Crystal Habit Modification of Strontium Sulfate. I. Habit-Modifying Action of Foreign Substances

By Sadaichi OTANI

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Crystals having spherical forms are often found in mineral spherulite which is recognized as a type of radiated crystals. Spherulites have also been prepared artificially by many workers. Popoff1) studied the two-dimensional spherulites of resorcinol and malonamide, while Lengyel2) investigated those of several inorganic substances. Three-dimentional spherulites of various inorganic substances were prepared by Morse and others3) by allowing the reacting solutions to be mixed through diffusion avoiding convection; their best spherulites having spherical forms were obtained in a gelatinous medium. Hence they considered the high viscosity of the medium to be one of the favorable conditions for spherulitic growth. From an ordinary solution, instead of the viscous medium, Patterson4) obtained spherulitic aggregates of calcium phosphate in the presence of the citrate ion, but the shape of the aggregate was far from being spherical. Recently Miura and his co-workers5) have succeeded in preparing fine spherical crystals of barium sulfate having nearly uniform size, from an aqueous solution containing citrate ion, and they pointed out the effective utilizations of such crystals in the fundamental study of colloid science and also in the industrial field.

The present author has been interested in the preparation of spherical crystals as well as in the mechanism of their formation, and several attempts have been made regarding these problems. The results obtained will be presented in two parts, of which the first deals with the habit-modifying effect of various substances upon the crystal of strontium sulfate, and the second with the characteristic behavior of the triphosphate ion in the course of deposition and dissolution of strontium sulfate, as well as the mechanism of spherulite formation.

Experimental

Reagents.—Strontium chloride of the reagent grade was purified by repeating three times the alternate crystallization of the dihydrate from a hot solution and then of the hexahydrate from a cold solution. Both potassium sulfate and sodium citrate of the analytical grade were recrystallized from their aqueous solutions. Sodium triphosphate (STP) was prepared by Bell's method6) and recrystallized from an aqueous solution by adding methanol. Both the EDTA and glycerol used were of the analytical grade. The polyvinyl alcohol (PVA) used had an average molecular weight of 8.5×10^4. Both oleylpyridinium chloride and polyethyleneglycol monostearate were furnished by the courtesy of Daiichi Kogyo Seiyaku Co. Ltd. Aerosol OT was of the commercially highest grade.

Procedure.—The crystals to be examined were precipitated by mixing a solution of strontium chloride with one of potassium sulfate, in the presence or absence of a third substance in a glass-stoppered flask. To diminish the influence of the container wall upon crystallization, the inside surface of the flask was coated with silicone by the diethyldichlorosilane-treatment. This prevented the precipitate from adhering to the container wall, and thus the crystal growth was not troubled with any steric disturbance of the wall. During mixing and crystallizing, the solutions were violently and continuously shaken with a motor-driven shaker, and the temperature was kept constant within the limits of ±0.1°C.

Foreign substances whose effects were to be examined were added either to the solution of strontium chloride or to one of potassium sulfate, prior to the mixing of these. Sodium citrate, EDTA or condensed phosphates, anyone of which was a complexing agent for metallic cations, was always added to the solution of strontium chloride.

Results

Crystals Grown from Mixtures of Strontium Chloride and Potassium Sulfate Solutions.—First of all, crystals deposited from the solutions prepared by mixing strontium chloride and potassium sulfate solutions without foreign substance were examined. Quite a number of samples were prepared by varying the concentrations and the mixing proportions of the solutions. The concentration range of strontium and sulfate, immediately after mixing, was $0.002\sim0.1$ M.

According to the crystal forms of these samples, they could be classified roughy into

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1) B. Popoff, *Latv. Farm. Zurn.*, **1934**, 1.

2) E. v. Lengyel, *Z. Krist.*, **97**, 67 (1937).

3) H. W. Morse, C. H. Warren and J. D. H. Donnay, *Am. J. Sci.*, **23**, 421 (1932).

4) D. Patterson, *Nature*, **173**, 75 (1937).

5) M. Miura, T. Nagakane and S. Masaki, *J. Sci. Hiroshima Univ., Ser. A*, **19**, 513 (1956).

6) R. N. Bell, "Inorganic Syntheses", Vol. 3, McGraw-Hill Inc., New York (1950), p. 101.

two large groups. Two microphotographs are shown in Fig. 1 for reference. Fig. 1a represents the crystals of a type obtainable from solutions containing a large excess of sulfate ion and Fig. 1b those of another type from the equivalent mixtures or solutions containing strontium ion in excess. By observing the extinction and retardation of polarized light between the crossed nicols, the orientations of the crystallographic axes were determined, and indicated in the photographs.

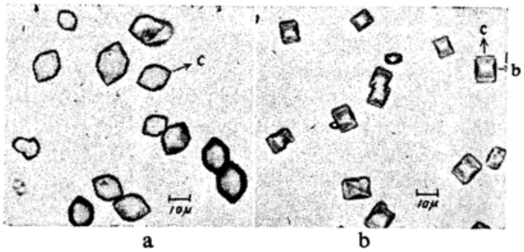


Fig. 1. Two samples of crystals grown from mixtures of $SrCl_2$ and K_2SO_4 solutions.

a : 0.017 M $SrCl_2$, 0.10 M K_2SO_4
b : 0.10 M $SrCl_2$, 0.017 M K_2SO_4

Effect of Several Additives. — To inquire whether the viscosity of the medium is an essential factor to the habit modification as reported by Morse and others[3], the effects of glycerol and PVA were tested. In the concentration ranges up to 27% with glycerol and up to 0.4% with PVA, none of these gave any significant influence on the habit of crystals formed.

Then the effects of some surface active agents were examined. Addition of oleylpyridinium chloride or polyethylene glycol monostearate caused a slight increase in the size of the crystals deposited, but the crystal form was hardly influenced by these surface active agents within the concentration limit of 1.0% in each case. Anionic surface active agent Aerosol OT, however, produced a voluminous white precipitate which might be its strontium salt.

Effect of Sodium Citrate.—Sodium citrate, even at a very low concentration, has a remarkable effect on the deposition rate and the shape of the crystals. The larger the amount of sodium citrate added, the slower was the deposition rate and the smaller the size of the crystals formed. The shape of the crystals was altered by the addition of sodium citrate in such a way that the edges and corners of the polyhedrons shown in Fig. 1 gradually vanished as the amount of citrate was increased, resulting finally in thin ellipsoids. However, because of the low solubility of strontium citrate, there was a limit to the concentration of the citrate ion in solution, above which the voluminous needle-shaped precipitate appeared.

In Fig. 2 the microphotographs of two samples are shown. These were obtained at 25°C from two separate solutions containing equal amounts of sodium citrate. Both of the solutions from which these crystals were deposited had the same concentration with respect to either of the essential salts as in the previous case (Fig. 1). The electron micrographs of these samples are shown in Fig. 3. Several slenderer figures appearing in Fig. 3a represent the oblique projections of thin ellipsoids (cf. Fig. 7b). Fig. 3b was taken after chromium shadowing at an angle of approximately 22° to the plane of the supporting

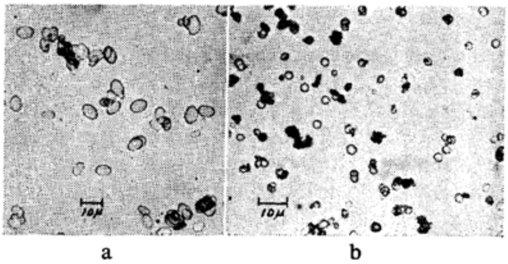


Fig. 2. Two samples of crystals grown from samples solutions containing sodium citrate.

a : 0.071 M $SrCl_2$, 0.10 M K_2SO_4, 0.003 M sodium citrate
b : 0.10 M $SrCl_2$, 0.017 M K_2SO_4, 0.003 M sodium citrate

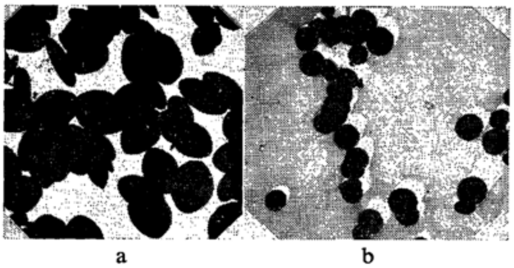


Fig. 3. Electron micrographs of the two a and b shown in Fig. 2.

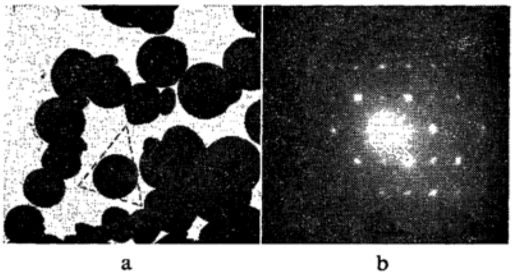


Fig. 4. Electron micrograph (a) of the sample as one shown in Fig. 2b, and the diffraction pattern (b) of the selected crystal in (a) (surrounded with the triangle).

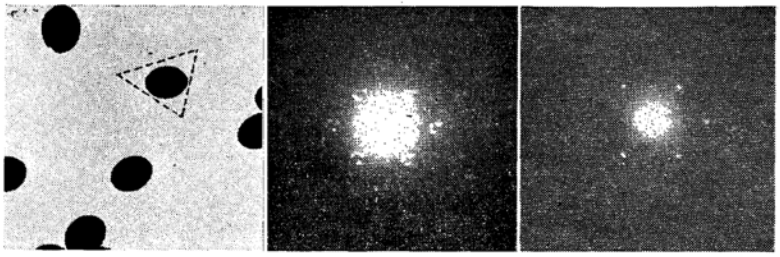
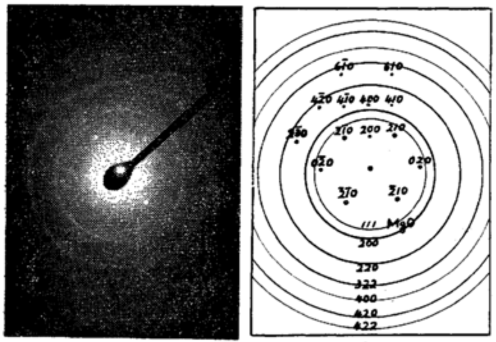

a b c

Fig. 5. Electron micrograph (a) of the same sample as one shown in Fig. 2a, and the diffraction pattern (b and c) of the selected crystal in (a) (surrounded with the triangle).

film. This micrograph shows that the crystals are flat and nearly disk-shaped (cf. Fig. 7a).

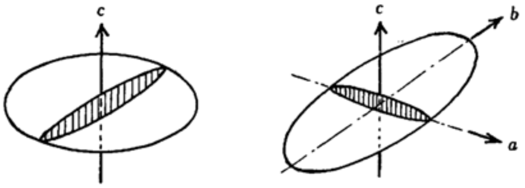
These crystals were then examined by means of an electron microdiffraction technique. The selected-area diffraction of any particle examined gave always an N-pattern as one shown in Fig. 4b or 5c, indicating that these individual crystals are single crystals. For the analysis of the diffraction patterns, the interplanar spacings were determined by comparing these patterns with the Debye-Scherrer rings of magnesium oxide which were taken under a similar condition. For this purpose, the sample crystals and magnesium oxide smoke were mounted together on a supporting film. That is to say, the film on which the sample crystals had already been mounted was exposed to the smoke of burning magnesium. Fig. 6a represents the diffraction pattern of the selected area where both a sample crystal and a large number of fine crystals of magnesium oxide are involved. The Miller indices corresponding to these spots and rings are indicated in Fig. 6b. From this result it is ascertained that the direction of the electron beam in this case was parallel to the *c* axis of the crystal.



a b

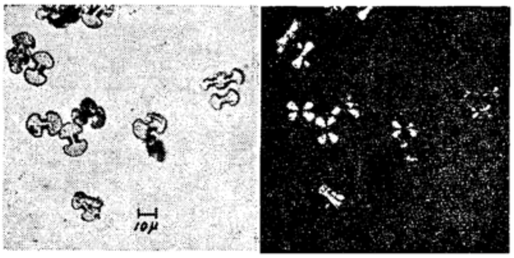
Fig. 6. Diffraction pattern of a selected area where a sample crystal and MgO smoke are mounted together.

Fig. 4b represents the diffraction pattern of the selected crystal shown in Fig. 4a which shows the electron micrograph of the same sample as the one in Fig. 2b. Fig. 5a represents the electron micrograph of the same sample as the one shown in Fig. 2a, and Fig. 5c shows the diffraction pattern of the selected crystal shown in Fig. 5a. Fig. 5b was taken at a current of the intermediate lens which was a little larger than in the case of Fig. 5c. Comparing these three photographs in Fig. 5 with each other, one can easily understand the relation between the orientation of the particle shown in the electron micrograph and that of the same particle in the diffraction pattern. From the fact that the patterns shown in Figs. 4b and 5c coincide with the N-pattern appearing in Fig. 6a, it is revealed that the nearly flat surfaces of these thin ellipsoidal crystals are parallel to the (001) plane. The direction of the largest



a b

Fig. 7. Shapes and crytsallographic axes of ellipsoidal crystals obtained from solutions containing sodium citrate. Shaded parts indicate the cross sections.



a b

Fig. 8. Crystals grown from a solution containing EDTA. (0.013 M $SrCl_2$, 0.05 M K_2SO_4, 0.025 M EDTA.)

a: with lower nicol only
b: with crossed nicols

diameter of the crystals shown in Fig. 5a or 2a coincides with that of *b* axis. The axial directions of these crystals are illustrated in Fig. 7.

Effect of EDTA.—The crystal habit of strontium sulfate was significantly influenced by EDTA, and it was found that spherulitic aggregates were obtained from a solution containing a relatively large amount of EDTA. One of the remarkable examples is shown in Fig. 8. These photographs were taken with a polarizing microscope with lower nicol only (a) and with the crossed nicols (b). From these photographs, the crystals are seen to be nearly two-dimentional spherulites.

Effect of Condensed Phosphates.—The effects of sodium triphosphate (STP) and sodium hexametaphosphate (SHMP) were examined at 25°C. A quite minute amount of these phosphates exerted a great influence on the deposition rate and the crystal habit.

The relation between the composition of the solution and the habit of the crystals obtained in the presence of STP are illustrated in Figs. 9 and 10. Small circles in Fig. 9 indicate the initial concentrations of the three components, strontium chloride, potassium sulfate and STP, the ionic product $[Sr^{2+}][SO_4^{2-}]$ being fixed at 0.001 M^2. After examining many solutions having various compositions plotted in the figure, the whole area of the diagram can be divided roughly into six regions A, B,……F. The characteristic behavior of the solution falling in each of these regions is described as follows.

Region A.—The effect of STP is insignificant on both the deposition rate and the crystal habit.

Region B.—Deposition is retarded noticeably and crystalline aggregates having irregular shapes make their appearance among remarkably modified single crystals (Fig. 10a).

Region C.—Retardation of the deposition becomes more significant, and a relatively small number of larger aggregates having irregular shapes (*primary product*) appear in the earlier stage of the process, and later the solution becomes intensely turbid with the deposition of fine single crystals (*secondary product*). Fig. 10b illustrates the primary product.

Region D.—Crystal deposition is retarded as well, and crystallization occurs stepwise as in Region C, but the primary product is composed of nearly spherical aggregates as shown in Fig. 10c.

Region E.—Spontaneous crystallization is inhibited for a long period of time. However, if the solution was seeded with the crystals obtained from a solution falling in Region D, the seed crystals grow up to larger spheres. The secondary fine crystals also are deposited later.

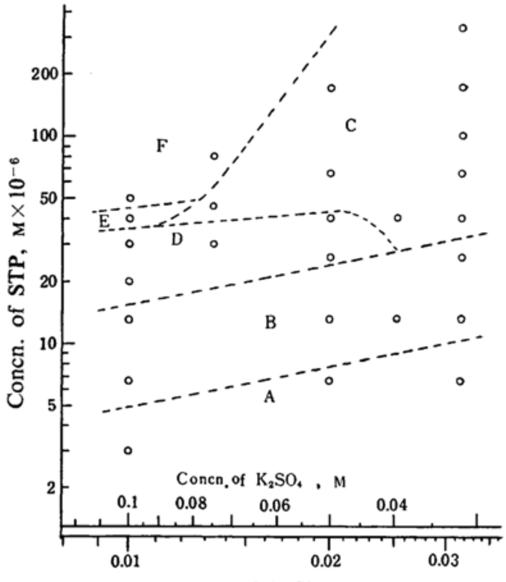
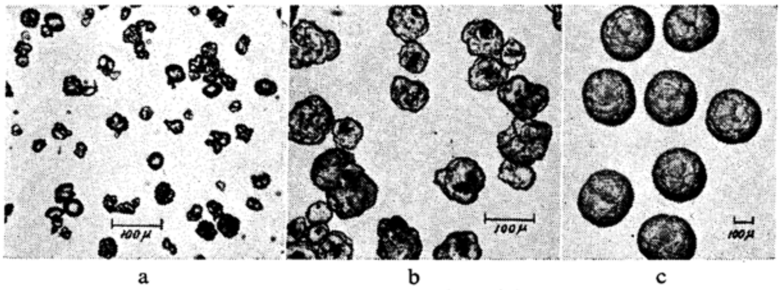


Fig. 9. Composition diagram of $SrCl_2$-K_2SO_4-STP-H_2O system.
$[Sr^{2+}][SO_4^{2-}] = 0.001$ M^2



a b c

Fig. 10. Crystals grown from solutions containing STP.

a: 0.01 M $SrCl_2$, 0.1 M K_2SO_4, 1.3×10^{-5} M STP (Region B)
b: 0.032 M $SrCl_2$, 0.032 M K_2SO_4, 6.3×10^{-5} M STP (Region C)
c: 0.01 M $SrCl_2$, 0.1 M K_2SO_4, 3.0×10^{-5} M STP (Region D)

Region F.—Both spontaneous crystallization and the growth of the seed added are inhibited almost completely.

As the present author was interested in the preparation of spherical crystals, the favorable compositions of the solutions were inquired into for the purpose of examining this process, and it was found that there were the following restrictions on the selection of available compositions. (a) The concentration of STP must be high enough to cause marked habit modification, though there is an upper limit above which no crystallization occurs. (b) The favorable concentration of strontium sulfate is limited to a certain narrow range; below this range crystallization is prevented by so small an amount of STP that the habit-modifying effect does not come into question, while above this range it is impossible to maintain the concentration of STP of sufficiently large value because of the precipitation of sparingly soluble strontium triphosphate. It may be concluded, therefore, that the solution containing a large excess of sulfate ion and a sufficient amount of STP should be recommended for the preparation of well-formed spherical crystals.

Fig. 11, which shows the splinters obtained by crushing the spherical crystal between a pair of microscope slides, makes it clear that the spherical crystal is a kind of spherulite. The arrangement of crystallites can be visualized from microscopic observation of a thin section of the spherulite. Fig. 12a shows a section of a spherulite grown by treating a seed spherulite several times successively with newly prepared solutions of the composition falling in Region E. Fig. 12b illustrates the central portion of the same section in a larger magnification. Fig. 12c shows a micrograph taken with the crossed nicols.

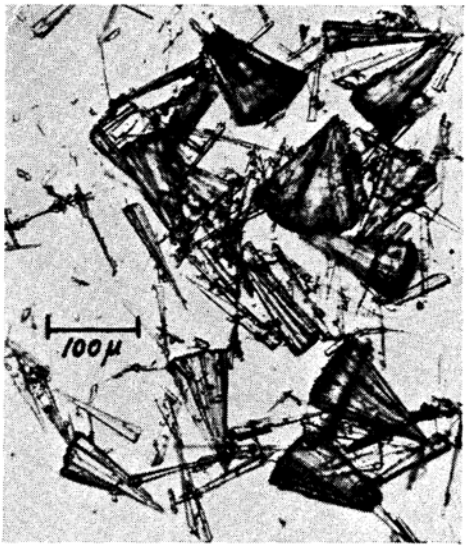


Fig. 11. Splinters of spherulite shown in Fig. 10c.

By certain X-ray examination, it was ascertained that the spherulite was constructed of needle- or wedge-shaped crystallites, each of which was elongated in the direction of *c* axis. The X-ray study was reported in another paper⁷⁾.

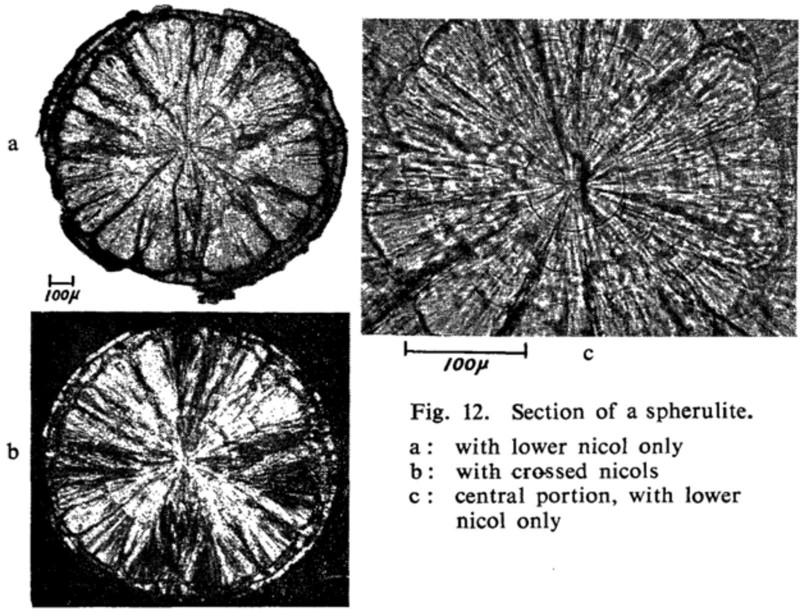


Fig. 12. Section of a spherulite.

a : with lower nicol only
b : with crossed nicols
c : central portion, with lower nicol only

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7) Y. Takano and S. Otani, *J. Sci. Hiroshima Univ., Ser. A*, 23, 109 (1959).

The effect of SHMP was also significant and similar to that of STP, and spherulite was obtained from solutions containing a large excess of sulfate and an appropriate amount of SHMP in its concentration range $(3\sim6)\times10^{-5}$ M.

Discussion

Lambert and Hume-Rothery[8] studied the crystal habit of strontium sulfate precipitated by mixing the strontium chloride solution with sulfuric acid at various concentrations and temperatures. They also investigated the effect of various foreign ions on the precipitation rate, but did not mention the effect on the habit modification. The crystal habits of their products are somewhat different from what was noticed in the present experiments. This discrepancy may be attributed to the difference in the composition of solutions; particularly the difference in acidity may play a dominant role.

From many experimental evidences which have been reported and those of the present work, it is known that the effect of a foreign substance on the crystal habit is very complicated. For example, the citrate ion caused the formation of spherical crystals of barium sulfate[5] on the one hand, and of nearly disk-shaped single crystals of strontium sulfate on the other hand. Another example is the case of spindle-shaped crystals of barium sulfate obtained by Takiyama[9] in the presence of EDTA, which, in the case of strontium sulfate, caused the formation of nearly two-dimensional spherulites.

It is self-evident that the shape of a crystal depends on the relative growth rate in one direction to that in another direction. The growth rate may be affected by the adsorption of foreign substances on crystal faces. According to the peculiarity of each crystal face, the nature and the degree of adsorption may be varied from face to face. Thus a peculiar habit modification might be interpreted by the relation between the crystal structure of the substance to be crystallized and the molecular or ionic structure of the foreign substance added.

The effect of viscosity itself on the crystal habit seems to be insignificant from the experimental results obtained with glycerol or PVA. Referring to the evidence that spherulite can be obtained from ordinary solutions in the presence of a certain impurity, the adsorption, but not the high viscosity, may be the dominant factor for the spherulitic growth. Morse and others' results[3] that the gelatinous medium favored the spherulitic growth may also be attributed to the adsorption of the gelatin itself or of some other impurities possibly involved in it. The mechanism of the spherulitic growth will be discussed in detail in the following paper.

Summary

The effect of various impurities on the crystal habit of strontium sulfate were investigated. Solutions containing citrate ion produced a nearly disk-shaped single crystal whose nearly flat surface was parallel to the (001) plane. Nearly two-dimensional spherulite is obtainable from a solution containing EDTA. A minute amount of sodium triphosphate or sodium hexametaphosphate caused the deposition of a relatively large spherulite having a spherical form, which is composed of numerous needle- or wedge-shaped crystallites elongated in the direction of *c* axis. The habit-modifying action of impurities is discussed in detail.

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Department of Chemistry
Faculty of Science
Hiroshima University
Hiroshima

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[8] B. Lambert and W. Hume-Rothery, *J. Chem. Soc.*, **1926**, 2937.

[9] K. Takiyama, This Bulletin, **31**, 950 (1958).