Japan's Participation in Research on Crystals*

By Isamu Nitta

Department of Chemistry, Kwansei Gakuin University, Uegahara, Nishiomiya 662, Japan

The historical development of Japanese participation in the study of diffraction by crystals and in structure analysis is traced from 1912 to 1972. Contributions to dynamical theory, polytypism, electron diffraction, and crystal imperfections (including order–disorder) have been particularly important.

This year is the sixtieth anniversary of Laue's discovery in 1912. It is generally accepted that with this discovery the age of modern crystallography began. I should like to begin my historical account of this epoch by dividing it into three periods: the first up to the end of the twenties, the second the next two decades, and the third from the fifties to the present.

As soon as the very important news of Laue's discovery reached Japan, T. Terada at the Department of Physics, University of Tokyo, carried out the following experiment. Using an X-ray beam with quite a large cross section, he examined visually, with a fluorescent screen, the movement of each diffraction spot as a specimen crystal was gradually turned. He used crystals of rocksalt, fluorite, quartz, mica, gypsum, cane sugar, and others. In this way, he came independently of the Braggs to the reflexion idea. This experiment was reported in the year following that of Laue's discovery.

In the same year Nishikawa & Ono (1913) at the same Department of Physics presented a very noteworthy report on the X-ray diffraction photographs obtained from fibrous, lamellar and granular substances. They studied specimens of the fibrous substances asbestos, silk and *asa* (in Japanese), a kind of hemp. As typical lamellar materials, they studied talc and mica. The granular substances they studied included marble, finely pulverized rocksalt, quartz and others. Fig. 1 shows an example of the photographs they obtained. This is the one from asbestos, the direction of the fibre being perpendicular to the incident X-ray beam. This diagram is nothing other than the so-called fibre diagram of the present day, the only difference being that the continuous X-ray spectrum from a platinum anticathode was used. Fig. 2 shows another photograph of the same specimen with the fibre axis inclined to the incident beam. Using the reflexion law and assuming, in the present terminology, a uniaxial orientation of the assemblage of minute crystals, they accounted for the behaviour of the obtained diffraction patterns. Furthermore, they investigated diffraction patterns of rolled sheets of metals, such as copper, iron, zinc and other metals, and studied the effect of annealing on these sheets. Thus their study may be looked upon as an embryo of later applications of X-ray diffraction methods to metallurgy, or metallography, and polymer science.

Two years later, in 1915, Nishikawa determined, independently of W. H. Bragg, the crystal structures of spinel and magnetite from their Laue photographs. In this work he showed for the first time the usefulness of the theory of space groups for systematic analysis of a crystal structure. Toward the end of the First World War, he was sent abroad by the newly established Institute of Physical and Chemical Research, Tokyo. He stayed for some time at Cornell University, where he became acquainted with R. W. G. Wyckoff, then a graduate student of chemistry. He taught Wyckoff how to analyze crystal structures.

In the beginning of the nineteen twenties Nishikawa returned to the Institute of Physical and Chemical Research, and continued his studies in the field of X-ray crystallography. Then Y. Sakisaka and I were his senior students. Using an ionization-chamber spectrometer, Sakisaka carried out a series of significant experimental studies on the effect of surface treatments, such as grinding, etching, and many others, on the rocking curve of reflexion intensity. I, as a graduate of the chemistry course, began to be engaged in the crystal analysis of organic compounds, such as iodoform, pentaerythritol, and others. Some time later S. Kikuchi joined Nishikawa's group. In a remarkably short period of time, by making an incident cathode ray beam pass through a very thin film of mica, he was able to obtain beautiful electron-diffraction photographs, corresponding to X-ray Laue diagrams. An even more important discovery was that of interesting new patterns, later called Kikuchi lines and Kikuchi bands. His experiments were carried out immediately after those of Davisson and Germer and of G. P. Thomson. Kikuchi's new findings were probably of even greater significance than those of these other scientists. They impressed the minds of young physicists in Japan so deeply that the later history of the development of diffraction crystallography was inclined considerably to the electron side rather than to the X-ray side.

At about the same time S. Nishikawa and K. Matsukawa made a very notable experiment with a single crystal of zincblende to show that the intensity law of Friedel does not hold for the region of anomalous X-ray dispersion. This was in 1928, just before I was sent abroad for further study. When I first called upon D. Coster in Groningen, he proposed to me that I work on

---

* *Editorial note*: This paper is based, with the minimum of editorial change, on the Congress Discourse delivered by Professor Nitta at Kyoto on 27 August 1972.
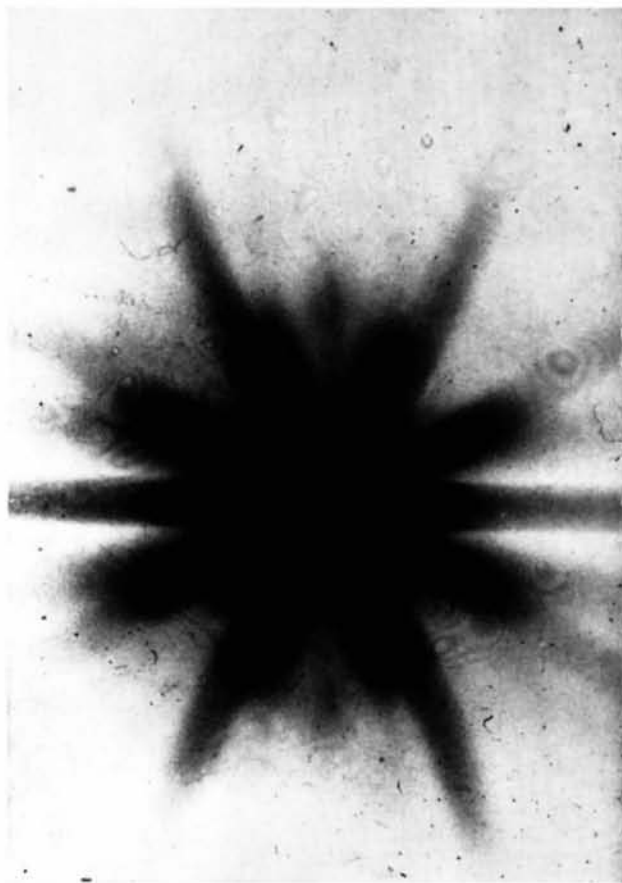
Fig. 1. X-ray diffraction from asbestos (Nishikawa & Ono, 1913).

Fig. 2. X-ray diffraction from asbestos (Nishikawa & Ono, 1913).
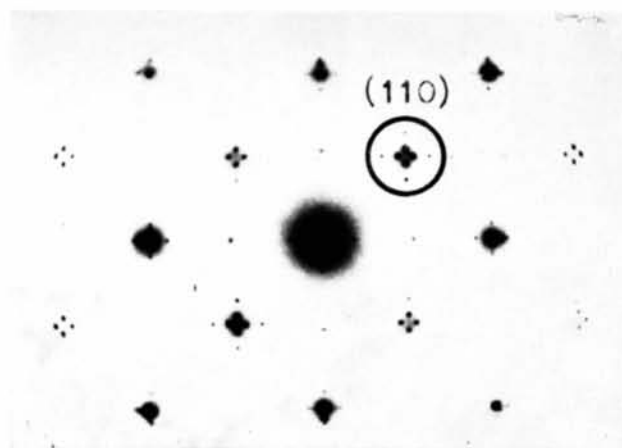

Fig. 8 Electron diffraction from CuAu II. (Ogawa & Watanabe, 1954).

the same problem of the anomalous dispersion effect on the reflexion intensity from zincblende, without knowing that my teacher and colleague had already made such a study.

In addition to the Nishikawa school, about which I have just spoken, I should mention some other forerunners in the application of X-rays to the fields of metal physics and mineralogy in Japan. Professor K. Honda at the Department of Physics, Tohoku University, was a great pioneer in the physics of magnetism and metals, and led a division for research on iron and steel, which in 1922 became the present Research Institute for Iron, Steel and Other Metals. Since the very beginning, the Honda school, or the Research Institute, has made, and is still making, numerous valuable contributions in the fields mentioned. I shall give two examples. One is the X-ray study of the solubility of hydrogen in palladium carried out by M. Yamada in 1923. The other is S. Kaya's experiment of single crystal magnetization of iron, performed in 1926. The latter example shows that the technique of the production of large single crystals of metals had progressed far in Japan by that time. At the Department of Physics of Kyoto University, U. Yoshida, with the collaboration of S. Tanaka, T. Fujiwara, K. Tanaka and others, began in the mid-twenties a series of X-ray investigations on the fine texture of worked metals.

Turning to mineralogy, S. Kôzu and Y. Endö at Tohoku University made an X-ray examination of adularia and moonstone of the feldspar group in the early twenties. T. Ito, a graduate of the geology course, University of Tokyo, went to Europe in the mid-twenties. He studied first the geometrical theory of crystal structure under P. Niggli in Zürich, and then the crystal analysis of minerals under W. L. Bragg in Manchester. On returning to Japan, he became Assistant Professor at the Mineralogical Institute, University of Tokyo, and continued research in the field of crystal analysis of minerals. This concludes my story of diffraction crystallography in Japan in its germinal, or first, period, up to the end of the twenties.

In discussing the next period, covering the two decades of the thirties and forties, I shall first mention the development of the dynamical theory of diffraction in this country. This resulted from the experimental studies on electron diffraction by crystals. These studies were first of elementary or basic nature; then they were extended to problems of oxidation on crystal surfaces, the structure of metallic films formed by evaporation upon crystal surfaces, and so on. The hitherto unknown patterns found in the experiments necessitated, for their interpretation, recourse to Bethe's dynamical theory of electron diffraction put forward in 1928. Thus, those who were engaged in the experiments began to form a group studying intensively the dynamical theory. S. Miyake and R. Uyeda were the leaders. The group, which later became called 'the electron diffraction group', had a considerable influence upon the subsequent development. It is interesting that the importance of the dynamical theory of X-ray diffraction put forward much earlier by C. G. Darwin and P. P. Ewald was first widely recognized in Japan after Bethe's theory of electron diffraction.

In the field of research on metals and alloys, Z. Nishiyama, an old student of Professor Honda, began his X-ray study on the structure of martensite in the early thirties. He found lattice-orientation relationships in the transition from the face-centred cubic to the body-centred cubic structure. His studies of martensite and its transition continued for a very long time at the Institute of Scientific and Industrial Research, attached to Osaka University. After the War, he used electron-microscopic methods in addition to find some types of twin and stacking faults in martensite. T. Fujiwara, originally of the Kyoto school, later at Hiroshima University, is known for his topographic studies of imperfect structures of metals, using a divergent X-ray beam. He is also known for his convenient method of producing metal single crystals with desired crystallographic orientation irrespective of the outer shapes of the specimens. With such crystals, he observed anisotropic growth velocities along different crystallographic directions.

In passing, I would like to mention the following studies. During the Second World War, T. Ogawa found, independently of foreign scientists, that barium titanate and the like showed remarkable ferroelectricity. This stimulated active studies on titanates and other ferroelectric materials by him and many others. At the same time, studies on piezoelectric materials were made. Some tried to look for new materials to substitute for natural quartz or Rochelle salt in certain applications. For these applications it became necessary to develop methods for producing large single crystals. Speaking of such crystal growing, it should be added that T. Noda at Nagoya University attempted from the prewar time to grow good large crystals of artificial mica and graphite.

Turning now to mineral structures, T. Ito had carried out a series of X-ray analyses, of which a detailed account was published in 1950 in a book in English entitled *X-ray Studies on Polymorphism*. From his studies of certain silicate minerals, Ito drew attention to the significance of extremely fine twinning with respect to space-group theory. Thus he explained the structural relationships between the rhombic pyroxenes and diopside; anthophyllite and tremolite; zoisite and epidote; and others. In his book he also proposed a general method of indexing a powder photograph regardless of its crystal symmetry. Ito's line of research was later continued by his students, R. Sadanaga, Y. Takéuchi, N. Morimoto and many others and extended to structure analyses and phase-transition studies of various silicates, sulphides and sulphosalts.

In the early thirties, I moved from the Institute of Physical and Chemical Research to the newly established Department of Chemistry, Osaka University, where I continued crystal-structure analysis of organic

compounds. Then I began to extend my study to the problem of the relationship between structure and properties of crystals. I shall mention one particular example. In 1937, independently of F. L. Llewellyn, E. G. Cox and T. H. Goodwin, T. Watanabé and I determined the crystal structure of pentaerythritol by the two-dimensional Fourier method. Then we studied, by means of powder photographs, the structure of the high-temperature cubic phase, which is formed at about 184°C from the room-temperature tetragonal phase. This motivated, during many subsequent years, a series of measurements, by S. Seki, R. Kiriyama and others of our group, of the thermodynamic, electrical and optical properties of the two phases.
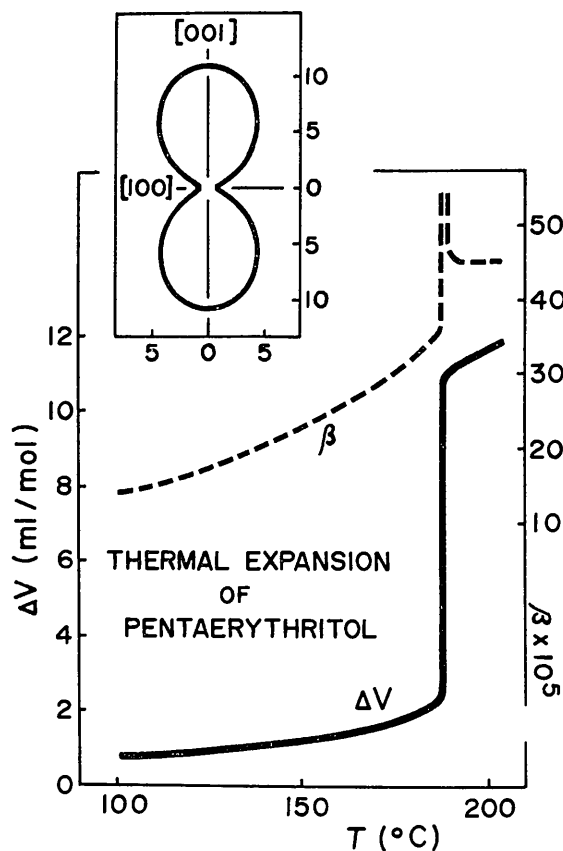
Fig. 3 illustrates the structure of the room-temperature modification. On the left, the molecular conformation, of symmetry $\bar{4}$, is shown. On the right, a part of the hydrogen-bonded layer of the crystal, viewed along the c axis, is represented. On passing through the transition point, the hydrogen bonds between molecules are broken, and, at the same time, the molecules become flexible, owing to rotation about the carbon–carbon and carbon–oxygen single bonds. In addition, the molecules as a whole undergo some rotation about their central carbon atoms. Thus, in the cubic phase, the molecules, arranged in the face-centred manner, assume a statistically averaged shape having cubic or higher symmetry. Fig. 4 gives the results of the thermal expansion measurements. On the left is shown a polar diagram of the linear expansion coefficient averaged over a certain temperature range for the tetragonal phase. Its minimum value is along the hydrogen-bonded molecular layer, while its maximum, which is more than sixteen times as large as the minimum, is in the direction perpendicular to the layer. The lower curve in a solid line is the dilatometric volume–temperature curve, showing a remarkable increase in volume at the transition point. In the middle is the temperature dependence of the thermal expansion coefficient derived from the dilatometric curve. Fig. 5 gives the heat capacity–temperature curve with a sharp rise at the transition point. This and the preceding curves show definitely that the transition is of the first order, when the used sample is very carefully purified. As to the thermodynamic quantities, it is noteworthy that, whereas the entropy of transition has the large value of 22·8 e.u., the entropy of melting is only 3·2 e.u. Fig. 6 shows the temperature variation of the dielectric constants. For the tetragonal phase there are different values for the axes a and c, while above the transition point the anisotropy disappears and the dielectric constant rises suddenly with marked dispersion for different frequencies, resulting from violent thermal motion of the molecules in the cubic phase. Finally, Table 1 shows measured and literature values of the principal refractive indices for pentaerythritol and its tetra-acetate and tetranitrate derivatives, all crystallizing practically with a tetragonal body-centred lattice. With these values, using Ewald's theory of lattice optics, we derived separate contributions to the double refraction for light due to the anisotropy of lattice arrangement and to the anisotropy of the molecular polarizability.

At about the same time as our structure investigation of pentaerythritol, J. Timmermans in Belgium proposed the name 'plastic crystals' for those organic compounds which show remarkable plasticity and give ex-

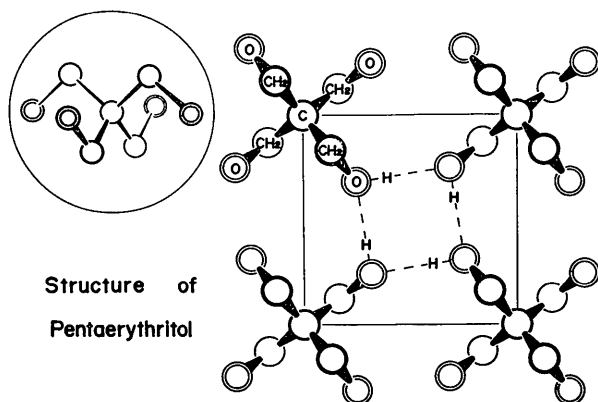**Structure of**

Pentaerythritol

Fig. 3. Crystal structure and molecular conformation of pentaerythritol.

Fig. 4. Thermal expansion of pentaerythritol (Nitta, Seki, Momotani, Suzuki & Nakagawa, 1950).

A C 29A – 1*

traordinary low values of entropy of melting in contrast with rather large values of entropy of transition for the lower transition point. From what I have shown, it follows that the cubic phase of pentaerythritol may be looked upon as a complex example of such plastic crystals. Generally in such crystals, polyatomic molecules are in violent rotational or reorientational motion, so that the substance may be said to be in a partially molten state. In fact, later n.m.r. investigation proved this quite clearly. Using the broad-line technique, T. Yukitoshi, H. Suga, S. Scki and J. Itoh performed a proton-magnetic-resonance experiment in 1957 on solid hexamethyldisilane $(CH_3)_6Si_2$ in the temperature range from about $-180\,°C$ to about $+20\,°C$. Fig. 7 shows their result: the temperature variation of the width of the absorption line. From the narrowing of the line, it is concluded that the six methyl groups are undergoing reorientational motion around the Si–C bonds even at liquid-air temperature. Furthermore, above about $-120\,°C$ the line width decreases markedly. This change is attributed to the onset of internal rotation around the Si–Si bond. On passing the transition point at $-51.3\,°C$ from phase II to phase I, which is cubic body-centred and plastic-crystalline, the line width shows a considerable and abrupt drop. This is due partly to the onset of reorientation of the molecular axis and partly to the rapid increase in self-diffusion of the molecules. At the melting point, the line width does not show any observable change. Further investigations on the state of plastic crystals should be of considerable interest.

The third period of our history began with Japan's adherence to the International Union of Crystallography. At the Second General Assembly and International Congress held in Stockholm in 1951, Japan joined the Union. Before going into research topics, I should mention the new establishment in 1957 of the Research Institute for Solid State Physics, attached to the University of Tokyo. It consists of about twenty research divisions. In addition to a few divisions of theoretical nature, there are divisions of crystallography (two divisions), solid materials (including production of pure single crystals), low temperature, high pressure, lattice imperfections, plasticity, ferroelectrics and quantum electronics, semiconductors, magnetism (two divisions), optical properties, radio and microwave spectroscopy, surface properties, molecular physics, nuclear phenomena in the solid state, and nuclear radiation. This list of research divisions shows the recent trend of research in Japan on crystals.

Coming to research topics, I find it difficult to discuss the third period of this general historical review in an impartial and thorough manner, even if description of most recent activities is omitted, since they are covered in the program of this Congress. I hope you will excuse me for picking a very limited number of topics out of the numerous ones in the ever expanding frontiers of crystallography and related fields. First, I shall refer to the intensive study of the dynamical theory of X-ray and electron diffraction, which has led to various fruitful results by S. Miyakc, R. Uycda, S. Takagi, K. Kohra, N. Kato, Y. Kainuma, and many others. On the electron side, these include the three-wave approximation, the violation of Friedel's law, the theory of Kikuchi patterns, diffraction by a finite crystal, thermal diffuse patterns, and so on, all connected closely with experimental findings. I shall not proceed further along this line, because there will be later a general lecture by Professor R. Uyeda on electron diffraction and microscopy in Japan. On the X-ray side, theories have been
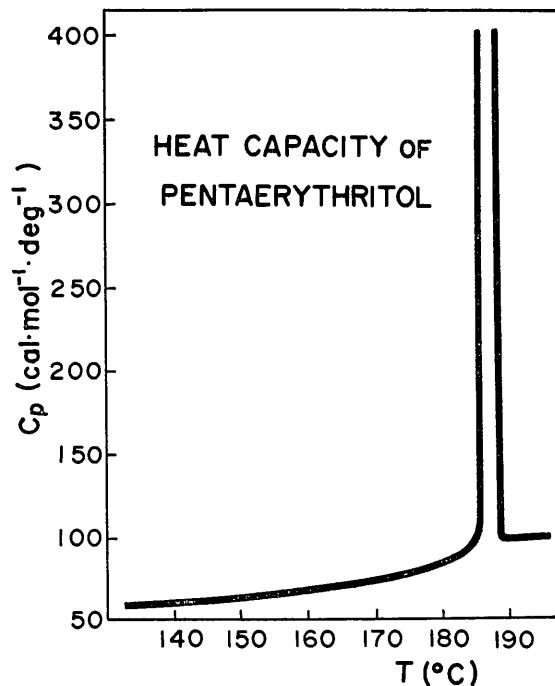

Fig. 5. Temperature dependence of heat capacity of pentaerythritol (Nitta, Seki & Momotani, 1950).

Table 1. *Double refraction of pentaerythritol and its derivatives*

Data are taken from Nitta (1940).

	$C(CH_2OH)_4$	$C(CH_2ONO_2)_4$	$C(CH_2OCOCH_3)_4$
a (Å)	6.604	9.386	12.00
c (Å)	8.779	6.714	5.506
ω (Na D)	1.555	1.554	1.433
ε (Na D)	1.515	1.553	1.483
α_ξ (Å)	12.37	23.60	31.76
α_ζ (Å)	11.65	20.87	18.08

developed for spherical waves instead of plane waves, diffraction by a wedge-shaped crystal and by a distorted crystal, and so forth. In connexion with these theoretical investigations, it should be remarked that N. Kato observed with A. R. Lang the so-called X-ray 'Pendellösung' fringes. K. Kohra tried to produce an X-ray

Fig. 6. Temperature dependence of dielectric constants of pentaerythritol (Kiriyama, Yabumoto & Nitta, 1954).

Fig. 7. Temperature dependence of n.m.r. absorption linewidth of hexamethyldisilane (Yukitoshi, Suga, Seki & Itoh, 1957).

beam with a divergence angle of a hundredth of a second so as to be able test some theoretical conclusions. Here, it may be added that considerations based on the dynamical theory are very important for the interpretation of the patterns obtained by various methods of X-ray topography. In Japan, as elsewhere, these are now widely applied to investigations of imperfections and secondary structures in crystals of semiconductors, ferroelectrics, magnetic materials, metals and others.

In 1961, there was held in Kyoto, a joint international Conference on Magnetism and Crystallography. The part concerned with electron and neutron diffraction was sponsored by the International Union of Crystalolgraphy. With regard to neutron diffraction, there was a great delay in commencing experimental studies in Japan. This delay was a result of the delay in constructing atomic reactors, chiefly because Japanese people were extremely sensitive about radioactivity from the experience of the last War. Since the symposium was held about the time of the completion of an atomic reactor of CP-5 type at the Japan Atomic Energy Research Institute in Tokai-mura, north-east of Tokyo, the topic of neutron diffraction was included to stimulate and encourage Japanese scientists to neutron diffraction and related studies by learning from foreign researchers their valuable experiences. Starting in 1961 N. Kunitomi, H. Katsuraki, S. Hoshino and others conducted neutron-diffraction studies in three groups. Their studies were those on uranium–$3d$-transition-metal alloys, magnetic structure of alloys such as manganese–tellurium (1:1), iron–germanium (1:1), and so on. On the other hand, S. Hoshino, Y. Saito and others analyzed crystal structure of deuterated oxalic acid dihydrate. This crystal is not isomorphous with the widely known structure of ordinary oxalic acid dihydrate, though both crystallize in the monoclinic system. Also, in the third period now being discussed, very active theoretical investigations were begun on magnetic anisotropy, interaction, arrangement or orientation of spins by T. Nagamiya, K. Yoshida, A. Yoshimori, J. Kanamori, T. Moriya and many others. These studies led to neutron-diffraction studies on more or less complicated magnetic structure, such as those of screw type.

Turning to researches on metals and alloys, S. Ogawa, at the Research Institute for Iron, Steel and Other Metals began a study in the early fifties on very thin single-crystal films of some ordered alloys formed by vacuum evaporation onto the cleaved surface of rock salt. For this he used the transmission electron-diffraction method, and found that reflexions showed splittings into satellites. He explained such a phenomenon as due to the existence of long-period domains, resulting from some periodic antiphase shifts of the ordered lattice. The ordered alloys he studied were: CuAu II, Cu_3Pd, Ag_3Mg, gold–zinc system and so on. Fig. 8 shows an example of the electron-diffraction photographs he obtained. This is from CuAu II. Ogawa further studied this phenomenon using X-ray diffraction and transmission electron-microscopic methods, and
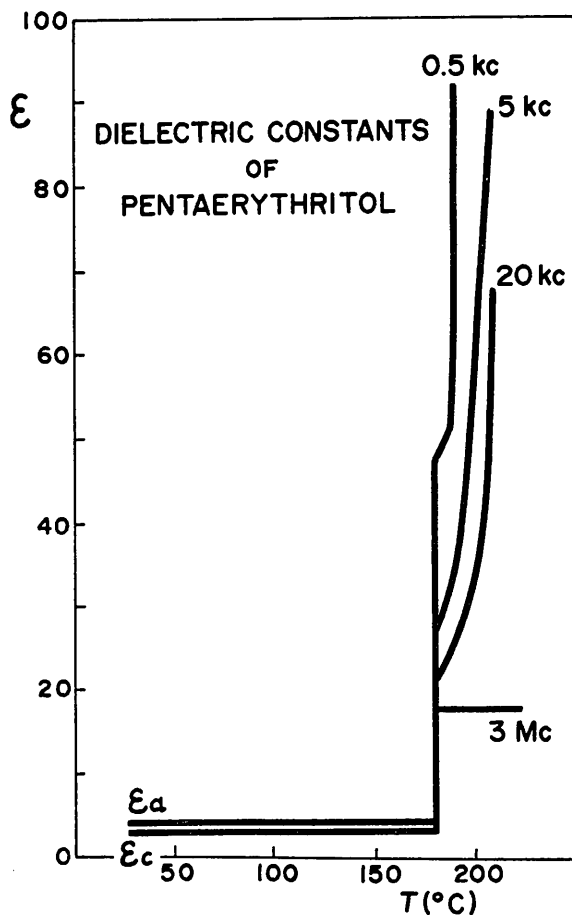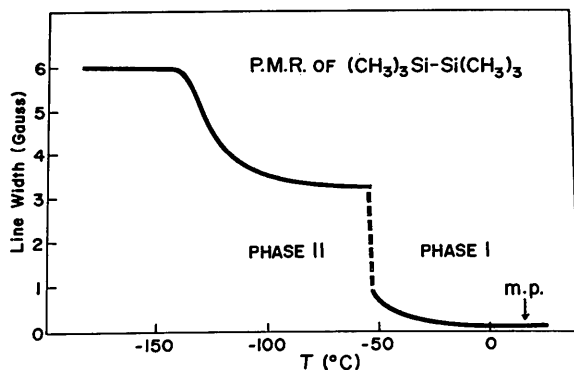
made valuable contributions to the knowledge of ordered alloy structure. Such an antiphase domain structure contains lattice defects or irregularities of a specific kind. Speaking of defect structures, I shall next mention the investigations of J. Kakinoki. In the mid-fifties, Kakinoki became interested in the theory of X-ray diffraction due to stacking faults. Since then he has studied and developed the theory in a very general and systematic manner for various cases extending to higher ranges of stacking influence. His general theory clarifies the meaning of various expressions and concepts appearing in preceding theories put forward by other researchers. I should like to add further that, in the late forties, T. Matsubara proposed a theory of diffuse X-ray scattering by a partially ordered crystal. T. Oda subsequently applied this theory to the case of cubic tetranitromethane by taking into account the short-range order. Matsubara's general theory became recently recognized again when people began studying the X-ray diffuse scattering by ferroelectric crystals in the neighbourhood of their transition points.

It is here needless to remark that crystal analysis of more or less complicated structures owes its rapid and great development to advances in the mathematical theories of the analytical procedures, computing tools, experimental techniques and instrumentation. In these respects, Japan cannot be said to have contributed much. However, Y. Okaya and K. Sakurai made some proposals on the use of simpler inequality methods, and, some time later, S. Naya and T. Oda tried to formulate in a general manner the statistical method of the direct determination. Concerning the Patterson function method, Y. Saito and Y. Okaya with R. Pepinsky devised the so-called P_c and P_s functions, which can be utilized advantageously in the structure determination of a non-centrosymmetric crystal showing anomalous X-ray dispersion. For such a crystal, it is well known that, in 1951, the X-ray anomalous dispersion effect was first applied by A. F. Peerdeman, A. J. van Bommel and J. M. Bijvoet to the determination of the absolute configuration of the tartrate ion. A few years later, Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya determined the absolute configuration of an isomer of tris-ethylenediamine cobaltic ion showing (+) activity for the D-line. This is the first example of the X-ray determination of the absolute configuration of a metal complex ion. Fig. 9 shows a drawing of the configuration determined for that ion.

Next, with regard to organic structures, the analysis group at Osaka University continued to analyze simple compounds, hydrogen-bonded structures, intermolecular compounds and others, all of some significance to structural chemistry. Some of the group aimed at analyzing organic natural products. However, at that time in Japan, we could not yet avail ourselves of electronic computers for such a purpose. As an example of this precomputer time, I may mention the research on kainic acid, which is the most active component for destroying intestinal worms isolated from a kind of sea weed. The

analysis confirmed it as 2-carboxyl-3-carboxymethyl-4-isopropenylpyrrolidine, a five-membered ring with three side chains. This may be looked upon as a limit of molecular complexity, which can be solved without recourse to an electronic computer. Such a computing tool became at length available to Japanese crystallographers in the early sixties, and from then on there was a sudden increase in the number of the analyses of more or less complex natural products. These were carried out by the Osaka school and also by Y. Iitaka and his group at the University of Tokyo.

Meat of some kind of puffer or globe fish is a famous favourite food of Japanese people. However, it is not rare for one who has eaten the fish to be poisoned to death by a strongly toxic substance in it. The poison was crudely isolated long ago and named 'tetrodotoxin'. In 1963–64 the chemical structure of this toxin was derived
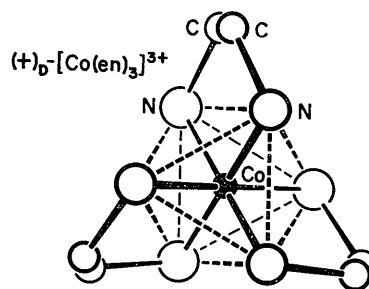

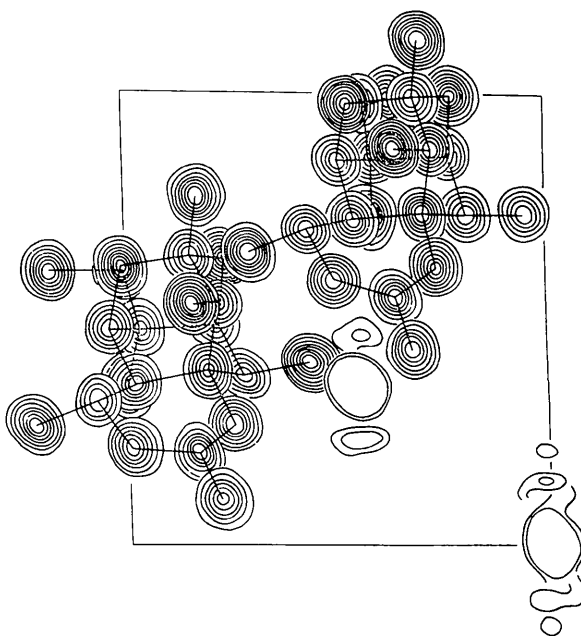Fig. 9. Absolute configuration of d-[Co en₃]³⁺ (Saito, Nakatsu, Shiro & Kuroya, 1954).

Fig. 10. Electron-density distribution of tetrodotoxin hydrobromide. (Furusaki, Tomiie & Nitta, 1970).

on the basis of X-ray analyses of four derivatives by three independent research groups of organic chemists and crystallographers. One of these groups was formed by cooperation between the University of Tokyo and the Sankyo Company. The second group was a joint activity of Nagoya Univsersity and Kwansei Gakuin University. The third was the Woodward group at Harvard University. Very recently the crystal structure

Fig. 11. Framework of the tetrodotoxin ion.

$$a = 15.42 \ \mathring{A}$$

r : right-handed , l : left-handed
R : rectus , S : sinister

Fig. 12. The helical structure of isotactic poly(t-butylethylene oxide).

of tetrodotoxin itself was directly analyzed as its hydrobromide by the late Tomiie and his collaborators. Fig. 10 shows the electron-density map of this crystal. The map shows two molecules in the asymmetric unit. Fig. 11 gives the stereochemical perspective of the molecule. An important characteristic of the molecule is its dioxaadamantane skelton, which decomposes in various ways according to different chemical treatments. It is of interest to compare the structure of tetrodotoxin itself with those of the four derivatives by prior X-ray analyses. However, I shall not discuss this topic further.

In addition to these natural products, Y. Iitaka, M. Kakudo, K. Tomita and others have been engaged in the X-ray analysis of other biologically important substances. For instance, the Kakudo group at the Institute for Protein Research, attached to Osaka University, has very recently completed the analysis of bonito ferrocytochrome c at 2·3 Å resolution.

On the other hand, the X-ray method has long been utilized in Japan in the field of polymer science, ever since I. Sakurada and Y. Go introduced the German technique in the early thirties. In recent years, H. Tadokoro, Y. Chatani and others at Osaka University have determined a considerable number of structures of synthetic linear polymers in various kinds of conformation. Fig. 12 shows, as an example, the structure of isotactic poly(t-butylethylene oxide) containing, in each monomer residue, an asymmetric carbon of the rectus or, its antipode, sinister chiral configuration. This example is that of the racemic mixture of the rectus polymer and the sinister polymer chains. In the unit cell of the space group symmetry $P\bar{4}n2$, there are two rectus chains in the left-handed helix of 9 monomers in 4 turns and two corresponding sinister chains in the right-handed helix all arranged along the c axis in a bisphenoidal $\bar{4}$ manner.

Since electronic computers of world-famous as well as Japanese makers began to be used in Japan for crystallographic purposes, various programs for such crystallographic computing have been actively put forward. T. Sakurai at the Institute of Physical and Chemical Research made efforts under cooperation of many other Japanese crystallographers to make up such programs systematically and compiled them in a 'Universal Crystallographic Computation Program System (UNICS)', published in 1967.

In summary, I have covered, though very roughly, some historical features of development in Japan in the two main fields of crystal-diffraction study and crystal-structure analysis as well as a number of research topics related closely to these. For obvious reasons, the advances in these fields have further led to increased research on the relationships between structure and properties, such as lattice-dynamical, electrical, magnetic, optical, and others; on imperfections and secondary structures; on crystallography at extraordinary pressures and temperatures; and on many other research topics. However, it is of course beyond my reach to widen the present review further along the lines mentioned.
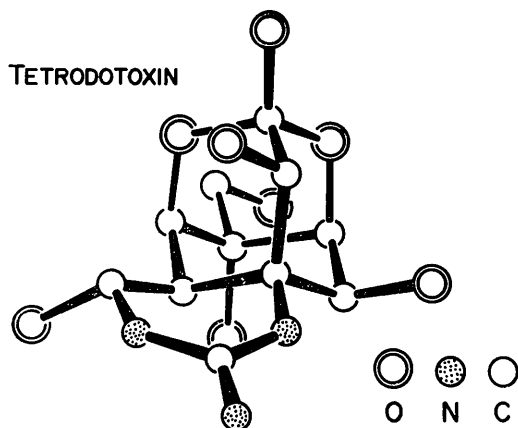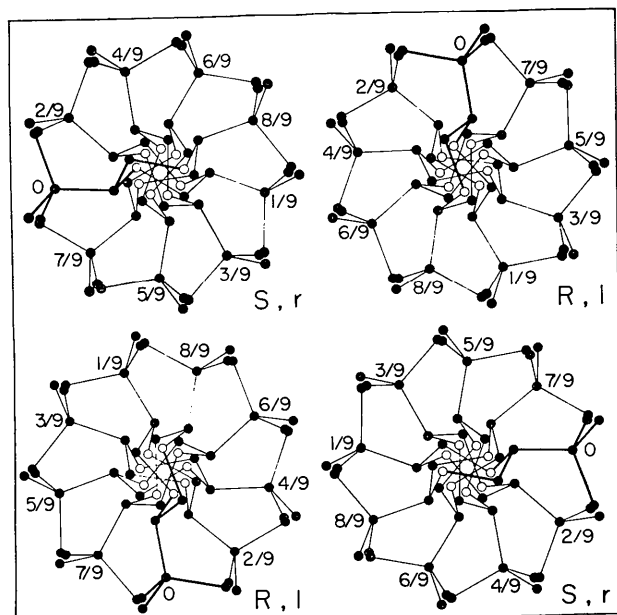
Although it is true that the world history of modern crystèllography is now rather old, its continuing achievements have provided indispensable knowledge and tools for the future progress of science in general. On the other hand, it is also true that the frontiers of crystallography and related fields are ever growing into innumerable branches so rapidly and so manifoldly that it cannot be denied that one is likely to be lost in orientation in the midst of such a wealth of scientific activities.

References

FURUSAKI, A. TOMIIE, Y. & NITTA, I. (1970). Bull. Chem. Soc. Japan, 43, 3332–3341.

KIRIYAMA, R., YABUMOTO, S. & NITTA, I. (1954). Bull. Chem. Soc. Japan, 27, 115–119.

NISHIKAWA, S. & ONO, S. (1913). Proc. Math. Phys. Soc. Tokyo, 7, 131–298.

NITTA, I. (1940). Sci. Papers Inst. Phys. Chem. Research, Tokyo, 37, 114–130.

NITTA, I., SEKI, S. & MOMOTANI, M. (1950). Proc. Japan. Acad. 26, No. 9, 25–29.

NITTA, I., SEKI, S., MOMOTANI, M., SUZUKI, K. & NAKAGAWA, S. (1950). Proc. Japan. Acad. 26, No. 10, 11–1c.8.

OGAWA, S. & WATANABE, D. (1954). J. Phys. Soc. Japan, 9, 475–488.

SAITO, Y., NAKATSU, K., SHIRO, M. & KUROYA, H. (1954). Acta Cryst. 7, 636.

YUKITOSHI, T., SUGA, H., SEKI, S. & ITOH, J. (1957). J. Phys. Soc. Japan, 12, 506–515.

Structure Determination of a $MoO_2Cl_2.H_2O$ Polytype by Interpretation of Non-Space-Group Extinctions*

By H. SCHULZ

Institut für Kristallographie und Petrographie, ETH, CH-8006 Zürich, Sonneggstrasse 5, Switzerland

AND F. A. SCHRÖDER

Lehrstuhl für Anorganische Chemie der Universität, D-7800 Freiburg i. Br., Albertstrasse 21, Germany (BRD)

Based on the magnitude of intensities obtained by X-ray diffraction, the reflexions of $MoO_2Cl_2.H_2O$ can be divided into so-called main reflexions (strong intensities) and so-called superstructure reflexions (weak intensities). A comparison of the structure determined with the main reflexions only (designated as structure A) and of the structure determined with the superstructure reflexions only (designated as structure B) shows that structure A is not the superposition or average structure of structure B, but that structures A and B are polytypes. This means that the basic structure element, the coordination polyhedron of the Mo atoms, being an irregular octahedron, is very similar in both structures. The octahedra are however combined with each other in different ways in the two structures.

1. Structure A

Structure A was determined by Atovmyan & Aliev (1971) and Schröder & Nørlund Christensen (1972). It crystallizes in space group $Pmn2_1$. The cell dimensions are $a=9.23$, $b=3.89$, $c=91$ Å. The projection of the structure on (100) is shown in Fig. 1(a). The main feature of structure A is the coordination polyhedron around Mo in form of an irregular octahedron. The Mo atom is displaced from the centre into a tetrahedral environment, which must be considered as the essential bonding polyhedron. The four atoms forming the corners of the tetrahedron are mainly bonded to the corresponding Mo atom. In Fig. 2 the sequence of

the polyhedra in structure A for two unit cells is shown. Each unit cell contains two octahedra. Each octahedron is part of a chain running parallel to the b axis. The octahedra have two common edges. The two chains can be considered as antiparallel.

During the collection of the data three crystals were investigated, all of which showed besides the reflexions corresponding to structure A, additional superstructure reflexions which are considered separately in this paper.

2. Explanation of the terms, position of gravity, ideal position and real position

In the following, some general considerations are outlined: Fig. 3 shows in (a) an arrangement of two Mo atoms in cell A. In (b) four cells A are put together in

---

* Part VIII of Contributions to the Chemistry of Molybdenum and Tungsten. For part VII see: Z. anorg. algem. Chem. (1972), 392, 107.