CHAPTER 23

Japan

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As described in Part V, the history of fifty years of X-ray diffraction in Japan was inaugurated by T. Terada, who found in 1913, immediately after Laue's discovery and also quite independently of W. L. Bragg, the law of X-ray reflection based on his original visual as well as photographic observation of the movement of the Laue spots as the crystal was being turned.[1] In his diffraction experiments using an X-ray bulb of the Müller-Uri type operated with a Toepler influence machine, he examined single crystals of rocksalt, fluorite, quartz, mica, gypsum, borax, tourmaline, epidote, penninite, cane sugar, etc. For the visual observation with a fluorescent screen he used a very wide beam of X-rays collimated by a diaphragm with a circular aperture 5–10 mm in diameter. Terada continued his diffraction studies for about one year, investigating the effect of the bending of rocksalt [2] and analyzing to some extent the crystal structure of alum.[3]

The second name appearing in this history is that of S. Nishikawa, of whom we have spoken in detail in Part V and whose rôle was of primary importance to the progress of diffraction studies in Japan. As already mentioned, Nishikawa published in 1913 his first paper, with S. Ono, on the study of diffraction photographs of fibrous substances such as asbestos, silk and *asa*(*Cannabis sativa*—a kind of hemp), of lamellar substances like talc and mica, and of granular substances such as marble, finely pulverized rocksalt, quartz, etc., using continuous X-rays.[4] Moreover, Nishikawa studied diffraction patterns of rolled sheets of metals such as copper, iron, zinc, etc., and the effect of annealing them. Such a study is nothing other than that of the diffraction characteristics of polycrystalline textures, which has later found many applications in the fields of metallography, polymer science and other sciences. His earliest introduction of the theory of space groups as a general and logical means for crystal analysis

appeared in his paper in 1915 on the crystal structure of some crystals of the spinel group and magnetite.[5] In this way began the first page of the history of X-ray diffraction in Japan.

Now, in order to describe the development, it may be convenient first to name the schools or the regional research groups in more or less the chronological order of their origin. These include the Nishikawa school, the Honda school, the Kyoto school, the Ito school in Tokyo, the Osaka school, the Hiroshima school and the Nagoya school. Besides these, there may be given names of individuals who were known to be active in the early period. They are G. Asahara, S. Kôzu, A. Ono and others.

We begin briefly with the Nishikawa school in Tokyo, as it has already been described in Part V in some detail. In the early twenties, within the so-called Nishikawa Laboratory in the Institute of Physical and Chemical Research, Nishikawa was engaged in analysing some orthorhombic crystals by means of an ionization chamber spectrometer, and his early students, Y. Sakisaka, I. Nitta, Z. Ooe and S. Shimura carried out structure analyses of crystals of inorganic compounds, minerals and compounds of metallographic importance. A little later, Nishikawa, Sakisaka and I. Sumoto, using a double crystal spectrometer as well as Laue photographs, investigated the effects of various physical treatments of crystals on the reflection intensities from the point of view of extinction and crystal imperfection. Thus they investigated the effect of surface grinding,[6] that of thermal strain or inhomogeneous temperature distribution,[7] and that of piezoelectric vibration.[8] Such investigations were later extended by his students, E. Fukushima, Y. Kakiuchi, S. Miyake, S. Yoshida and others. Fukushima studied the effect of inhomogeneous elastic deformations under an external force.[9] Kakiuchi examined that of long impressed strong electric fields.[10] Miyake observed an anomalous change in the intensity of reflection from Rochelle salt on passing the Curie point.[11] Yoshida found that the relative intensities of X-ray spectral lines changed with the degree of imperfection of the crystal used for spectrometry.[12] T. Muto made a theoretical calculation of the intensity of reflection from an alloy with a disordered structure.[13]

Since Kikuchi's experiments of electron diffraction by crystals carried out in the Nishikawa Laboratory in 1928, most of Nishikawa's students in the Institute of Physical and Chemical Research and in the Department of Physics of the University of Tokyo turned to this field. Thus K. Matsukawa, M. Miwa, T. Muto, T. Yamaguti, K. Shinohara,

S. Nakagawa, S. Miyake, Ryozi Uyeda and others played important parts in the development of wide studies on electron diffraction by crystals. Shinohara noticed that, in order to elucidate the observed Kikuchi-lines, -envelopes and -bands, one should start from the dynamical theory put forward by Bethe.[14] Besides Kikuchi, Shinohara and Nakagawa, T. Yamaguti also determined precisely the inner potentials of a series of crystals by the rotating crystal method with a knife-edge.[15] The interesting complexities of electron diffraction by crystals led Miyake and Uyeda to study very keenly and thoroughly the dynamical theory developed by Bethe, Harding, Laue and others. Their effort had a very favourable influence upon the later development of younger students, and there was gradually formed a strong electron diffraction group. Of the younger students graduating before 1945, the names of S. Takagi, K. Kimoto, G. Honjo, H. Yoshioka, K. Kohra, N. Kato and Y. Kainuma will be given. To the experimental development too, contributions of Miyake and Uyeda have been made in various respects. The instrumentation for the study of electron diffraction has been greatly improved by them before and after the War. In this connection it may be added that the manufacture of electron microscopes in Japan has greatly benefited from the co-operation of electron diffraction scientists possessing long and valuable experiences. As for theoretical development, there have been published important papers on such topics as the problem of simultaneous reflection, including the violation of Friedel's law (Miyake, Uyeda and Kohra); an anomalous phenomenon found by Kikuchi and Nakagawa (Miyake, Mieko Takagi and Kohra); determination of phase angles (Miyake and K. Kambe); dynamical theory for a finite polyhedral crystal (Uyeda and Kato), explanation of Kikuchi patterns (Kainuma); theory of absorption (Yoshioka); effect of thermal vibration (S. Takagi), etc.

The Nishikawa school, which had started as an important center of X-ray diffraction, changed its character, as described above, to become an active center of electron diffraction. In the meantime the school branched in many lines. Thus in 1933 Kikuchi and Nitta went to Osaka University, with the former beginning nuclear research and the latter continuing X-ray diffraction work. Around 1940 Miyake entered the Kabayashi Institute of Physical Research, Tokyo, and there he carried out X-ray and electron diffraction studies. In 1948 he became a professor of physics at the Department of Physics, Tokyo Institute of Technology, and led a group of scientists in both fields of X-ray and electron diffraction. Honjo, Mrs. Mieko Takagi (formerly

Miss Mieko Kubo), S. Hoshino and others were the members of the group. Uyeda remained in the University of Tokyo up to 1942, when he became a professor of physics at the Department of Physics, Faculty of Science, Nagoya University. There he formed the Nagoya school which is very active in the field of electron diffraction. Among the scientists of the Nagoya school the names of Kimoto, Yoshioka, Kato and Kainuma have already been given above. Speaking of the Nagoya school, it is to be added that a colleague of Uyeda, Y. Morino (1908–) began a series of electron diffraction studies of gas molecules with M. Kimura and others. Morino became later a professor of chemistry at the University of Tokyo. Coming back once again to Miyake, he became very recently a research professor at the newly established Institute for Solid State Physics, which is attached to the University of Tokyo, and is working there with his colleagues, Y. Saito, S. Hosoya, S. Hoshino and others.

In the Tokyo region, G. Asahara (1891–) was active, in the early period under review, as the leader of the Asahara Laboratory, Chemistry Division, Institute of Physical and Chemical Research. As mentioned in Part V, Nishikawa and Asahara began the X-ray study of metals at Cornell University in 1920. On returning to his Institute in Tokyo, Asahara soon published his X-ray studies of graphite and amorphous carbon [16] and of thallium.[17] Of his research group, H. Nakamura examined by means of X-rays the structure of electrolytic brass,[18] and T. Sasahara studied the solid solution system KCl—KBr [19] and also the structure of α-thallium.[20] Tokunosuké Watanabé (1904–) determined the crystal structure of northupite, brominated northupite and tychite.[21] By the time he published this paper, Asahara had retired from the Institute and had been succeeded by H. Shiba. Besides the two groups of Nishikawa and Asahara, M. Majima, S. Togino and K. Yamaguchi in the Engineering Division of this Institute were also active in carrying out X-ray studies of metals. S. Yamaguchi made independently a series of electron diffraction studies of metals and chemical reactions on their surfaces.

Next to the above groups in Tokyo, it will be appropriate to turn to the Sendai region, where the Tôhoku University is located. The application of the X-ray method was first attempted by S. Kôzu (1880–1955), a professor of petrology of the Faculty of Science, Tôhoku University. In collaboration with Y. Endö, a physicist, he began in 1921 his notable X-ray study of the felspar group, especially

adularia and moonstone.[22] Later Kôzu and K. Takané made structure determination of cancrinite, bronzite, vesuvianite, diaspore, enargite, etc.[23] In the Research Institute for Iron, Steel and Other Metals, founded by K. Honda (1870–1954) and attached to Tôhoku University, the X-ray method was introduced by M. Yamada. The first two X-ray papers by Yamada published in 1923 were a note on the reflection of X-rays from a fluorite crystal [24] and on the occlusion of hydrogen in palladium.[25] As is well known, Honda led in his Institute a large number of scientists in the fields of metallurgy, metallography and physics of magnetism for a long period of time. He was also one of the sponsors of the *Zeitschrift für Kristallographie.* Honda's students who were engaged in X-ray metallographic studies are, besides M. Yamada and Y. Endö mentioned above, A. Ôsawa, S. Sekito, S. Ôya, K. Endo, T. Sutoki, Z. Nishiyama and many others. They made use of the X-ray diffraction method for the identification or confirmation of a definite phase, for the determination of equilibrium phase diagrams, the study of occlusion of gases in metals, solid solution formation, phase transformation, etc. E. Matsuyama improved the high-temperature camera, and I. Edamoto constructed an X-ray tube with oscillating target. I. Obinata, who had made an X-ray study of the β-phase of Cu-Al alloy at the Ryojun College of Engineering and then worked with E. Schmid and G. Wassermann at the Kaiser-Wilhelm-Institut für Metallforschung on the solid solubility in the Pb-Sn system, the plastic deformation of metal single crystals, etc., joined the Honda school. Shiro Ogawa (1912–), who is known with M. Hirabayashi, D. Watanabe and others for his studies of antiphase domains of some alloys, is leading the research group of X-ray and electron diffraction in the Institute.

In Kyushu University X-ray work dates back to 1922, when A. Ono (1882–), at the Department of Mechanical Engineering, College of Engineering, attempted an X-ray examination of the inner structure of strained metals such as copper, aluminium, and α-iron from the standpoint of material testing. The results of this investigation were reported in a series of papers from 1922 to 1930.[26] In his third report in 1925 he noted that the findings of G. I. Taylor and C. F. Elam (1925) and of M. Polanyi and E. Schmid (1925) about the slip resistance of crystals stood in conformity with his view concerning the cause of strain-hardening.

Kyoto University did not stand behind in the introduction of the X-ray method to various fields of scientific studies. This was mainly by virtue of M. Ishino and U. Yoshida in the Department of Physics,

College of Science. Thus in 1925 S. Tanaka (1895–) and T. Fujiwara (1897–), students of Yoshida, published, respectively, papers on the X-ray study of the polycrystalline texture of rolled platinum sheet[27] and of aluminium and copper wires.[28] In 1927 Yoshida proposed some experimental devices which facilitate the determination of the orientation of crystal axes.[29] Yoshida introduced many students to the X-ray investigation of metallurgical and various other problems. Such students are K. Tanaka, J. Tsutsumi, S. Shimadzu, G. Okuno, K. Hutino, M. Kabata, S. Nagata and others. H. Hirata, G. Shinoda, and C. Matano of Kyoto University are also known for their X-ray studies, mainly of metallographical and metallurgical problems, during the decade around 1930. I. Sakurada (1904–) of the College of Engineering, Kyoto University, once a student of Hess at the Kaiser-Wilhelm-Institut für Chemie, Berlin-Dahlem, began a series of X-ray investigations of natural and synthetic high polymers with Hutino. K. Tanaka (1904–) became the professor of physics succeeding Yoshida and the leader of the X-ray and electron diffraction group at the Kyoto College of Science. A book on X-ray crystallography written by Yoshida and Tanaka appeared in the thirties and was of great help to young students who wanted to advance in this field. E. Suito, who has for many years been engaged in electron microscopic studies of fine powder systems, has extended his study into electron diffraction at the Institute for Chemical Research attached to the University.

Now we pass on to the Ito school in Tokyo. T. Ito (1898–) finished in 1923 his student course of geology at the University of Tokyo, and went to Kyoto University for further study in petrology. After a short time he was called back to the University of Tokyo, and in 1925 went to Zurich to work with P. Niggli at the Eidgenössische Technische Hochschule. There he formed his thorough background of structural crystallography, and studied especially the topological structure analysis of the Niggli school. His paper on the diamond lattice complex in the orthorhombic system appeared in 1928.[30] The next year he visited W. L. Bragg in Manchester and learned the methods of X-ray crystal analysis. His X-ray papers, with J. West, on the crystal structure of hemimorphite [31] and of bertrandite [31] were published in 1932. When he came back to Tokyo, he became professor of mineralogy, University of Tokyo, and since then has been very active in the field of X-ray crystallography. Influenced by the study of Kôzu mentioned above, he has long been interested in problems such

as crystal structures of rock-forming minerals, especially the felspar group, mode of twinning, theoretical extension of space groups, etc. In 1950 he published a book entitled *X-ray Studies on Polymorphism* (Maruzen, Tokyo), which covers the work done in his school during the last War and was not published elsewhere. In 1949 Ito devised a new general method of lattice determination based on the Debye-Scherrer pattern. This is a development of the old idea of C. Runge (1917). In Ito's method use is made of the method of lattice reduction devised by Delaunay (1933), which Ito had noticed quite early. His students active in the X-ray analysis of minerals and organic compounds are R. Sadanaga, Y. Takéuchi, N. Morimoto, Y. Iitaka, K. Doi and others. Sadanaga succeeded Ito after his retirement. M. Nakahira, who was once with Nishikawa and then with G. W. Brindley, later became a lecturer in the Department of Mineralogy of the University. Nakahira and T. Sudo, of the Tokyo University of Education, are known for their X-ray investigations of clay minerals.

In the Osaka region, Osaka University was established in the early thirties. In the Department of Applied Physics and Precision Machinery, Faculty of Engineering, S. Tanaka, G. Shinoda, K. Kojima and S. Nagata, all from the Kyoto school, have been engaged in applications of X-ray methods to metallographic and other problems and in the instrumentation for X-ray and electron diffraction studies. In the Department of Chemistry, Faculty of Science, I. Nitta and T. Watanabé, both from the Institute of Physical and Chemical Research already mentioned, undertook the project of crystal analysis of organic compounds. In 1937 two-dimensional Fourier syntheses of electron density distribution in tetragonal pentaerythritol were carried out by them for the first time in Japan. They became interested in hydrogen-bonded structures of mainly organic crystals and also in orientational and rotational disorder in molecular crystals; the latter are related to the phase of the so-called plastic crystals of J. Timmermans (1938) and form a significant approach to the physics and chemistry of the liquid state. The X-ray and other physico-chemical studies of such problems have been made by them and their students such as R. Kiryama, S. Seki, K. Sakurai, T. Oda, I. Taguchi, K. Osaki, Y. Saito, M. Kakudo, S. Hirokawa, R. Shiono, Y. Okaya, Y. Tomiie, M. Atoji, and many others. In 1952 Okaya and Nitta published a paper containing an elementary derivation of linear inequalities for phase determination. Sakurai devised a graphical method applicable to the Harker-Kasper inequalities. Recently

Taguchi, S. Naya and Oda developed a theory of inequalities in a general manner by use of matrix theory. Y. Saito and K. Nakatsu determined absolute configurations of some complex salts. T. Matsubara of the Department of Physics made some improvements in the theory of X-ray diffuse scattering by using matrix calculations, and together with Oda applied these to some actual cases of plastic crystals. It is to be added that Ryuzo Ueda, who is now a professor of the Department of Applied Physics, Waseda University, Tokyo, was before with Nitta and Watanabé. Dating back to 1935, Y. Go, once with O. Kratky in the Kaiser-Wilhelm-Institut für Faserstoff-forschung and then with K. H. Meyer at the University of Geneva, returned to Japan and joined the staff of the Department of Chemistry of Osaka University bringing the technique of the Weissenberg goniometer. He established a laboratory of polymer science and began X-ray and electron diffraction studies of polymers with S. Nagata and J. Kakinoki. After the War the latter became a professor of physics of Osaka City University, and there he has led a group in X-ray and electron diffraction studies. Recently Kakinoki and Y. Komura developed the theoretical calculation of intensities from irregular layer lattices by use of a matrix method. The Institute of Industrial and Scientific Research attached to Osaka University was opened in 1939. There Z. Nishiyama, already mentioned as a student of Honda, carried out X-ray studies of martensite, of age-hardening of alloys and of the nickel oxide structure. He has trained Y. Shimomura, S. Nagashima and others. K. Kojima, from the Kyoto school, has been engaged in the determination of internal stress in metallic materials by means of X-ray diffraction, along with S. Karashima.

In Hiroshima University, until very recently T. Fujiwara, (1897–) as a professor of physics, Faculty of Science, was active in research and teaching of metal physics using X-ray methods. As already mentioned he is a student of U. Yoshida of Kyoto University. He is known for his studies of divergent beam X-ray photographs and for growing single metal crystals. Incidentally, T. Imura, now at the Institute of Solid State Physics, University of Tokyo, developed the study of divergent beam photographs in the Department of Metallurgy, University of Osaka Prefecture. S. Yoshida is one of the best known among the students of Fujiwara and has followed the same line as his teacher. In the same Department H. Tazaki is also known for his structure analysis of boric acid and other inorganic compounds.

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