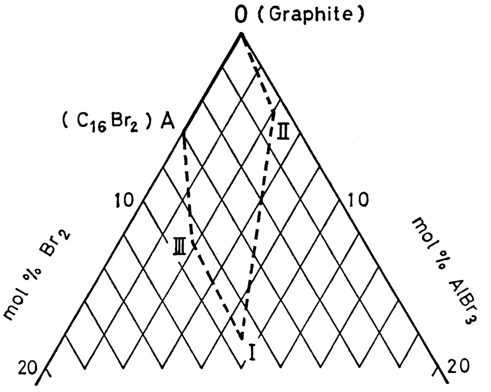

Fig. 3. Phase diagram of the ternary system of graphite $AlBr_3$–$Br_2$ (25°C).

*(2) Formation and Stability of the Ternary Compounds.* It is well-known[3,11] that aluminum chloride ($AlCl_3$) and chlorine form ternary lamellar compounds with graphite. Hennig[3] interpreted the role of the third component chlorine as follows. In the system, graphite–$AlCl_3$, $AlCl_3$ can not raise the charge-transfer with the carbon layers by itself, which is necessary for the formation of lamellar compounds with graphite. When chlorine is added to the system, it forms an ionic bonding with the carbon layers and stabilizes the neutral $AlCl_3$ molecules in the interstices of the carbon layers. The ratio of $AlCl_3$ to Cl in the compound was found to remain nearly three up to the saturation compound of the first stage.

The ternary compound in the present study, graphite–$AlBr_3$–$Br_2$, is very similar system to that of graphite–$AlCl_3$–$Cl_2$. $AlBr_3$ does not react with graphite by itself and requires bromine for the occurrence of lamellar reaction. The mole ratio of $AlBr_3$ to Br was also found to be nearly three up to the compound of the second stage (compound II). The situation is, however, different for the compound of the first stage. The atomic composition of the lamellar compound with $AlCl_3$–$Cl_2$ was reported to be approximately $C_9AlCl_3 \cdot Cl_{0.3}$,[3] whereas that with $AlBr_3$–$Br_2$ is $C_9AlBr_3 \cdot Br_2$. The ratio of $AlBr_3$ to Br does not remain three for the first stage, decreasing to nearly 1/2, which means that the mole ratio of $AlBr_3$ to $Br_2$ is unity. The difference in composition of both

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[10] T. Sasa, Y. Takahashi, and T. Mukaibo, *Carbon*, **9**, 407 (1971).

[11] W. Rüdorff and R. Zeller, *Z. Anorg. Allgem. Chem.*, **279**, 182 (1955).

compounds of the first stage may be attributed to the fact that chlorine is scarcely absorbed by graphite at room temperature by itself,[12] while bromine is easily absorbed in the same condition.

The bromine content of the first stage compound of graphite–$AlBr_3$–$Br_2$ is far higher than that of $C_8Br$. Figure 2 shows that the bromine content of the ternary compound increases with the increase of $AlBr_3$ content from the value corresponding to $C_8Br$ to that of compound I *via* compound III. It is obvious that the coexistence of $AlBr_3$ molecules stabilizes the bromine molecules in the graphite crystal, in the same way as bromide stabilizes $AlBr_3$. $AlBr_3$ and $Br_2$ are considered to be complementary with each other in the lamellar reaction with graphite. It is also remarkable that although the activity of bromine in the system decreases when the composition changes from $C_8Br$ to compound I, the bromine content in the lamellar compound increases due to the stabilizing effect of $AlBr_3$ on $Br_2$ molecules. It should be noted that in the case of the ternary compound, graphite–bromine–chlorine $C_8Br_xCl_{1-x}$,[1] the bromine content of the compound is known to decrease as the activity of bromine in the system decreases.

In the system, graphite–$AlCl_3$–$Cl_2$, the stabilization of chlorine by $AlCl_3$ is also observed. Although chlorine is hardly intercalated in graphite above room temperature, a considerable amount of chlorine is found to be intercalated in graphite in the presence of $AlCl_3$. The energy of stabilization by the coexistence of aluminum halide in both cases may be attributed to a kind of solvation energy between halogen molecules and aluminum halide molecules.

*(3) Arrangements of Reactant Molecules in an Interstice of Graphite Layers.* Table 4 shows that the carbon layer spacings containing reactant molecules have similar values in the three compounds in spite of different molecular compositions. It is considered that the skeleton of $AlBr_3$ determines the layer spacing in all the three cases, because $Br_2$ molecules are too small to maintain such a large layer spacing as 10 Å.

The arrangements of reactant molecules in an interstice of graphite layers are investigated in several graphite lamellar compounds,[13–15] and found to be analogous to that of pure reactant solid. The structural analysis was carried out on the assumption that the skeleton of $AlBr_3$ in an interstice of graphite layers is analogous to that of pure solid of $AlBr_3$. It is known that in the crystal of $AlBr_3$,[16] Br atoms form trigonal layer planes and Al atoms are distributed in the interstices of Br layers. The experimental value of the spacing of carbon layers of compound I, 10.24 Å, was found to coincide with the calculated value, if it is assumed that two Br layers of $AlBr_3$ are included in an interstice. The structure factors calculated based on the assumed stacking sequence of the reactant molecules gave qualitative agreement with the experimental values (Table 1). The quantitative agreements, however, were not satisfactory.

The composition of $C_9AlBr_3\cdot Br_2$ and the interlayer spacing of 10.24 Å give a density of 4.4 g/cc for the reactants in the interstices of graphite layers. This is much higher than the density of solid $AlBr_3$, 3.01, or liquid $Br_2$, 3.10. The arrangements of the molecules in an interstice of graphite layers should be deformed considerably from those in pure reactant solids to give dense packings corresponding to 4.4 g/cc.

## Conclusion

Aluminum bromide and bromine were found to form ternary lamellar compounds with graphite. Three phases of the ternary system were found to exist with the changes of activity of $AlBr_3$ and $Br_2$ in the system at 25°C. The first phase (compound I), which has the highest reactant contents among the three, has the approximate composition $C_9AlBr_3\cdot Br_2$, and a lamellar structure of the first stage where every interstice of graphite layers is intercalated with reactants and expands from 3.35 Å to 10.24 Å. The second phase (compound II) formed at a lower activity of bromine than that for compound I, has the composition of $C_{24}AlBr_3\cdot Br_{0.3}$, and the structure of second stage with $I_c$ of 13.35 Å. The third phase (compound III) formed at the activity of bromine between compound I and $C_8Br$, has a non-stoichiometric composition of $C_{5-6}Br(AlBr_3)_{0.2}$, and a structure of the second stage similar to compound II. The bromine content of the ternary compounds was found to increase with the increase of $AlBr_3$ content from $C_8Br$ to compound I through compound III. It is concluded that $AlBr_3$ and $Br_2$ stabilize with each other complementarily in graphite crystal.

The authors are grateful to Mr. M. Iwakura for his collaboration in the experimental work.

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12) A. Herold, *Bull. Soc. Chim. Fr.*, **1955**, 999.

13) J. M. Cowley and J. A. Ibers, *Acta. Crystallogr.*, **9**, 421 (1956).

14) W. T. Eeles and J. A. Turnbull, *Proc. Roy. Soc.* **A 283**, 179 (1965).

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16) R. W. G. Wyckoff, "Crystal structures", Vol.2, 7 g, Interscience Publishers, New York, N. Y. (1960).