

# On the Crystal Structure and Crystalline Configuration of the Normal and Modified Si-Al Alloys

By

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## Abstract

The cooling curves and the micro-structures of various sand-cast specimens were preliminarily examined in connection with the normal and modified Si-Al alloys, to find out the characteristic modifying effects of a series of substances analogous in some peculiar respects to sodium. By way of revising and completing the conclusion thus arrived at, the X-ray investigation was then carried out, in connection with the crystal structures and the crystalline configurations of the same alloys.

As the consequence of these researches, it became clear on the one hand, that the micro-structures of the alloys inform us very little with regard to their actual crystalline configurations: Moreover, on the other hand, the peculiarities of the substances efficacious for the modification of Si-Al alloy, were confirmed not always to be in good accordance with those generally accepted, by the present theories of modification.

## Introduction

The marked increase of the industrial importance of Si-Al alloys during the last few years is mainly due to the improvement in their mechanical properties, caused by the modifying process of adding a small quantity of sodium or sodium fluoride. Accordingly, a number of metallographical investigations by means of the thermal analysis and microscopical test have hitherto been made to find out the reason why such a modification should take place. The crystal structures and crystalline configurations of Si-Al alloys were also examined by Jeffries,<sup>1</sup> Shinoda<sup>2</sup> and others utilizing X-rays, and as the consequences

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1. *Chem. and Met. Eng.*, **29**, 360 (1922)

2. Suiyokwai-Shi, Department of Mining and Metallurgy, Kyoto Imperial University, No. 5, **5** (1927)

of these X-ray examinations, the mechanism of modification above stated was in certain respects conclusively demonstrated.

Notwithstanding these, there remains still unknown with regard to this subject, even whether or not the micro-structures of the alloys are really in good accordance with their actual crystalline configurations; much more are further experiments needed to arrive at a general conclusion. Owing to such a lack of evidences, the mechanism of modification of Si-Al alloys, which has generally been attributed to the formation of ternary constituents or under-cooling phenomenon by the present thermodynamical considerations, seems hardly to be explainable in terms of the crystallographical theory of the space-lattice. So, the writer was induced to carry out the present investigation, not only by way of continuing the foregoing researches on the growth of metallic crystals<sup>1</sup> or on the Si-Al alloys<sup>2</sup> performed in our laboratory, but as one of the extensions of the previous ones with regard to the subject under consideration.

In the present investigation, the cooling curves and the micro-structures of several sand-cast specimens were preliminarily examined with regard to the normal Si-Al alloys by the ordinary metallographical methods. Essentially the same experiment was repeated in connection with those of the modified Si-Al alloys, which were prepared by adding various substances analogous to sodium in some peculiar respects. Then, the crystal structures and crystalline configurations of these two kinds of specimens, normal and modified, were examined with X-rays.

The experimental results thus obtained, were found not to be legitimately explainable by the theories of modification nowadays, as will be described below.

### Specimens

In this experiment, the normal and modified Si-Al alloys of various compositions, cast at 750°C into a U-shaped sand mould (10 mm. in inner diameter and 100 mm. long), were used as the specimens. To obtain the specimens of the normal alloys, the melt was usually made to contain 7, 13 and 22 per cent. of silicon respectively, by melting the intermediate Si-Al alloy (containing about 22 per cent. of silicon)

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1. e. g., H. Hirata and Y. Tanaka; These Memoirs, A, 17, 143 (1934)

2. H. Kotô; The Anniversary Volume dedicated to Prof. Masumi Chikashige, 303 (1930)

with pure aluminium (purity 99.8 per cent.) in a morganite crucible lined with alundum cement. While, those of the modified ones were prepared by adding a small quantity of sodium or another modifier as given in the second column of Table I at 800°C, to the molten normal alloy containing 13 per cent. of silicon. The properties analogous to sodium and the other peculiarities of these modifiers are noted in the first column of the same table; whereas, the third column of Table I represents the amounts of the modifiers added to prepare the modified specimens mainly used in the present experiment. To secure unity in the experimental data obtained, all the experiments were made with the vertical portion of U-shaped ingot.

Here, it is noticed that the compositions of the specimens and the amounts of the modifiers sometimes varied from those above mentioned, according to the purposes of researches, as will be stated later.

Table I

|               | Modifier | Amount added (Wt.-%) | Micro-structure  |   | Modifying Effect               |
|---------------|----------|----------------------|--|---|--------------------------------|
|               |          |                      | Primary Crystal  | Eutectic  |                                |
| Alkali Metals | Na       | 0.1                  | nil  | Silumin structure   | most remarkable                |
|               | Na       | 0.5                  | nil  | ditto   | ditto                          |
|               | Na       | 1                    | very small quantity of Al crystals   | ditto   | somewhat inferior to the above |
|               | Na       | 3                    | Al crystals  | ditto   | more inferior to the above     |
|               | Li       | 0.1                  | dendritic Al crystals  | Si comes to appear in a fine globular form  | remarkable next to Na          |
|               | Li       | 0.5                  | dendritic Al crystals and large quantity of crystalline substance supposed to be of $Si_2Li_6$ | ditto   | ditto                          |
|               | K        | 0.1                  | Si crystals  | almost unaltered with that of the normal alloy  | almost inappreciable           |
|               | K        | 0.5                  | very small quantity of Si crystals   | The central part of the ingot is composed of the eutectic containing very fine globular grains of Si, while in the other parts, Si is crystallized in a fine needle-shape | somewhat appreciable           |
|               | K        | 1                    | ditto  | Si is mostly crystallized in a fine needle-shape  | rather remarkable              |

Table I (Continued)

|  | Modifier | Amount added (Wt.-%) | Micro-structure  |   | Modifying Effect             |
|--|----------|----------------------|--|---|------------------------------|
|  |          |                      | Primary Crystal  | Eutectic  |                              |
| Alkaline Earth Metals                          | Ca       | 0.1                  | The amount of the primary crystallized Si decreases in comparison with that of the normal alloy  | Si comes to appear in somewhat finer needle-shaped crystals than those of the normal alloy  | somewhat appreciable in part |
|  | Ca       | 0.5                  | very small quantity of dendritic Al crystals   | The eutectic being mainly composed of Si crystallized in a needle-shape of considerable dimensions, is partly of the fine structure | rather remarkable in part    |
|  | Mg       | 0.1                  | primary Si crystals surrounded by Al   | The eutectic contains needle-shaped Si crystals of considerable dimensions  | almost inappreciable         |
|  | Mg       | 0.5                  | very small quantity of Al crystals   | The eutectic consists mainly of Si crystallized in a needle-shape   | rather remarkable in part    |
| The volatile Elements as Na                    | Te       | 0.1                  | Si crystals  | The eutectic contains needle-shaped Si crystals   | nil                          |
|  | Te       | 0.5                  | ditto  | ditto   | ditto                        |
|  | As       | 0.1                  | ditto  | ditto   | ditto                        |
|  | As       | 2                    | The amount of the primary crystallized Si decreases in comparison with that of the normal alloy, and primary crystals of Al come to appear surrounding Si crystals | Si comes to appear in somewhat finer needle-shaped crystals than those of the normal alloy  | somewhat appreciable in part |
| The Elements insoluble to both Al and Si as Na | Bi       | 0.1                  | Si crystals  | The eutectic contains needle-shaped Si crystals   | nil                          |
|  | Bi       | 4.5                  | ditto  | ditto   | somewhat appreciable in part |
|  | Sb       | 0.1                  | ditto  | ditto   | nil                          |
|  | Sb       | 0.5                  | ditto  | ditto   | somewhat appreciable in part |

In this table, the normal Si-Al alloy containing 13 per cent. of silicon is called the "normal alloy" for short.

## Experimental Results

### I. Micro-structure, Cooling Curve and Dilatation

The micro-photographs of some of the normal and modified specimens used in this experiment, are reproduced in Plate I. With regard to these two series of specimens, the binary constitutional diagram for the normal Si-Al alloys has already been determined by Fraenkel<sup>1</sup>, Edwards<sup>2</sup> and others.<sup>3</sup> Moreover, despite the lack of any complete ternary constitutional diagram corresponding to the modified ones, their constitutions may also be inferred from the experimental results obtained by Mathewson,<sup>4</sup> Gwyer,<sup>5</sup> Williams<sup>6</sup> and Assmann<sup>7</sup>, dealing with the binary systems as those of Na-Al, Bi-Al, Bi-Si and Li-Al respectively. It is conceivable from these diagrams that all the specimens of the normal and modified alloys under consideration are mainly composed of the eutectic, except for those of the normal ones containing respectively 7 and 22 per cent. of silicon, these two exceptions being presumed to bear the considerable amounts of the primary crystallized aluminium or silicon.<sup>8</sup>

As can be seen in Figs. 1, 2 and 3, Plate I, the micro-structures of the normal alloys show us, that they are composed not only of the eutectic containing needle-shaped crystals of silicon, but also of various amounts of the primary crystallized aluminium or silicon. Furthermore, the aspects of these primary crystallized substances are observed to vary with the increasing amounts of silicon contained in the specimen: i. e., in Fig. 1, Plate I, which is taken with the specimen of the normal alloy containing 7 per cent. of silicon, the primary crystals are observed to consist of the comparatively large irregular grains of aluminium;

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1. Zeits. f. anorg. Chem., **53**, 154 (1908)

2. Chem. and Met. Eng., **28**, 165 (1923)

3. e.g., Roberts; J. Chem. Soc., **105**, 1383 (1914)

Rosenhain, Archbutt and Hanson; Eleventh Report to the Alloys Research Committee of the Institution of Mechanical Engineers, (1921)

B. Ôtani; J. Inst. Met., **36**, 243 (1926)

A. G. C. Gwyer and H. W. L. Phillips; J. Inst. Met., **36**, 283 (1926)

4. Zeits. f. anorg. Chem., **48**, 191 (1906)

5. Zeits. f. anorg. Chem., **49**, 311 (1906)

6. Zeits. f. anorg. Chem., **55**, 1 (1907)

7. Zeits. f. Metallk. **18**, 51 (1926)

8. In this paper, aluminium containing very small amount of silicon ( $\alpha$ -solid solution of silicon in aluminium) and silicon containing very small amount of aluminium ( $\beta$ -solid solution of aluminium in silicon) are respectively called "aluminium" and "silicon" for short.

while, Figs, 2 and 3, Plate I indicate that the specimens containing 13 and 22 per cent. of silicon respectively, bear the polyhedral grains of the primary crystallized silicon, and the whole amount of these primary crystals increases more markedly in the latter specimen containing 22 per cent. of silicon, than in the former one containing 13 per cent. of the same element.

From the foregoing argument advanced in connection with the normal alloys, it became clear that their micro-structures coincide fairly well with the constitutional diagram of Si-Al system. Not only these, but the micro-structures of the modified alloys, which were partly reproduced in the figures following Fig. 4, Plate I, and tabulated in the third column of Table I, also indicate the predomination of the eutectic, as was previously inferred from the constitutional diagrams. Consequently, we may conclude that all the specimens of the normal and modified alloys examined are of usual micro-structure.

If we inspect the micro-photographs of the modified specimens in Plate I more minutely, the modifying effect of adding each element can easily be detected from the refinement of their micro-structures. The effect thus confirmed is shown in the fourth column of Table I.

In this table, not only sodium but the other alkali metals examined, such as lithium and potassium, are also found to be very efficacious for the modification of Si-Al alloy. Furthermore, it is seen that calcium and magnesium, belonging to the alkaline earth metals, come the next to these alkali metals in the conspicuousness of their modifying effect.

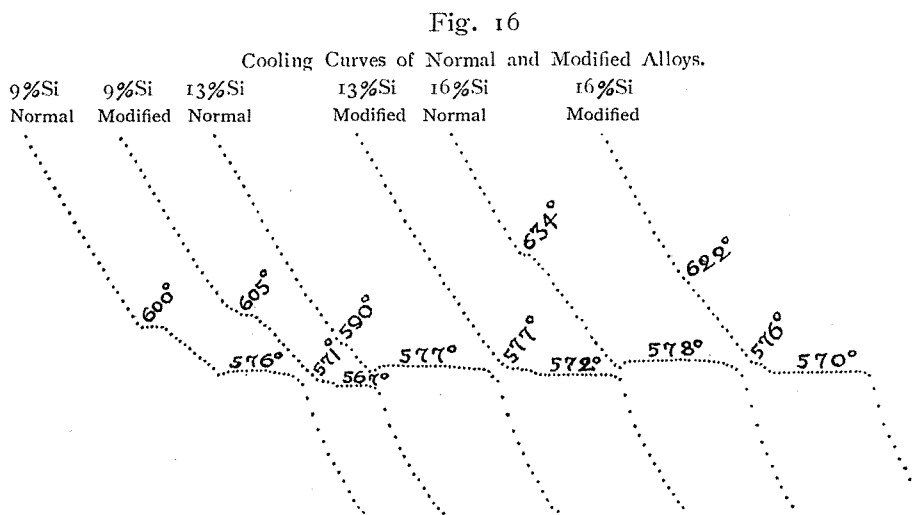
Contrary to the elements above mentioned, phosphorous, sulphur, selenium, tellurium and arsenic, which bear resemblance to sodium in their volatility, give rise to so slight a modification generally as to be hardly appreciable. Even in the special cases when these volatile elements were found somewhat efficacious for the modification, the aspects of the modifying effect considerably differed from that caused by sodium: e. g., the modifying effect of tellurium could only be detectable with the addition of the comparatively larger amount (about 5 per cent.), than those added in the cases of the alkali or alkaline earth metals. These facts above confirmed, can hardly be explainable by attributing the modifying agent of sodium to its volatility.

The modifying effects of adding bismuth and antimony, which are miscible neither to aluminium nor silicon, were also examined microscopically and tabulated again in the fourth column of Table I. As can be seen in this table, these two elements were also confirmed

not to be efficacious for the modification, as the volatile ones. Moreover, with regard to the modifying effects of some other elements belonging to this category, such as lead, cadmium and thallium, the same examination was carried out, but no sign of the modification could be observed even in these cases. Thus, the ternary constituents theory, which attributes the modifying agent of sodium to its separation from the molten Si-Al alloys by cooling, may hardly be said to explain the mechanism of modification at large.

To make the further confirmation on the mechanism of modification of Si-Al alloys, the thermal analysis was made in connection with the normal and modified alloys both containing less than 16 per cent. of silicon. Some of the cooling curves thus obtained are reproduced in Fig. 16.

As can be seen in Fig. 16, the results of the thermal analysis above stated were found to be essentially the same as those given by B. Ôtani,<sup>1</sup> who disproved the under-cooling theory of modification of



Si-Al alloys: i. e., the fair agreements between the cooling curves obtained by both series of examinations can be observed, not only with respect to the fact that the temperature of primary crystallization of the alloy modified with sodium is higher than that of the corresponding normal alloys in the aluminium side, but with regard to many other points. Especially, it is noticed that the curves obtained in connection

1. Loc. cit.

with the normal alloys in Fig. 16, similarly as those given by B. Ôtani, have the more remarkable indentations indicating the under-cooling of the specimens at the temperatures of primary and eutectic crystallization, than the curves corresponding to the modified ones containing a small quantity of sodium. Thus, the under-cooling theory of modification of Si-Al alloys, as well as the considerations based upon the volatility of sodium or the formation of ternary constituents before mentioned, seems to be exceptional, if not unreasonable, in this respect.

Here, it may be advisable to append the results of our examination on the abnormal dilatations of various specimens, which was carried out by means of the improved differential self-photographing dilatometer.<sup>1</sup> Some of the dilatation curves thus obtained by making use of pure aluminium as the standard, are shown in the annexed figure, Fig. 17.

Among these curves in Fig. 17, that represented by A was taken with the sand-cast specimen of the normal alloy left as it is. From this curve, the specimen above mentioned is seen to expand abnormally at about 350°C on heating. But, such an abnormal dilatation could no more be detectable from the curve represented by B, which was taken with the specimen once used in the former examination. These facts above mentioned show us without doubt, that the abnormal dilatation above stated is of the irreversible variety.

The dilatation curves following C in Fig. 17 were similarly taken as the curve A in the same figure, with some of the sand-cast specimens of the modified alloys. As may be seen in these curves, the abnormal dilatation observed with the specimen of the normal alloy can also be detected even with those of the modified ones containing the third elements. But, it is noticed that this abnormal dilatation came to appear the less markedly in the curves taken with the specimens of the more modified structure, as was observed with some of the specimens containing the alkali or alkaline earth metals.

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1. D. Uno, S. Yoshida and S. Katori; A Report of the Institute for Chemical Research, Imperial University, Kyoto, **3**, 152 (1933)



Fig. 17 a

The Differential Dilatation Curves of the Normal and Modified Alloys containing 13 per cent. of silicon.

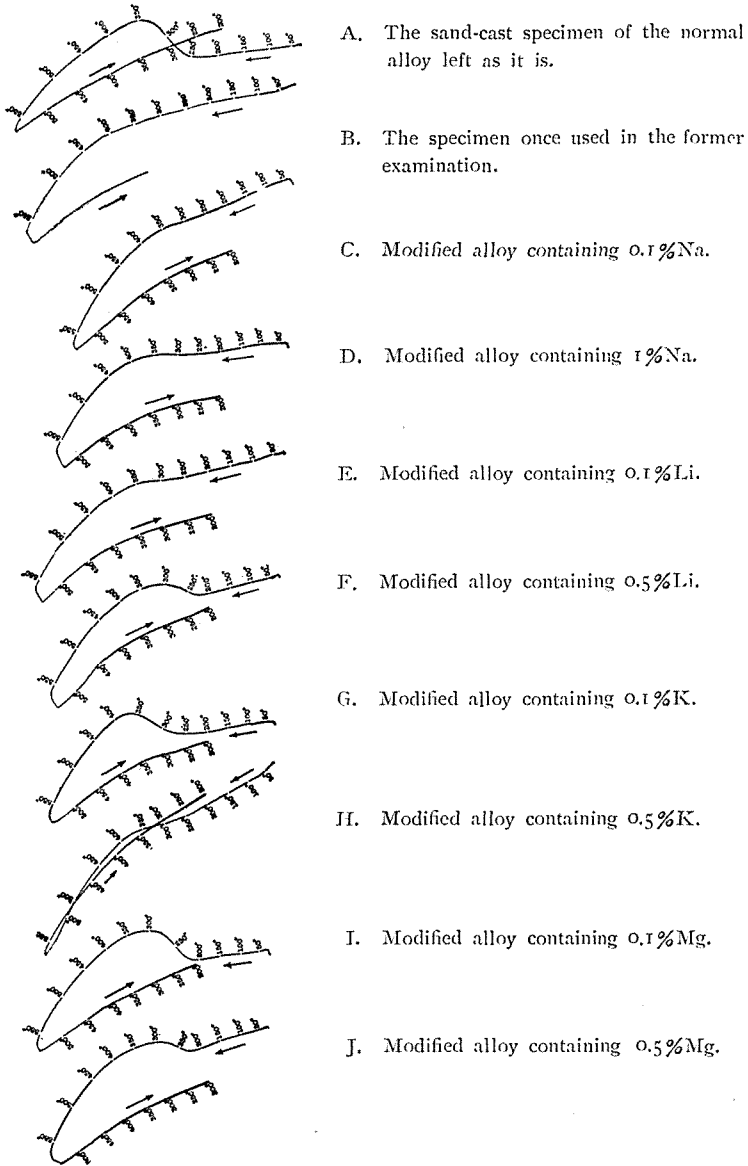
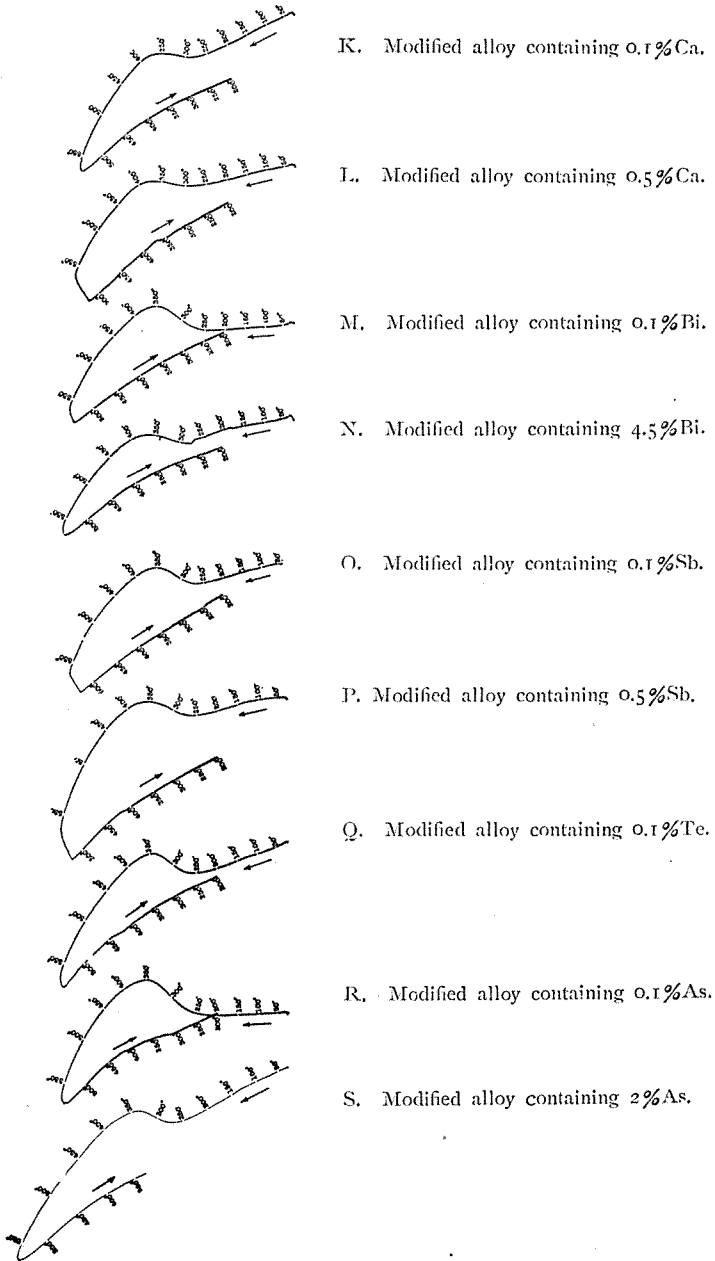


Fig. 17 b

The Differential Dilatation Curves of the Normal and Modified Alloys containing 13 per cent. of silicon.



## II. Crystalline Configuration

X-ray examination was first carried out by means of Laue's method, as was the case with Shinoda<sup>1</sup>, to see whether or not the micro-structure of the specimens above mentioned gives any accurate information in connection with the actual size and configuration of the micro-crystals. In this research, only the Si-Al alloys of the normal form of various compositions, and those modified by adding a small quantity of sodium, lithium, and bismuth respectively, were used as the specimens. To utilize the specimens in this examination, two series of thin plates (about 3 mm. in thickness) were respectively cut out from the vertical portion of each ingot, parallel and perpendicularly to its longitudinal axis and polished until they were reduced to about 1 mm. in thickness. When the planed surface of the specimens was set perpendicularly to the incident X-ray beam, two series of the diffraction patterns could be obtained; the one is given rise by the incidence of X-rays parallel to the longitudinal axis of ingot (named longitudinal incidence for convenience sake), while the other corresponds to the normal incidence (named transversal incidence).

Some of the diffraction patterns thus obtained are reproduced in Plates II and III. It is noticed that not only those here reproduced, but all the patterns due respectively to the longitudinal and transversal incidences of X-rays to the same specimen, were also found not essentially different to each other.

As can be seen in Figs. 18 and 19, Plate II, both diffraction patterns produced by the transversal and longitudinal incidences of X-rays to the normal alloy containing 7 per cent. of silicon, consist of an irregular assemblage of somewhat elongated Laue's spots. Thus, we may conclude from the presence of elongated Laue's spots in both figures above mentioned, that the specimen under examination is composed of crystals of comparatively large size, and bears a fibrous nature of weak degree.

Figs. 20 and 21, Plate II are the diffraction patterns taken with the alloy containing 13 per cent. of silicon in a similar way as Figs. 18 and 19, Plate II. The prominent parts of these patterns consist of several long radiating bands and a number of Debye-Hull's rings. Thus, it can be concluded from the presence of radiating bands in Figs. 20 and 21, Plate II, that the specimen under consideration is

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1. Loc. cit.

partly composed of a fibrous structure: But, the presence of Debye-Hull's rings shows us that the considerable portion of it consists of an irregular aggregation of the micro-crystals smaller than those in the former specimen containing 7 per cent. of silicon. By the aid of an improved Yoshida's crystallographic globe,<sup>1</sup> the axis of the fibre in this case was found to coincide with the normal to one of the icositetrahedral faces (211) of the cubic crystal. While, Debye-Hull's rings in the same figures were confirmed to be due to the molybdenum  $K_{\alpha}$  radiation reflected from the prominent atomic planes (111)<sub>1</sub>, (100)<sub>1</sub>, (110)<sub>1</sub>, (113)<sub>1</sub>, (111)<sub>2</sub>, (100)<sub>2</sub>, (133)<sub>1</sub> and (120)<sub>1</sub> of the aluminium crystal. Here it must be understood that the numerical suffixes used in the symbols ( )<sub>1</sub> and ( )<sub>2</sub>, denote the order of the spectrum.

In short, the specimen containing 13 per cent. of silicon may be said to be made up by the more irregular arrangement of the micro-crystals, which are of the smaller dimension than those of the specimen containing 7 per cent. of silicon.

Such a violation of the regularity of the crystalline configuration due to the increasing amount of silicon, was observed more markedly in the specimen containing 22 per cent. of silicon. The diffraction patterns occurring from this specimen are reproduced in Figs. 22 and 23, Plate II. As is seen in these figures, both diffraction patterns corresponding to the transversal and longitudinal incidences of X-rays, consist mainly of a number of Debye-Hull's rings, which were conceived to be due to the same atomic planes of aluminium, as in Figs. 20 and 21, Plate II. The predomination of such Debye-Hull's rings in Figs. 22 and 23, shows us without doubt that this specimen is nothing but an aggregation of the finer micro-crystals without any regularity.

From the foregoing argument in connection with the normal alloys, we may conclude that the smaller amount of silicon contained in the specimen, the more favourable were the conditions for the formation of large crystals and regular structures, at least within the scope of our investigation. The above conclusion does not agree so well with the results of the microscopical examinations, according to which the size of crystallites, as can be seen in Figs. 1, 2 and 3, Plate I, remains nearly unaltered by the increasing amount of silicon contained in the specimen.

1. U. Yoshida; Japanese J. Phys., 133 (1927), and S. Takeyama; These Mem irs. A, 11, 467 (1928)

Such a discrepancy of the crystalline configuration to the micro-structure, could be observed more markedly by taking into account the diffraction phenomena due to the modified specimens. As the case in point, we may refer to the diffraction patterns in Figs. 24, 25, 26, Plate II and Fig. 27, Plate III, which were given rise by the specimens modified with a small quantity of sodium. The diffraction patterns above mentioned consist mainly of a set of short radiating bands<sup>1</sup> or somewhat elongated Laue's spots, associated with several Debye-Hull's rings: While, in the patterns taken with some of the specimens of the normal alloys, nothing but Debye-Hull's rings could previously be detected, as was the case with the specimen containing 22 per cent. of silicon (see Figs. 22 and 23, Plate II). Thus, it may be said that the crystalline configuration is more regulated in these modified specimens than in some of the normal alloys. Furthermore, contrary to the results of the microscopical examination, the predomination of Laue's spots in Fig. 26, Plate II and Fig. 27, Plate III, instead of Debye-Hull's rings in Figs. 22 and 23, Plate II, shows us that the crystallites constituting the modified specimens with 3 per cent. of sodium, are at least of the larger dimension than those of the normal alloy containing 22 per cent. of silicon.

Not only with the specimens above mentioned, but with some other specimens, the same inconsistency of the diffraction pattern to the micro-structure was also observed; e. g., such an inconsistency can easily be seen by comparing Figs. 28 and 30, Plate III, or Fig. 26, Plate II and Fig. 34, Plate III. Thus, we may conclude that the micro-structure of Si-Al alloys informs us very little with regard to the actual crystalline configuration.

In our foregoing consideration, there remains still doubtful, if the procedure of cutting and polishing the specimens would inflict too much mechanical distortions upon the crystalline configuration of their surfaces, to give rise to any reliable diffraction figure. By way of removing the effect of such an infliction, the writer once tried to etch off the outer portion of each specimen by pickling it in the mixture of hydrochloric and hydrofluoric acid, before the X-ray examination. But, owing to the unequal corrosion of the constituents of the specimens, it was found impossible to do so without changing their composition. Therefore,

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1. The angular distribution of these radiating bands can also be realized by the rotation of a cubic crystal within a certain angle, around the normal direction to one of its (211) planes.

the writer was obliged to estimate the effect under consideration by comparing the diffraction patterns taken with two kinds of the specimens of pure aluminium: The one was prepared in the similar way as the specimens of Si-Al alloy examined, while to obtain the other, the specimen of pure aluminium thus prepared was pickled in hydrochloric acid. As the consequence of this estimation, it was confirmed that the diffraction patterns given rise by these two kinds of specimens were essentially the same. This shows us that even in such a comparatively soft metal as pure aluminium, the effect of the mechanical distortion is very slight; still less it should be the case with the comparatively hard alloys as were used in the present research.

### III. Crystal Structure

Despite the remarkable difference in their constitutional diagrams with aluminium and silicon, the alkali metals such as sodium and lithium were microscopically found to bear resemblance in their conspicuous modifying effects on the structure of Si-Al alloys, as stated before. In this respect, the more accurate confirmation with regard to the relation between the constitutional diagrams and the modifying effects, seems to be needed for a further consideration. Therefore, the writer repeated the X-ray examination, to make clear the crystal structure of Si-Al alloys corresponding to some of the phases in the constitutional diagrams.

In this experiment, not only the specimens of the normal form, but those modified by adding sodium and lithium respectively, were also examined after the ordinary powder method, with a quadrant spectrograph of 7.5 cm. in radius. Each one of these specimens was pulverised and then was sealed in a small glass tube to be mounted in the spectrograph. When the powdery crystals thus prepared were illuminated by the incident X-ray beam, the spectra of the molybdenum K characteristic radiation usually came to appear as shown in the figures of Plate IV. By measuring the distances of these spectral lines from the central one, we obtain the numerical values shown in Table II.

As can be seen in Figs. 37, 38 and 39, Plate IV, all the spectra of the normal alloys, were confirmed to be nothing but the superposition of two series of the spectral lines, each one of which was reflected respectively from the prominent atomic planes of the powdery crystals of aluminium and silicon. The increasing amount of silicon

Table II

| Indices of Al                         |                    | (III) <sub>1β</sub> | (III) <sub>1α</sub> | (100) <sub>1α</sub> |                    | new<br>line |                    | (110) <sub>1β</sub> | (110) <sub>1α</sub> |                    | (113) <sub>1β</sub> | new<br>line |                    | (113) <sub>1α</sub> | (111) <sub>2α</sub> |                    | new<br>line | new<br>line |  | (133) <sub>1β</sub>                      | (100) <sub>2α</sub> | (133) <sub>1α</sub> |  | (120) <sub>1α</sub> |  | (211) <sub>1α</sub> | (115) <sub>1α</sub><br>(111) <sub>2α</sub> |                    |      |      |
|---------------------------------------|--------------------|---------------------|---------------------|---------------------|--------------------|-------------|--------------------|---------------------|---------------------|--------------------|---------------------|-------------|--------------------|---------------------|---------------------|--------------------|-------------|-------------|--|--|---------------------|---------------------|--|---------------------|--|---------------------|--|--------------------|------|------|
| Pure Al                               |                    | 2.03                | 2.29                | 2.64                |                    |             |                    | 3.36                | 3.77                |                    | 3.99                |             |                    | 4.44                | 4.67                |                    |             |             |  |  | 5.24                | 5.41                |  | 5.91                |  | 6.10                |  | 6.70               | 7.15 |      |
| 7% Si alloy                           | 1.70               | 2.00                | 2.29                | 2.65                |                    |             |                    | 3.35                | 3.76                |                    | 3.95                |             |                    | 4.44                | 4.66                | 4.93               |             |             |  |  |                     |                     |  | 5.37                |  | 5.90                |  | 6.05               | 6.66 | 7.10 |
| 13% Si alloy                          | 1.70               | 2.03                | 2.28                | 2.65                | 2.84               |             |                    | 3.32                | 3.78                |                    | 3.98                |             |                    | 4.46                | 4.68                | 4.93               |             |             |  |  | 5.22                |                     |  | 5.40                |  | 5.92                |  | 6.06               | 6.70 | 7.13 |
| 22% Si alloy                          | 1.70               | 2.05                | 2.29                | 2.63                | 2.81               |             |                    | 3.29                | 3.75                |                    | 3.95                |             |                    | 4.42                | 4.61                | 4.87               |             |             |  |  | 5.16                |                     |  | 5.34                |  | 5.85                |  | 6.00               | 6.63 | 7.07 |
| Al alloy containing<br>5% Na          |                    | 2.02                | 2.28                | 2.64                |                    |             |                    | 3.35                | 3.78                |                    | 3.95                |             |                    | 4.45                | 4.66                |                    |             |             |  |  |                     |                     |  | 5.40                |  | 5.92                |  | 6.12               | 6.70 | 7.18 |
| Al alloy containing<br>20.4% Na       |                    | 2.03                | 2.30                | 2.67                |                    |             |                    | 3.37                | 3.79                |                    | 3.98                |             |                    | 4.47                | 4.68                |                    |             |             |  |  |                     |                     |  | 5.40                |  | 5.92                |  | 6.10               | 6.71 | 7.13 |
| Modified alloy<br>containing 0.1% Na  | 1.70               | 2.03                | 2.28                | 2.64                | 2.80               |             |                    | 3.29                | 3.76                |                    | 3.95                |             |                    | 4.43                | 4.65                | 4.90               |             |             |  |  | 5.20                |                     |  | 5.37                |  | 5.89                |  | 6.05               | 6.66 | 7.12 |
| Modified alloy<br>containing 3% Na    | 1.72               | 2.04                | 2.30                | 2.65                | 2.84               |             |                    | 3.30                | 3.79                |                    | 3.97                |             |                    | 4.45                | 4.65                | 4.93               |             |             |  |  | 5.21                |                     |  | 5.39                |  | 5.91                |  | 6.08               | 6.70 | 7.13 |
| Modified alloy<br>containing 5% Na    | 1.70               | 2.01                | 2.29                | 2.65                | 2.81               |             |                    | 3.32                | 3.77                |                    | 3.97                |             |                    | 4.45                | 4.66                | 4.91               |             |             |  |  | 5.22                |                     |  | 5.40                |  | 5.90                |  | 6.06               | 6.68 | 7.13 |
| Modified alloy<br>containing 20.4% Na |                    | 2.03                | 2.28                | 2.64                |                    |             |                    | 3.34                | 3.79                |                    |                     |             |                    | 4.47                | 4.68                |                    |             |             |  |  |                     |                     |  | 5.41                |  | 5.93                |  | 6.11               | 6.75 | 7.20 |
| Al alloy containing<br>2% Li          |                    | 2.06                | 2.30                | 2.68                |                    |             |                    | 3.38                | 3.82                |                    | 4.02                |             |                    | 4.48                | 4.74                |                    |             |             |  |  |                     |                     |  | 5.43                |  | 5.96                |  | 6.13               | 6.74 | 7.19 |
| Al alloy containing<br>7% Li          |                    | 2.05                | 2.29                | 2.65                |                    |             |                    | 3.37                | 3.77                |                    | 3.99                |             |                    | 4.45                | 4.69                |                    |             |             |  |  |                     |                     |  | 5.41                |  | 5.89                |  | 6.10               | 6.71 | 7.14 |
| Al alloy containing<br>17% Li         |                    | 2.11                | 2.41                | 2.71                |                    | 2.87        |                    | 3.43                | 3.81                |                    |                     | 4.26        |                    | 4.53                |                     |                    | 4.92        | 5.15        |  |  |                     |                     |  | 5.53                |  |                     |  |                    |      |      |
| Al alloy containing<br>20.4% Li       |                    |                     | 2.35                | 2.67                |                    | 2.84        |                    | 3.41                | 3.78                |                    |                     | 4.23        |                    | 4.48                | 4.68                |                    |             |             |  |  |                     |                     |  | 5.49                |  |                     |  |                    |      |      |
| Modified alloy<br>containing 0.1% Li  | 1.71               | 2.03                | 2.28                | 2.62                | 2.81               |             |                    | 3.30                | 3.75                |                    | 3.95                |             |                    | 4.40                | 4.63                | 4.93               |             |             |  |  | 5.19                |                     |  | 5.35                |  | 5.87                |  | 6.03               | 6.64 | 7.07 |
| Modified alloy<br>containing 0.5% Li  | 1.71               | 2.02                | 2.30                | 2.66                | 2.85               |             |                    | 3.32                | 3.79                |                    | 3.99                |             |                    | 4.44                | 4.66                | 4.91               |             |             |  |  | 5.21                |                     |  | 5.40                |  | 5.90                |  | 6.06               | 6.66 | 7.14 |
| Modified alloy<br>containing 2% Li    | 1.71               | 2.03                | 2.28                | 2.63                | 2.84               |             |                    | 3.31                | 3.78                |                    | 3.98                |             |                    | 4.42                | 4.65                | 4.92               |             |             |  |  | 5.20                |                     |  | 5.40                |  | 5.89                |  | 6.05               | 6.65 | 7.10 |
| Modified alloy<br>containing 17% Li   |                    |                     | 2.30                | 2.60                |                    |             |                    | 3.38                | 3.77                |                    |                     | 4.18        |                    | 4.43                |                     |                    |             |             |  |  |                     |                     |  | 5.41                |  |                     |  |                    |      |      |
| Modified alloy<br>containing 20.4% Li |                    |                     | 2.35                | 2.68                |                    |             |                    | 3.40                | 3.79                |                    | 4.00                | 4.21        |                    | 4.48                | 4.70                |                    | 4.85        | 5.10        |  |  |                     |                     |  |                     |  |                     |  |                    |      |      |
| Pure Si                               | 1.71               |                     |                     |                     | 2.80               |             | 3.28               |                     |                     | 3.96               |                     |             | 4.34               |                     |                     | 4.92               |             |             |  | 5.21                                     |                     |                     |  | 5.64                |  | 5.95                |  | 6.39               |      |      |
| Indices of Si                         | (III) <sub>1</sub> |                     |                     |                     | (110) <sub>2</sub> |             | (113) <sub>1</sub> |                     |                     | (100) <sub>4</sub> |                     |             | (133) <sub>1</sub> |                     |                     | (211) <sub>2</sub> |             |             |  | (115) <sub>1</sub><br>(111) <sub>2</sub> |                     |                     |  | (110) <sub>4</sub>  |  | (135) <sub>1</sub>  |  | (130) <sub>2</sub> |      |      |

contained in the specimens from 7 and 13 per cent. to 22 per cent., only intensifies the series of lines corresponding to the silicon crystals, but does not affect the position of any line in these spectra. Such an unalteration of the spectral lines indicates that the solubility between aluminium and silicon is extremely small. Consequently, this confirms the binary constitutional diagram of the Si-Al system previously determined, to be correct.

The spectral lines of the specimens of Si-Al alloys modified with various quantities of sodium, are reproduced in Figs. 42, 43, 44 and 45, Plate IV. For the convenience of comparison, similar examinations were also carried out with the specimens of aluminium containing the same amounts of sodium as above. Some of the spectral lines thus obtained with these specimens are shown in Figs. 40 and 41, Plate IV.

In two series of figures here reproduced, the unalteration of the positions of spectral lines irrespective to the composition, which has already been observed with the normal alloys, may also be found to hold even with regard to these specimens containing some sodium. Thus, we may conclude that not only aluminium and silicon are hardly soluble in the solid state to each other, but sodium is also insoluble to these two elements, as was suggested by the constitutional diagrams.

Nevertheless, this unalteration is violated in the case when lithium, instead of sodium, was added to the specimens: i. e., as can be seen in the spectra reproduced from Fig. 46 to Fig. 54, Plate IV, the deviation of the lines corresponding to aluminium and silicon, became markedly observable with the increasing amount of lithium. Furthermore, some new lines supposed to be caused by the compound of aluminium and lithium, appeared in the spectra of the specimens containing comparatively large amount of lithium. These facts indicate that the transformation of space lattices in the specimens took place with the addition of lithium.

The consideration confirmed above with regard to the specimens containing lithium agrees well with the binary constitutional diagrams of the Li-Al and Li-Si systems, according to which not only the solid solution extending to the comparatively wide scope in composition, but the intermetallic compounds between lithium and aluminium or lithium and silicon, such as  $\text{AlLi}$  or  $\text{Li}_6\text{Si}_2$ , should exist. Thus, notwithstanding the similarity in the modifying effects of sodium and lithium on Si-Al alloy as stated before, these two modifiers may be said to be entirely



different in their alloying properties to each component of Si-Al alloy. This confirms again our foregoing opposition to the theory of modification based upon the formation of ternary constituents.

### Summary

The experimental results which have hitherto been described in connection with the sand-cast specimens of various normal and modified Si-Al alloys, lead us to the following conclusions:—

(a) The crystal structure of these specimens as well as their micro-structure is in good accordance with the corresponding constitutional diagrams.

(b) The elements efficacious for modifying the specimens are not necessarily either volatile or immiscible to aluminium and silicon, as was suggested by the present theories of modification: But, they should partake of the chemical properties analogous to sodium.

(c) The cooling curves show us that the specimens of the normal alloys have undergone the more remarkable under-cooling phenomena than those of the modified ones containing a small quantity of sodium.

(d) There are some discrepancies between the actual crystalline configuration in the specimens and their micro-structure.

Among these four propositions (a), (b), (c) and (d), which were deduced as the necessary consequences of our experimental results, (b) could hardly be explained by attributing the modifying agents of the modifiers to their volatility. Also, from (a) and (b), some elements of the appreciable solubility to both aluminium and silicon, such as lithium, were found to be also efficacious for the modification of Si-Al alloy. Thus, Ôtani's<sup>1</sup> ternary constituents theory and Gwyer's<sup>2</sup> protective colloid theory, which attribute the conspicuous modifying agent of sodium to its small miscibility to both aluminium and silicon, may be said not to be applicable at least in the case of lithium. But, it is here noticed that the modifying agents of these two elements, sodium and lithium, to Si-Al alloy, are too similar to be conceived of as different mechanisms. Moreover, the proposition (c) was not in good accordance with the under-cooling theory of modification. In short, the foregoing propositions (a), (b) and (c) could hardly be explained by the theories of modification nowadays, without some special assump-

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1. Loc. cit.

2. Loc. cit.

tions. Not only these, but the proposition (d) showed us the necessity of further considerations before the mechanism of modification of Si-Al alloys is described in terms of the space-lattice theory on crystallography.

Contrary to the above, the elements belonging to the alkali and alkaline earth groups were found to partake remarkably of the modifying agent, as was pointed out by the proposition (b). This fact seems to suggest the concealment of some "atomistic", instead of "thermodynamical", causes giving rise to the modification of Si-Al alloy.

In conclusion, the writer wishes to express his thanks to Prof. D. Uno and Dr. H. Hirata for their kind guidance and invaluable advice. His thanks are also due to the Imperial Academy of Japan for the fund granted for the present investigations.

Institute of Metallography,  
Kyoto Imperial University.

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Plate I

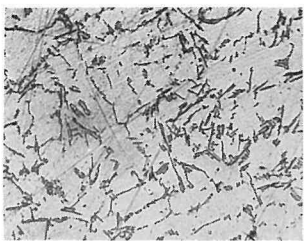


Fig. 1.—7% Si.  $\times 100$

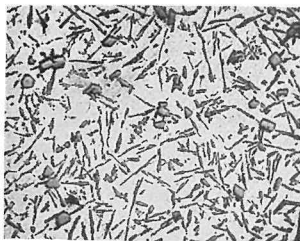


Fig. 2.—13% Si.  $\times 100$

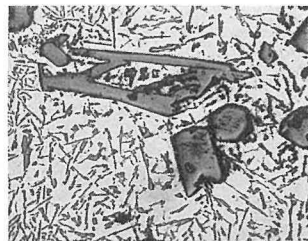


Fig. 3.—22% Si.  $\times 100$

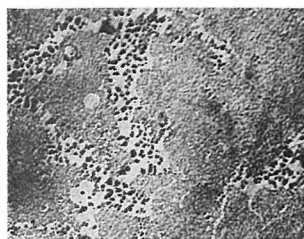


Fig. 4.—Modified with 0.1% Na.  
 $\times 100$

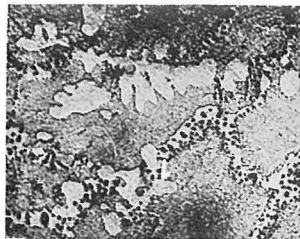


Fig. 5.—Modified with 3% Na.  
 $\times 100$

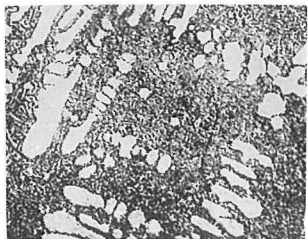


Fig. 6.—Modified with 0.1% Li.  
 $\times 100$

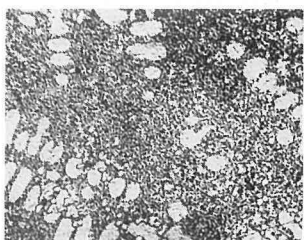


Fig. 7.—Modified with 0.5% Li.  
 $\times 100$

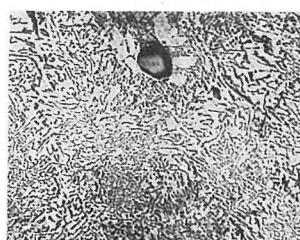


Fig. 8.—Modified with 1% K.  
 $\times 100$

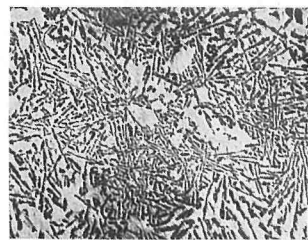


Fig. 9.—Modified with 0.5% Mg.  
 $\times 100$

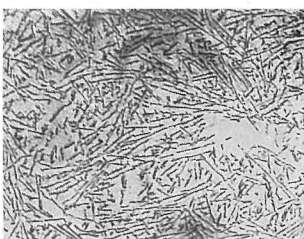


Fig. 10.—Modified with 0.5% Ca.  
 $\times 100$

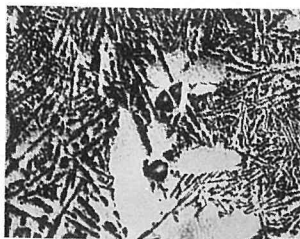


Fig. 11.—Modified with 2% As.  
 $\times 100$



Fig. 12.—Modified with 0.5% Te.  
 $\times 100$



Fig. 13.—Modified with 0.1% Bi.  
 $\times 100$

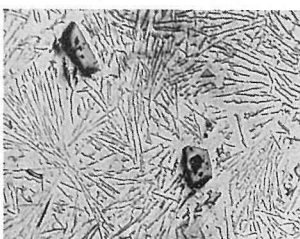


Fig. 14.—Modified with 4.5% Bi.  
 $\times 100$



Fig. 15.—Modified with 0.5% Sb.  
 $\times 100$

Plate II

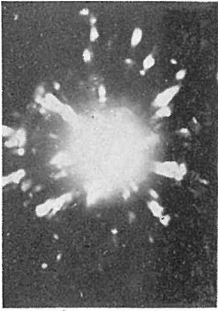


Fig. 18.—7% Si.  
Transversal Incidence.



Fig. 19.—7% Si.  
Longitudinal Incidence.

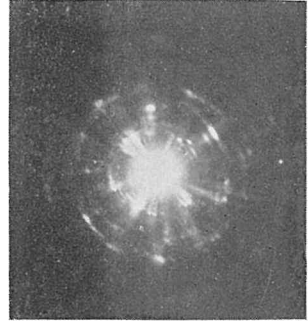


Fig. 20.—13% Si.  
Transversal Incidence.

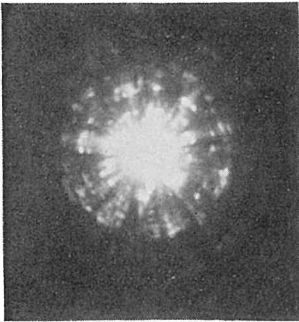


Fig. 21.—13% Si.  
Longitudinal Incidence.

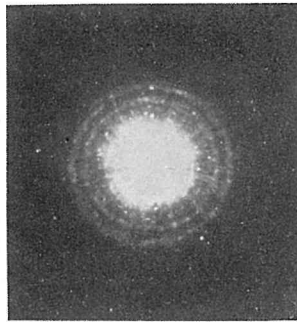


Fig. 22.—22% Si.  
Transversal Incidence.

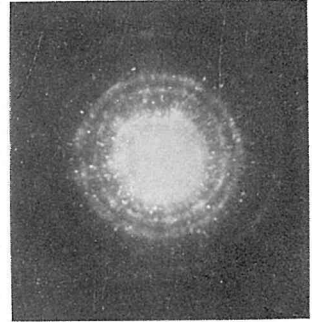


Fig. 23.—22% Si.  
Longitudinal Incidence.

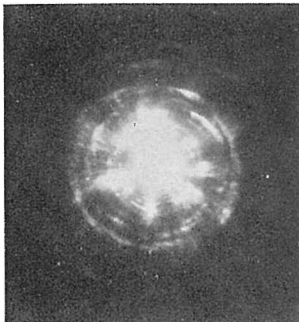


Fig. 24.—Modified with 0.1% Na.  
Transversal Incidence.

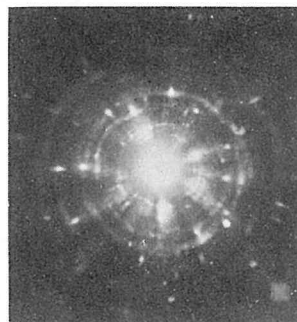


Fig. 25.—Modified with 0.1% Na.  
Longitudinal Incidence.

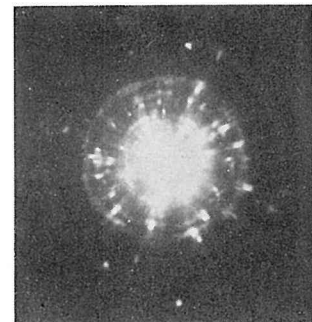


Fig. 26.—Modified with 3% Na.  
Transversal Incidence.

Plate III

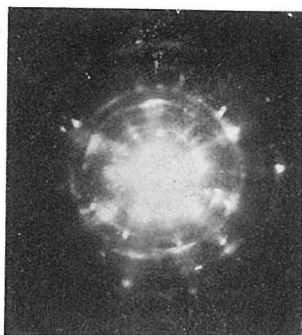


Fig. 27.—Modified with 3% Na. Longitudinal Incidence.

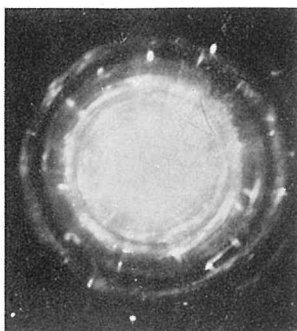


Fig. 28.—Modified with 0.1% Li. Transversal Incidence.

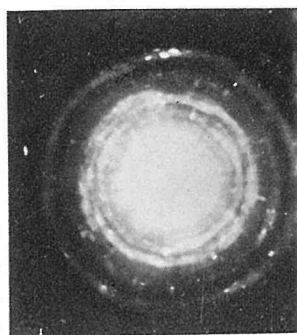


Fig. 29.—Modified with 0.1% Li. Longitudinal Incidence.

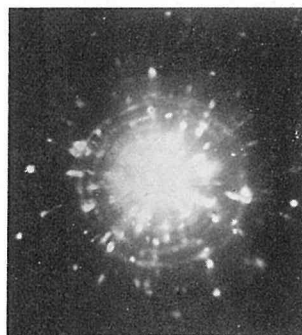


Fig. 30.—Modified with 0.5% Li. Transversal Incidence.

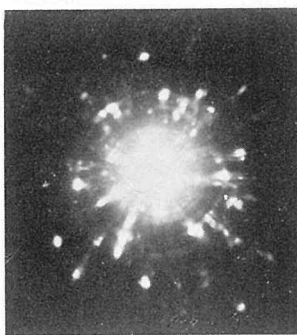


Fig. 31.—Modified with 0.5% Li. Longitudinal Incidence.

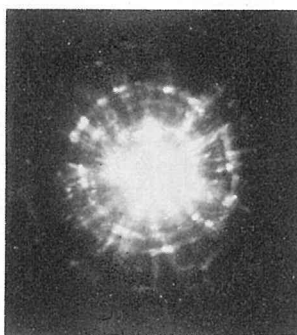


Fig. 32.—Modified with 0.1% Bi. Transversal Incidence.

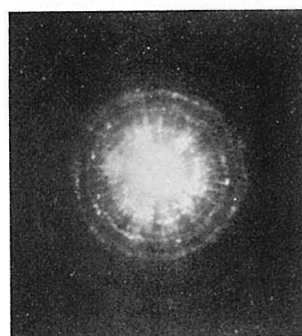


Fig. 33.—Modified with 0.1% Bi. Longitudinal Incidence.

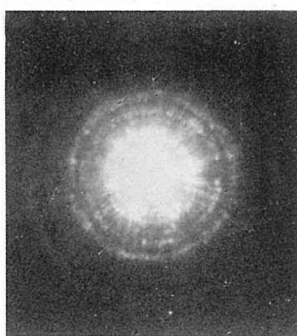


Fig. 34.—Modified with 4.5% Bi. Transversal Incidence.

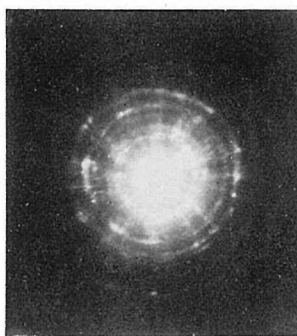


Fig. 35.—Modified with 4.5% Bi. Longitudinal Incidence.

