JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-II, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. II

Application and Technique of Electron Diffraction

Some Recent Developments in Electron Diffraction Technique

GORO HONJO

Tokyo Institute of Technology, Oh-okayama, Meguro-ku
Tokyo, Japan

A summary is given of recent developments in technique of electron diffraction and electron microscopy with respect to the following points: (1) The experimental studies of the dynamical effects in electron diffraction intensity have been refined to give results which can be compared with theories quantitatively, by making use of wide wavelength range which became available by the recent progress of high tension electron source. (2) The low temperature electron microscopy has been developed to a practice as routine in operation and as high in resolution as usual electron microscopy, by improvements of low temperature specimen holder and a device against contamination. (3) Specimen holders of electron microscope which can tilt the specimen around any desired axis across the specimen plane are developed to improve the performance of electron microscope as a tool of crystallography. (4) Chemical etching has been successfully applied to the preparation of thin single crystal films of non-metallic substances for use in electron optical studies.

Preliminary results of studies, making use of the technique, concerning the domain structure of barium titanate and unknown streak in electron diffraction patterns produced from germanium, silicon and barium titanate are also described.

The last ten years have added two new lines to the application of electron diffraction. One is the crystal structure analysis based on electron diffraction intensity data[1]. The other is the electron optical studies of lattice imperfections by observing diffraction effects in electron microscopic images[2]. By these developments, the electron diffraction has become to attract more general concerns of crystallographers than ever.

The electron diffraction, however, is still limited in the range of its application and its performance. Some of the limitations arise from the inherent nature of electrons making strong interaction with matters and having short wavelength. But not few of them seem to have been due to insufficient development in technique, especially, in the instrumentation of electron microscope as a tool of crystallography.

Among other recent developments in technique of electron diffraction, the present paper is concerned only with those made in the author's laboratory or by his initiative with regard to the following four points; (1) a use of high tension electrons in studies of dynamical effects in electron diffraction intensity, (2) specimen cooling technique, (3) specimen tilting device for electron microscope and (4) preparation of thin single crystal film of non-metallic substances.

(1) A use of high tension electrons

The increase of penetrating power of electrons by the development of high tension electron source is useful for electron works in crystallography in various points. For one thing it has extended the available range of wavelength, an important parameter in electron diffraction effects.

Incidentally, Japanese electron diffractionists owe the facilities for high tension electron source to the efforts made by Japanese electron microscopists, who started on making high tension electron microscopes about ten years ago, motivated by the need of larger penetrating power of electrons in the biological field at that time before the development of the ultra-microtome technique. They have yielded two high tension electron microscopes now operating: One in Hitachi Central Laboratories using a van de Graaf generator up to 350 kV[3] and the other in the Institute for Chemical Research of Kyoto

University using a cascade type generator up to 300kV manufactured by Shimadzu Co.[4]

Previously, advantage was taken by the present author and Kitamura of the former equipment to a study of the primary extinction effect in electron diffraction intensity[5]. More recently, the same was done by them of Shimadzu high tension generator to construct a new electron diffraction camera which can operate as routine as conventional ones in a wide range of accelerating voltage from 15 to 200kV. Kitamura has applied this camera to a further study of the primary extinction effect[6] and M. Takagi and S. Morimoto to a study of the anomalous intensity of (222)-reflection of germanium[7]. Previously, studies of such intensity anomalies due to the dynamical diffraction effects used to be done by changing particle size of specimens. The wavelength, however, can be changed and determined more accurately than the particle size and the effect of its change can be examined sample by sample. This advantage, combined with some improvements of the method of photographic intensity measurement[8),9)], provided the above experiments with very reliable results, which can be compared with theories quantitatively.

Fig. 1 reproduces photometer curves obtained by Kitamura. The sample was sodium fluoride prepared by vacuum evaporation and composed of crystallites of mean crystal size about 200Å having almost perfectly random orientation. It may be noted that the back grounds of the curves are flatted by the use of a s^1-sector and that all reflection peaks are clearly separated from each other, since higher odd-order reflections are vanishingly weak for this substance. From such photometer curves, the relative intensities of reflections were determined with fairly high accuracy, within 5% for low order strong reflections.

In the previous paper[5], a method was proposed to eliminate the primary extinction effect by extrapolating observed intensities to wavelength zero, presenting an observation for aluminium film which agreed with the prediction of the dynamical theory of the two-wave approximation[10),11)]. The two-wave approximation was subjected to a criticism[12] and various theories including the many-wave interaction have been developed[13),14)]. Therefore, it is interesting to examine by such a refined experiment how the real intensity deviates from the two-wave approximation. Fig. 2 reproduces an example of Kitamura's results of such examination[6]. The observed intensities are plotted in the logarithmic scale against wavelength λ squared. The observed values for shorter wavelength fall on straight lines approaching to limiting values which coincide with the calculated

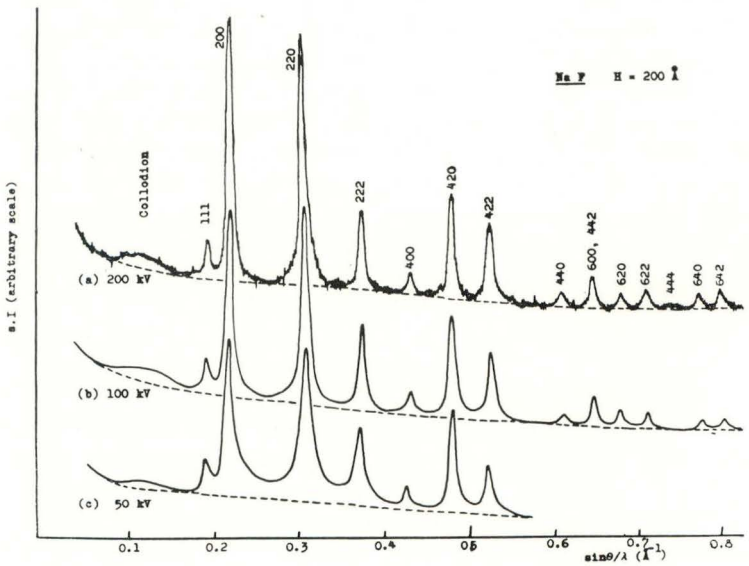

Fig. 1.

kinematical values indicated by arrows within the accuracy of the experiment. The shift of the abscissa for the limiting values from $\lambda^2=0$ to $\lambda^2=-h^2/m^2c^2$ is due to the relativistic correction pointed out by Miyake in this symposium[15]. The gradient of the linear trends, too, coincides well with those expected from the theory. The deviation from the straight lines of the observed intensity for longer wavelength can be explained very well if the decrease of the effective crystal size as a result of increasing absorption is taken into account. Thus, within the accuracy of the experiment and the reliability of the calculated intensities, the observation is in agreement with the theory of two-wave approximation and no complication which requires explicitely the many-wave theory was found.

Fig. 3 reproduces a part of the result of Takagi and Morimoto who studied the variation of the relative intensity of (222)-reflection from germanium with wavelength and crystal size[7]. Here again the data from the wide range of wavelength show a systematic result that the intensity approaches to the kinematical value, zero, with the decrease of wavelength. The observed values show a good agreement with the calculated values based on Hoerni's theory of systematic interaction[13] shown by the solid curve.

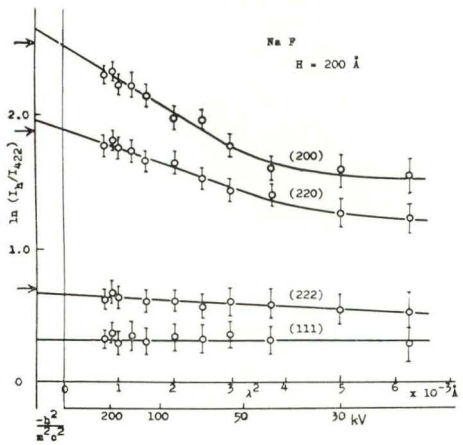

Fig. 2.

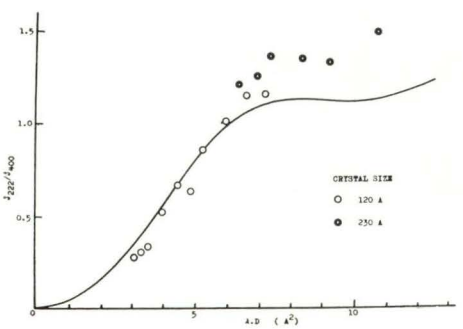

Fig. 3.

(2) **Low temperature specimen technique**

Specimen cooling, as well as specimen heating, is important for studies of various thermal effects. Specimen cooling, in addition, can extend the electron works to substances which are too volatile at ordinary temperature or too vulnerable to thermal damage due to electron irradiation. Thus, solid mercury[16], cubic ice[17] and solid hydrogen sulphide[18] have been brought into the reach of electron diffraction studies and highly crystalline order was found to exist in valonia microfibril[19]. A further study of the low temperature phase transition of solid hydrogen sulphide is reported by Kitamura and Harada in this symposium[20].

The low temperature technique for electron diffraction reported previously has been operating satisfactorily, but that for electron microscopy was not satisfactory, being laborious in operation and poor in resolution[16]. The later technique has been improved in the following points. Two types of specimen cooling devices have been developed. In one of them, due to the present author's idea[21], the whole device, refrigerant reservoir and specimen carrying part, has a symmetric construction around the optical axis and is pressed down upon usual specimen shifter during observation. In this way, thermal and mechanical fluctuations of specimen are lessened to such an extent that a pretty high resolution disclosing the lattice spacing of about 10Å (in copper phthalocyanine) becomes attainable. In the other type, developed very recently by Akabori *et al.* of Hitachi Co., the thermal contact between specimen carrying part and refrigerant reservoir is given by a bundle of thin metallic foils which do not transfer the vibration of the reservoir to specimen, and by it a resolution as good as the above one can be obtained. Specimen can be put in or taken out of the position for observation in these cooling devices at any time during their operation. This is

important not only to routine works but also to prevent specimen from contamination, because sufficient pre-cooling to absorb contaminating residual vapour can be made before specimen is inserted. This improvement preventing contamination is supplemented by a new device given by M. Watanabe and Nagahama of Japan Electron Optics Lab. Co. That is to sandwitch the specimen carrying mesh by two sheet meshes with proper spacings (1 mm, about ten times as large as the diameter of the holes in the meshes). If the holes of the three meshes are aligned by a guide, the outside meshes shield the specimen very effectively from the contamination without masking the field of observation.

By these improvements, the electron microscopy at low temperature has become a practice as routine in operation and as high in resolution as usual electron microscopy.

(3) Tiliting device for crystalline specimen of electron microscope

The performance of electron microscope in crystallography has been very much enhanced by the development of the method of selected area diffraction[22]. But the conventional electron microscopes are yet unsatisfactory from the crystallographic point of view, since their specimen can only be shifted in the plane perpendicular to the optical axis or, at best, can be tilted around a *given* axis of the device for stereo-micrographs. In the study of crystalline substance, where the three dimensional approach is essential, a device is required by which a specimen can be tilted around *any* desired axis. An ideal device to satisfy the requirement is difficult to be incorporated in electron microscopes. A device which can tilt a specimen around any desired axis across the specimen plane provides an approach to the requirement. A scheme for such a tilting device is given in Fig. 4 (a): A crystallite (or a part of a crystalline film) found in a field of an electron microscopic image is first rotated around an axis perpendicular to the plane of the specimen carrying mesh until the axis a—a′, around which the crystallite is desired to be tilted, becomes parallel to the mechanical tilting axis A—A′ of the device. Second, the specimen is shifted until the axis a—a′ coincides with the axis A—A′ and then tilted.

The first model of electron microscope with

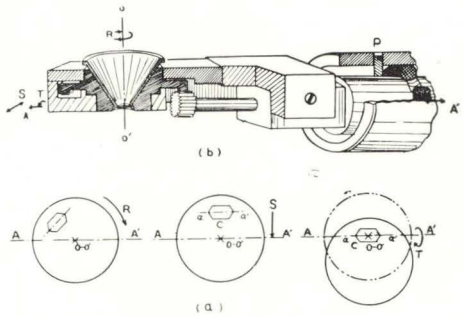

Fig. 4.

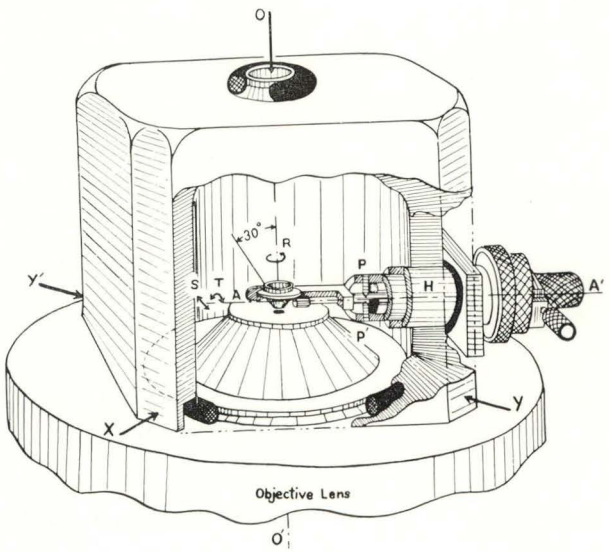

Fig. 5.

such a tilting device was realized by the present author and Kitamura using a specimen holder shown in Fig. 4 (b), which can give the above mentioned three motions to specimen and is attached rigidly to a wall of the specimen chamber movable in a plane perpendicular to the optical axis, and using a special objective lens as shown in Fig. 5. By this device, the orientation and position of a crystallite can be adjusted easily and finely, since the various modes of the specimen motions can be driven directly without mutual couplings. This microscope can resolve a moiré fringes of about 50Å.*

Recently, the above device has been modified, with the collaboration of Ashinuma and Watanabe of J. E. O. L. Co., so as to be incorporated in the conventional scheme of electron microscope, which is otherwise of satisfactory performance. The tilting over a range $\pm 30°$ by means of van de Graaf joint in the above scheme is replaced by that over a range $\pm 20°$ on a wedge (Fig. 6). The mechanism to give the specimen motions R, S and T in Fig. 4 (a) are mounted on the base B of usual specimen shifter and are driven through free joints. In the new device, an asymmetric objective lens having a very wide inner diameter, 20 mm, of upper pole piece

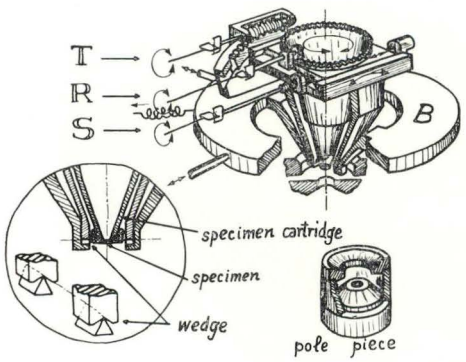

Fig. 6.

* In this model, the specimen position is about 4 mm above the top face of the objective lens pole piece. The resolution attainable by this model is limited partly on account of this high specimen position, but largely by the poor quality of the old voltage stabilizer, illuminating system etc. Even with such a high specimen position it is not impossible to get an enough resolution to observe lattice spacing of 10 Å as it has been proved by Masuda of Akashi Co.

plays an important role. This unusual objective lens devised by M. Watanabe has been proved to be able to give a very high resolution clearly disclosing the lattice spacing of about 10Å (Fig. 7). By virture of this lens, the fulcrum of the tilting is able to be set close to the specimen which is to be brought deep into the field of objective lens. The performance of the new scheme is pretty satisfactory and the additional mechanisms do not bring about serious trouble in obtaining a high resolution as above.

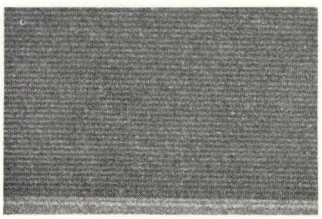

Fig. 7. An electron micrograph of copper phthalocyanine taken by the asymmetric objective lens described in the text. The lattice spacing of 9.8Å are clearly resolved.

Ono, with collaboration of Hitachi Co., is developing very recently a specimen tilting device of another scheme. It makes use of spherical contact of a radius of a few mm. Specimen is put at the centre of the sphere and tilted around the centre. The specimen is also brought into an objective pole piece similar to the above mentioned one.

(4) Preparation of thin single crystal films of non-metallic substances.

The technique to prepare thin single crystal films of metals and alloys by electro-chemical etching[23] has brought about a rapid progress of the recent electron optical studies of metals and alloys. The electron optical studies of non-metallic substances have been in an undeveloped state on account of lack of such a general method of specimen preparation for these substances. The method of usual chemical etching, however, seems to have a possibility to be developed as a general method.

The technique of chemical etching for germanium and silicon has been well developed in solid electronics. The technique has been successfully applid to the prepara-

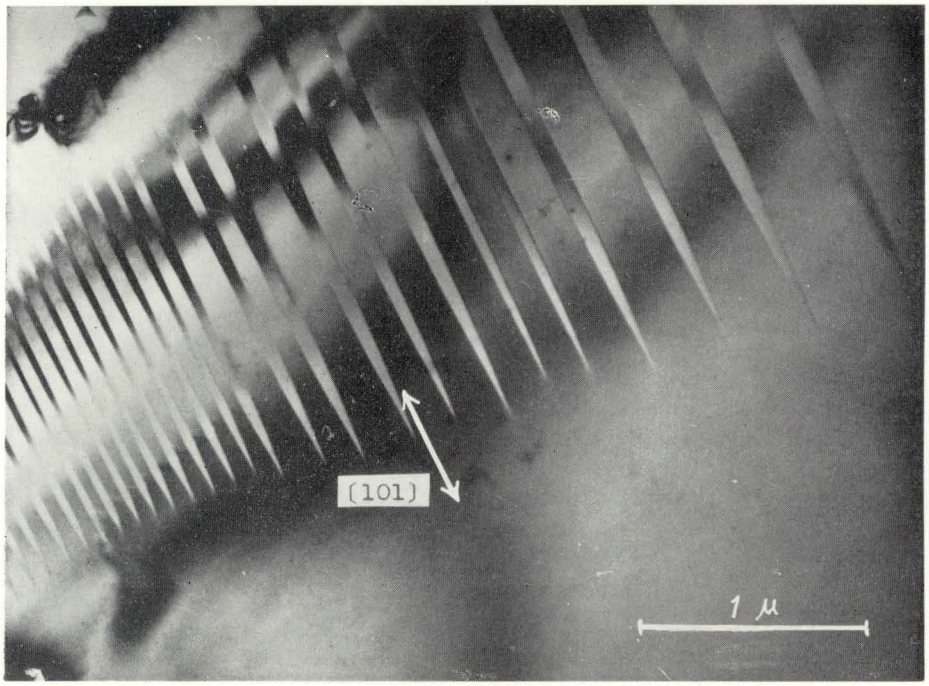

Fig. 8.

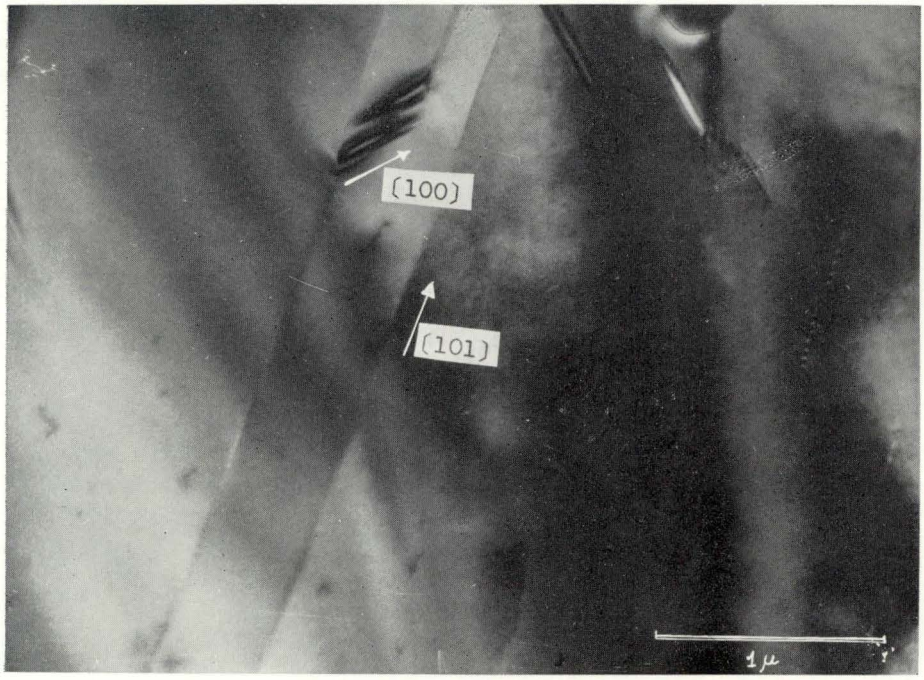

Fig. 9.

tion of thin single crystal film of these substances in a number of laboratories.[24),25)] In our laboratory the method of chemical etching has been applied further to ionic substances and Tanaka succeeded in preparing thin single crystal films of barium titanate and Kodera in preparing similar films of sodium and potasium chlorides. The etchants used are very common ones; hot phosphoric acid for barium titanate and water in alcohol for the latter two salts.

Finally, preliminary results of two new observations making use of the above technique are briefly described.

One is concerned with the domain structure of barium titanate. Fig. 8 reproduces an electron micrograph of a film of barium titanate. The domains in the micrograph have sharp boundaries along [101]-direction and they are proved to be *a*-domains with polarizations along the film plane, by inspecting splitting of reflection spots in selected area diffraction patterns and by observing the change of the contrast which occurs when the contrast-making reflection is changed: The boundaries were found to disappear when the image is formed by the reflection from the atomic plane common to the domains. For such observations the specimen tilting device mentioned above is indispensable. In another electron micrograph of a similar film (Fig. 9), small domains with striped

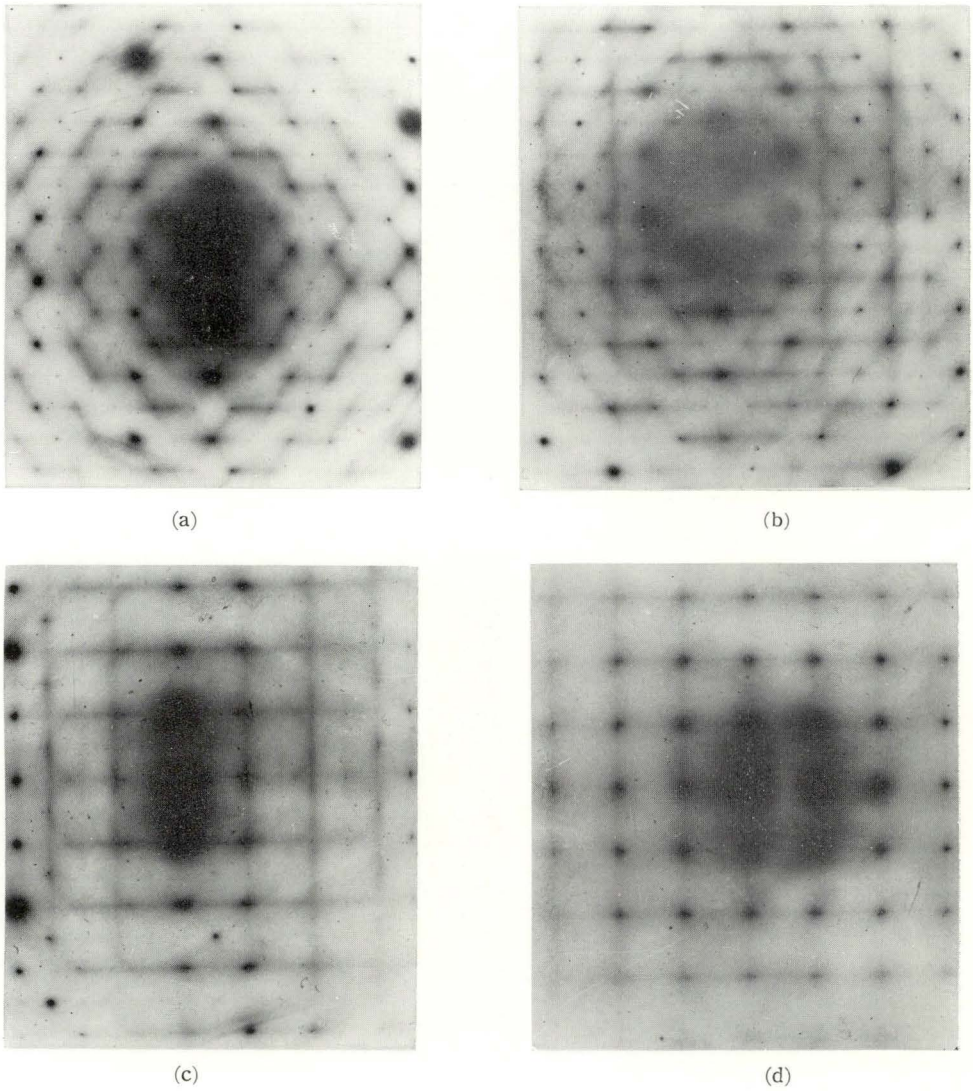

Fig. 10.

boundaries along [100]- and [010]-directions are seen beside the domains with the above mentioned sharp boundaries. The domains with striped boundaries are proved to be *c*-domain with polarization perpendicular to the film plane, the striped contrast of boundaries being the equal thickness fringes caused by the boundaries oblique to the film plane. A more interesting thing found in this micrograph is the interaction between dislocation and domain. Domain grows usually from the edge of the film or from other domain boundary. In this micrograph it is seen that two *c*-domains are growing from the ends of a dislocation.

The other observation is concerned with the anomalous streaks first found by Igaki[25] in the diffraction pattern from germanium and silicon single crystal films. He noticed a hexagonal net work of streaks binding the spots of net patterns produced by the films parallel to (111)-plane with electron incidence nearly perpendicular to the film plane. In our laboratory the same kind of streaks has been observed and studied from various angles with results suggesting that the streak is a general phenomenon, not being due to a trivial origin, such as, for example, surface topography caused by etching: Similar patterns appeared not only from film parallel to (111)- and (100)-planes but also from thin edges of broken fragments of crystal block. The streak seems to be concealed behind Kikuchi pattern when films are thick and is easier to be observed when use is made of high tension equipments. Fig. 10

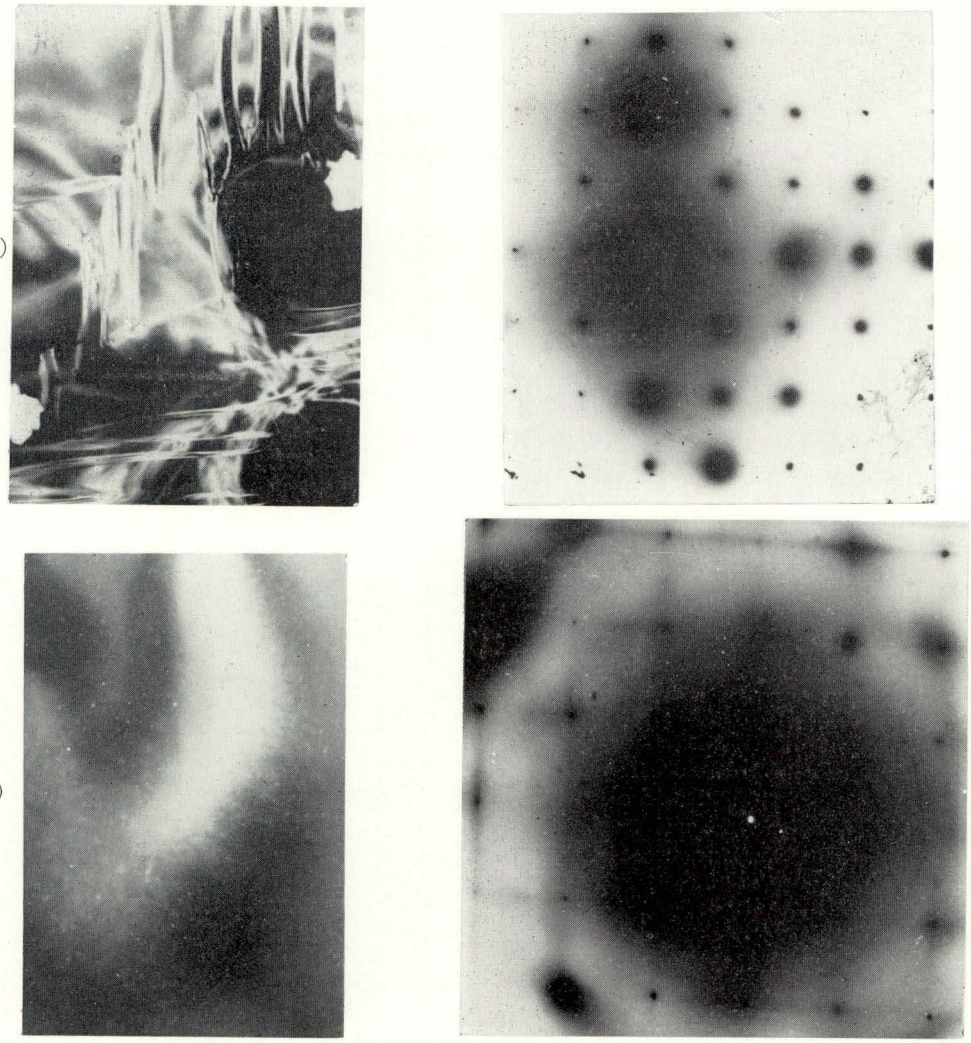

Fig. 11. Pairs of electron micrographs and diffraction patterns of barium titanate film taken at (a) room temperature and (b) 200°C.

reproduces a series of electron diffraction patterns from a germanium film taken by incidences of electrons parallel to the $(1\bar{1}0)$-plane and making angles (a) 14°, (b) −35°, (c) −49° and (d) −55° with the [111]-direction, respectively. The last incidence is parallel to [001]-direction. It may be seen that, besides hexagonal streaks appearing for the incidences near [111]-direction, there appear rectangular streaks for the incidences near [001]- direction. An important point to be noticed is that the streaks can be evidently seen in areas between Laue zones of different orders. The geometry of the streaks can be described as the intersections between Ewald sphere and hexagonal and rectangular net works of *walls*, standing perpendicularly to (111)- and (001)-net planes of reciprocal space, respectively. The intensity of the streaks varies not only from specimen to specimen but also from place to place in the same film. In connection with this fact the following observation for barium titanate film is of interest. It may be seen that streaks similar to those in Fig. 10 are strong in the diffraction pattern Fig. 11 (b) taken at a temperature above Curie point, while they do not appear in the pattern Fig. 11 (a) taken at room temperature.

Details of the studies on the domain structure in thin single crystal films of barium titanate and the streak patterns of various single crystal films will be reported elsewhere.[26),27)]

References

1 Z. G. Pinsker: *Diffractiya Electronov.* (1949) A. N. SSSR, Moscow. (Engl. ed. 1953 Butterworth Sci. Pub., London.).
B. Vainshtein: *Structurnaya Electronographiya* (1956) A. N. SSSR, Moscow.
J. M. Cowley: Acta Cryst. **6** (1953) 516, 522.

2 P. B. Hirsch, A. Howie and M. J. Whelan: Phil. Trans. Roy. Soc. London **252** (1960) 499.

3 B. Tadano, Y. Sakaki, S. Maruse and N. Morito: J. Electronmicroscopy Japan **4** (1956) 5.

4 K. Kobayashi, S. Suito, S. Shimadzu and M. Iwanaga: Electronmicroscopy Japan **7** (1959) 102.

5 G. Honjo and N. Kitamura: Acta Cryst. **10** (1957) 533.

6 N. Kitamura: J. Phys. Soc. Japan **16** (1961) 2254.

7 M. Takagi and S. Morimoto: In preparation.

8 M. Takagi: Acta Cryst. **10** (1957) 708.

9 M. Takagi, N. Kitamura and S. Morimoto: J. Phys. Soc. Japan **16** (1961) 792.

10 H. A. Bethe: Ann. Phys. **87** (1928) 55.

11 M. Blackman: Proc. Roy. Soc. **A175** (1939) 68.

12 S. Miyake: J. Phys. Soc. Japan **14** (1959) 1347.

13 J. A. Hoerni: Phys. Rev. **102** (1956) 1534.

14 J. M. Cowley and A. F. Moodie: Acta Cryst. **10** (1957) 609; **12** (1959) 353; Proc. Phys. Soc. London **71** (1958) 533.
K. Fujiwara: J. Phys. Soc. Japan **14** (1959) 1513.
F. Fujimoto: J. Phys. Soc. Japan **14** (1959) 1588.

15 S. Miyake, K. Fujiwara and K. Suzuki: In this Volume p. 124.
K. Fujiwara: J. Phys. Soc. Japan **16** (1961) 2226.
S. Miyake, K. Fujiwara, G. Honjo and N. Kitamura: J. Phys. Soc. Japan **16** (1961) 2336.

16 G. Honjo, N. Kitamura, K. Shimaoka and K. Mihama: J. Phys. Soc. Japan **11** (1956) 527.

17 G. Honjo and K. Shimaoka: Acta Cryst. **10** (1957) 710. K. Shimaoka: J. Phys. Soc. Japan. **15** (1960) 106.

18 N. Kitamura, Y. Kashiwase, J. Harada and G. Honjo: Acta Cryst. **14** (1961) 687.

19 G. Honjo and M. Watanabe: Nature (London) **181** (1958) 326.

20 N. Kitamura and J. Harada: In this Volume, p. 245.

21 M. Watanabe, I. Okazaki, G. Honjo and K. Mihama: The Report of Fourth International Conference of Electron Microscopy. Berlin, 1958.

22 H. Boersch: Ann. Phys. **27** (1936) 78..
A.C. Dorster, H. Nievwdrop and A. Verdoeff: Philps Tech. Rev. **12** (1950) 33.

23 R. D. Heidenreich: J. Appl. Phys. **20** (1949) 993. W. Bollmann: Phys. Rev. **103** (1956) 1588.

24 B. A. Irving: Brit. J. Appl. Phys. **12** (1961) 85.

25 K. Igaki: Bull. Univ. Osaka Pref. A **10** (1961) 53.

26 M. Tanaka, N. Kitamura and G. Honjo: In preparation.

27 G. Honjo, S. Kodera, E. Isobe, M. Tanaka, M. Takagi and N. Kitamura: In preparation.

DISCUSSION

A. L. Mackay: Have any semiconductor devices been tried for heating or cooling in electron microscope stages?

G. Honjo: No, we have not yet tried it.