GRAIN-BOUNDARY ENERGY AND GRAIN-BOUNDARY GROOVE ANGLES IN ICE

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Abstract. Relative grain-boundary energies in ice were measured as a function of mismatch angles made by the *c*-axes or *a*-axes in grains, using ice specimens having triple grain boundaries. It was found that the Read–Shockley equation for grain-boundary energy was valid for grain boundaries tilted between 0° and 15°. Angles of the solid–vapour grain-boundary groove in ice were measured by the use of micro-interferometry at grain-boundary grooves covered with extremely thin metalic foil. The data were compared with those measured by a silvered replica of grain-boundary grooves.

Résumé. *Energie aux limites entre grain et angle des cannelures aux limites entre grains dans la glace.* Les énergies relatives des surfaces limites entre grains dans la glace ont été mesurées en fonction des angles de mauvais raccordement faits par les axes *c* ou les axes *a* dans les grains, en utilisant des échantillons de glace présentant des lignes de limites triples. On a trouvé que l'équation de Read–Shockley sur l'énergie aux surfaces limites des grains était valable pour des limites de grains faisant un angle de moins de 15°. Les angles des canaux à l'interface solide–vapeur dans la glace furent mesurés par micro-interférométrie dans des canaux entre grains couverts d'une feuille de métal extrêmement fine. Les résultats furent comparés avec ceux obtenus par une réplique en argent des canaux aux limites des grains.

Zusammenfassung. *Korngrenzenenergie und Korngrenzen-Rillenwinkel in Eis.* Die relativen Korngrenzenenergien in Eis wurden als Funktion der von den *c*-Achsen oder *a*-Achsen der Körner gebildeten Versetzungswinkel gemessen, wobei Eisproben mit Dreifach-Korngrenzen benutzt wurden. Die Read–Shockley-Gleichung für Korngrenzenenergie erwies sich als gültig für Korngrenzenneigungen zwischen 0° und etwa 15°. Die Winkel von Korngrenzenrillen zwischen den Phasen fest und dampfförmig wurden mikrointerferometrisch an Rillen gemessen, die mit einer extrem dünnen Metallfolie überzogen waren. Die Daten wurden mit solchen verglichen, die an Silberabdrucken von Korngrenzenrillen bestimmt worden waren.

Introduction

Grain growth or grain coarsening in ice has been studied by a number of authors, Wakahama (1960), Roos (1966), Jellinek and Gouda (1969), and Suzuki (1969), but few measurements have been made of the grain-boundary energy of ice in spite of the fact that boundary energy plays an important role in these phenomena. First, this paper presents an attempt made to measure the grain-boundary energy in ice as a function of the angles formed by *c*-axes and *a*-axes in grains, giving evidence on the validity of the Read–Shockley Equation for grain boundary energy when ice grains are used. Secondly, this paper aims at proposing a new technique for the measurement of the solid–vapour grain-boundary groove angle in ice.

I. Grain-boundary energy in ice

Experimental method and preparation of triple grain boundaries

When polycrystalline ice is left alone for a long period of time at a temperature near the melting point, the interfacial tension acting in each grain boundary will pull into equilibrium with that acting in the adjoining boundaries. When ice crystals are grown from the melt, three grains almost always meet together at a point forming three boundaries in between. If interfacial tensions acting in three grain boundaries are in equilibrium at a triple junction, the following relationship should be satisfied:

$$\frac{\gamma_1}{\sin \theta_1} = \frac{\gamma_2}{\sin \theta_2} = \frac{\gamma_3}{\sin \theta_3} \qquad (1)$$

where γ_1, γ_2, γ_3 are the interfacial tensions or grain-boundary energies, and θ_1, θ_2, θ_3 the angles made by two boundaries. If one of these γ is known and three angles are measured, then the other energies can be obtained. In our experiments, for the sake of convenience, one of the triple boundaries was defined as the reference boundary and its interfacial energy was assumed as a unit.

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In order to prepare specimens of ice having triple boundaries, three blocks of seed single crystals of ice were attached on the surface of a large cylindrical brass block by freezing, as shown photographically in Figure 1 and diagramatically in Figure 2. The centre part of the brass block S can be rotated coaxially against the centre part of the block S' in such a way that their crystallographic axes could be oriented in the desired directions. The third seed crystal 3 was frozen onto S, but its relative crystallographic orientation against the seed crystals 1 and 2 was changeable by the rotation of S. The three seed crystals were dipped carefully in distilled water kept near the melting point of ice. When the brass block was
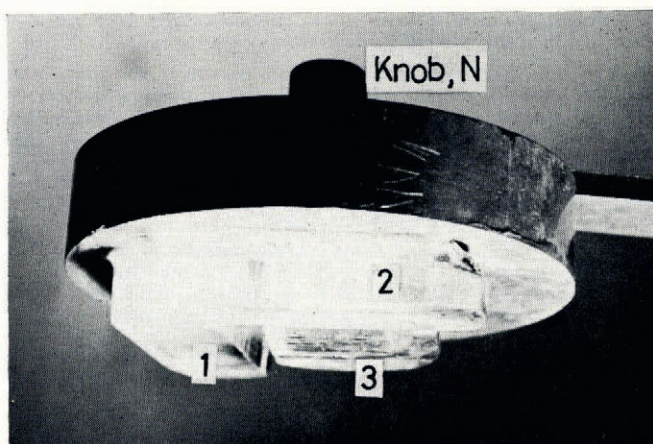

Fig. 1. Horizontal view of the crystal-growing device. Three seed crystals are attached on the surface of a brass block.

gradually cooled in a regulated cold box, the three seed crystals began to grow slowly, maintaining their original orientations. In a short time, they met at one junction, forming triple boundaries. When a block of ice having triple boundaries had grown to reach an acceptable length, it was taken out from the growing device and cut off carefully, leaving the seed crystals on the surface of the brass block. These seed crystals could be used again to develop ice blocks having triple boundaries. A thin plate (20 mm × 15 mm × 0.5 mm) was sliced from the block and placed on a clean glass slide in such a way that the line of the junction of triple boundaries was normal to the slide surface. Thus prepared, specimens were annealed in the atmosphere saturated with respect to ice at $-5°$ C for about 8 months.
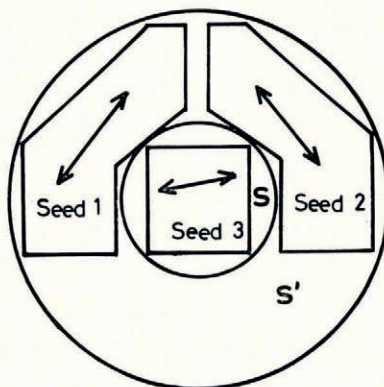

Fig. 2. Bottom view of the crystal-growing device. The seed crystal attached on S can be rotated against S'.

In our experiments, two types of specimen were prepared. In the first type, the c-axes in the three grains were distributed horizontally in the same plane as shown in Figure 3, and the boundary between grains 1 and 2 was chosen as the reference boundary. The angle ϕ_1 made by the c-axes in grains 1 and 2 was set at 50°, and the angles ϕ_2 and ϕ_3 made by the c-axes in grains 1 and 3 and in grains 2 and 3 were changed to desired values in every specimen by the rotation of grain 3. Accordingly, the ratio of the grain-boundary energy against the energy of the reference boundary, γ_2/γ_1 or γ_3/γ_1, could be measured as a function of ϕ_2 or ϕ_3.
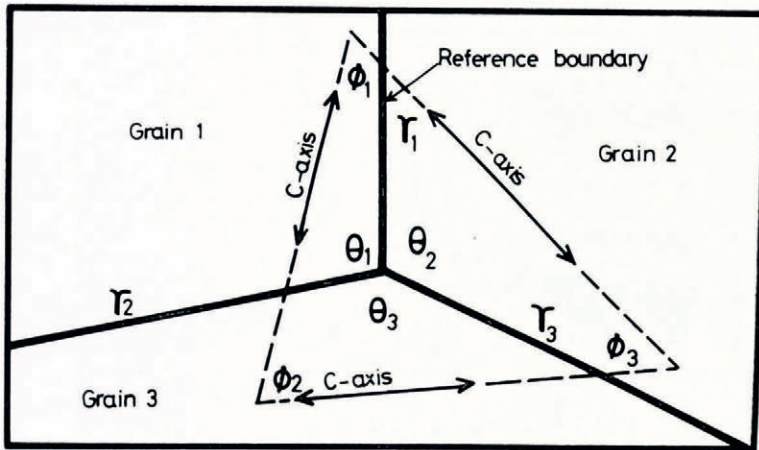

Fig. 3. *A schematic diagram of a specimen of ice having triple grain boundaries. The reference boundary is indicated.*

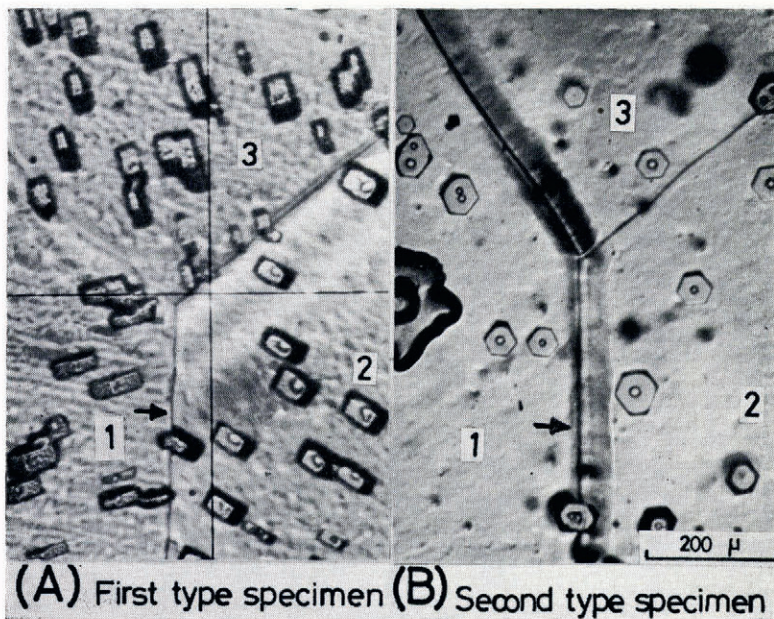**(A)** First type specimen **(B)** Second type specimen

Fig. 4. *(A) First type specimen (B) second type specimen. Thermal etch pits indicate the crystallographic orientations of each grain.*

The second type of specimen was prepared in order to measure grain-boundary energy as a function of mismatch angle made by the *a*-axes in grains. The *c*-axes in the three seed crystals were set perpendicular to the brass surface and the angle ϕ_1 made by the *a*-axes in seed crystals 1 and 2 was set in each case at 15° or 27°. The relative orientation of the *a*-axes of grain 3 against grains 1 and 2 was changed in each specimen from 0° to 30° by the rotation of grain 3.

In Figure 4, (A) and (B) show the first and second type of specimen. The reference boundary is indicated by an arrow in each photograph. Etch pits showing the crystallographic orientation of individual grains were produced by the evaporation of water molecules through a thin formvar film applied on the specimen surface (Higuchi, 1958). Note that in photograph (B), the boundary between grains 2 and 3 was less etched because of minor mismatching between the *a*-axes.

Experimental results

Figure 5 shows the relative grain-boundary energy measured as a function of mismatch angle between the *c*-axes in two grains in the first type of specimen. The ordinate indicates the ratio of the boundary energies, $R = \gamma_2/\gamma_1$ and γ_3/γ_1. As seen in this figure, the value of R scattered widely in the range of 0.7 to 1.4. When the angle made by the *c*-axes in two grains
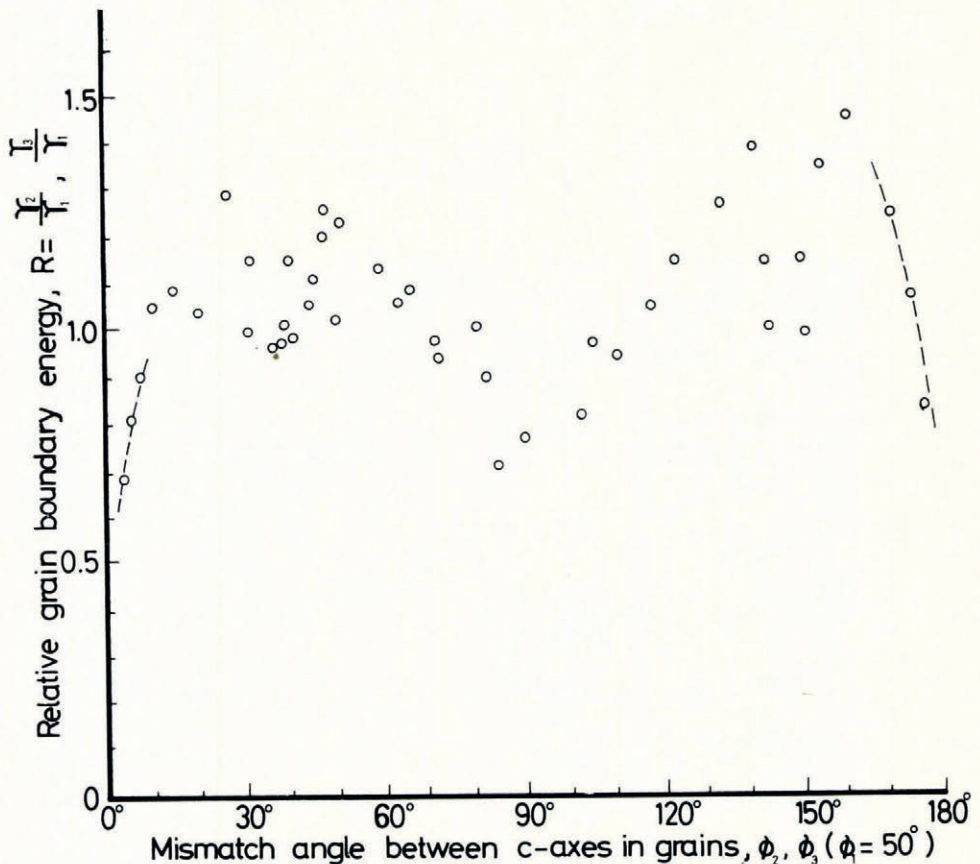

Fig. 5. *The value of relative grain-boundary energy obtained as a function of mismatch angle between the c-axes in two grains in the first type specimens.*

approached the limiting values $0°$ or $180°$, the value of R tended to decrease as shown by dotted lines.

Figures 6(A) and (B) show the value of R obtained as a function of mismatch angle between the a-axes in two adjoining grains in the second type of specimen. As seen in this figure, the grain boundary bounded by grains 1 and 2 was taken as the reference boundary, and the angle ϕ_1 made by the a-axes in the grains 1 and 2 was set at $15°$ in specimen (A) and
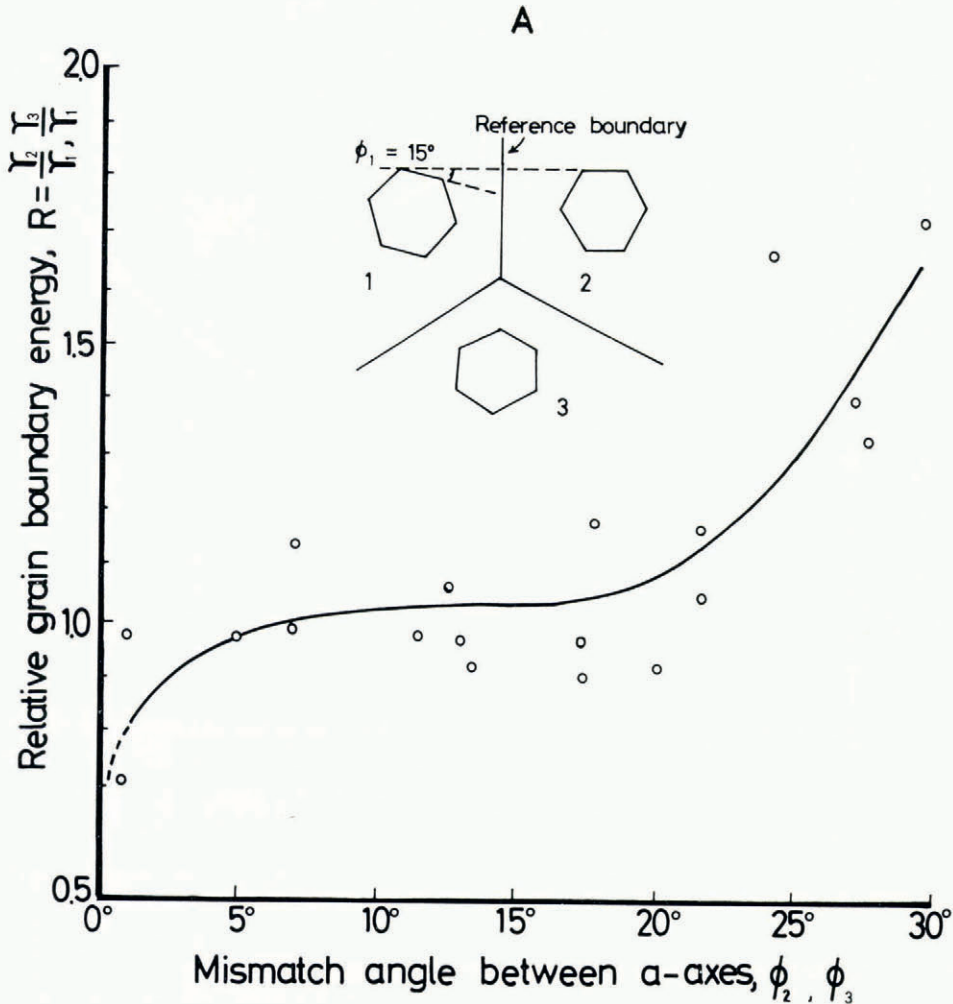
A

Fig. 6a

at $27°$ in specimen (B). In order to measure the value of $R = \gamma_2/\gamma_1$ and γ_3/γ_1 as a function of mismatch angle made by the a-axes in grains, the orientation of the a-axes in grain 3 was changed in the range between $0°$ and $30°$. The measured value of R was found to equal approximately unity in (A) and slightly less than unity in (B) for mismatch angles less than $25°$. This difference in R may be related to the difference of the energy of the reference boundary used in (A) and (B).

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Fig. 6b

Fig. 6. The relative boundary energy measured as a function of mismatch angle between the a-axes in two grains in the second type specimens.

Validity of the Read–Shockley equation for grain boundary energy in ice

According to Read and Shockley (1949), the energy E of a grain boundary which consists of an array of edge dislocations is given by

$$E = E_0\phi(A-\ln \phi) \tag{2}$$

where

$$E_0 = Gb/4\pi(1-\nu)$$

and

$$A = 4\pi(1-\nu)B/Gb^2$$

where G is the rigidity modulus, ν the Poisson's ratio, b the Burgers vector, B the core energy

of the edge dislocation, and ϕ the mismatch angle made by two crystallographic axes in adjoining grains. If ϕ is small, it is given by b/h, where h is the distance between two edge dislocations. Equation (2) suggests that if this equation is valid, there may be a linear correlation between E/ϕ and $\ln \phi$. Dividing Equation (2) by γ_1, we obtain

$$R = R_0\phi(A - \ln \phi) \qquad (3)$$
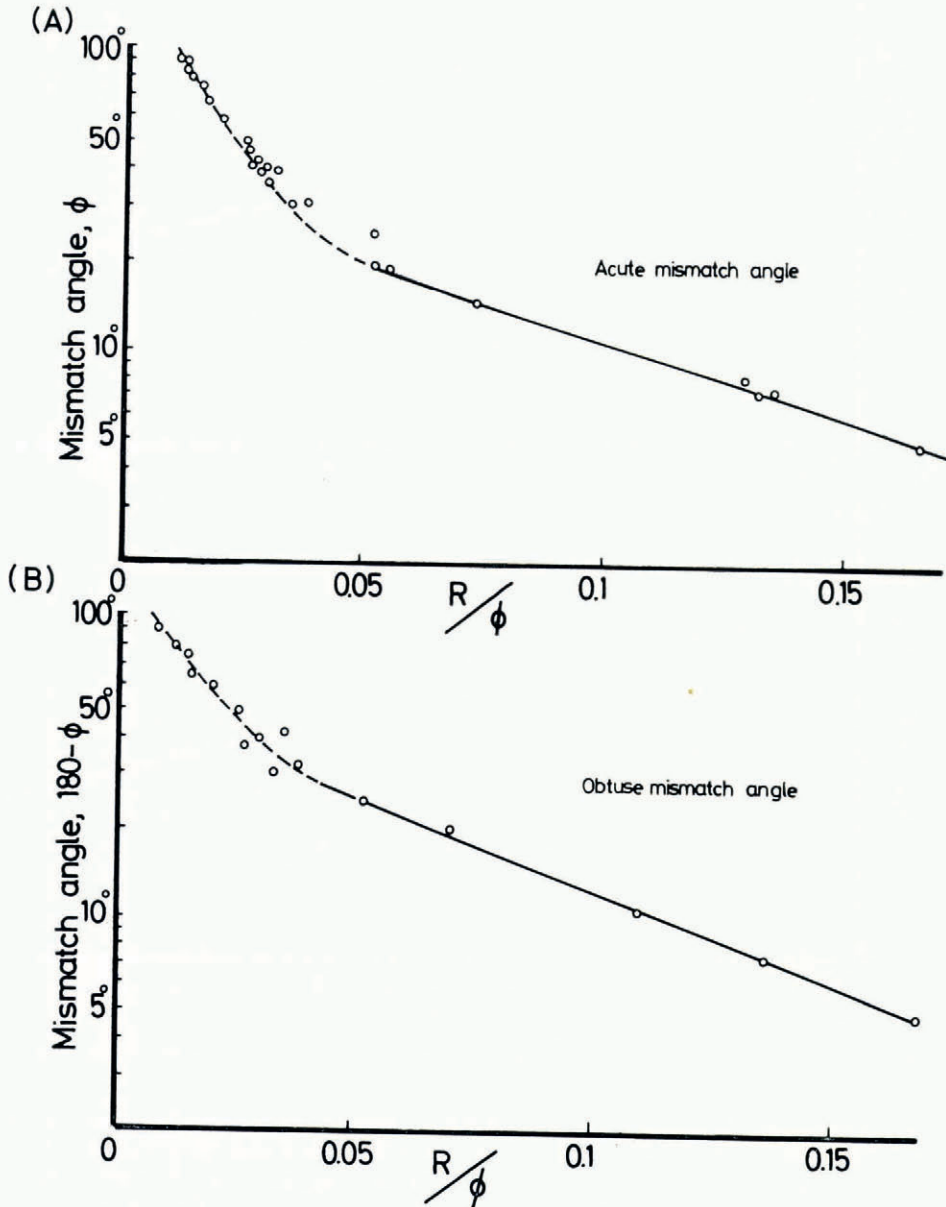
where $R = E/\gamma_1$ and $R_0 = E_0/\gamma_1$.

Fig. 7. Plots of R/ϕ versus $\ln \phi$. ϕ and $180° - \phi$ show the mismatch angle made by the c-axes in grains in the first type specimens.

To test Equation (3), plots were made of R/ϕ against $\ln \phi$ for the experimental data obtained. Figure 7 represents the relationship of R/ϕ against $\ln \phi$ for the first type of specimen. The plots of R/ϕ were made respectively against acute mismatch angles in (A) and the complementary angles of obtuse mismatch angles in (B). As seen in Figure 7(A) and (B), the linear correlation is maintained for the c-axes mismatch angles less than 20°. Figure 8
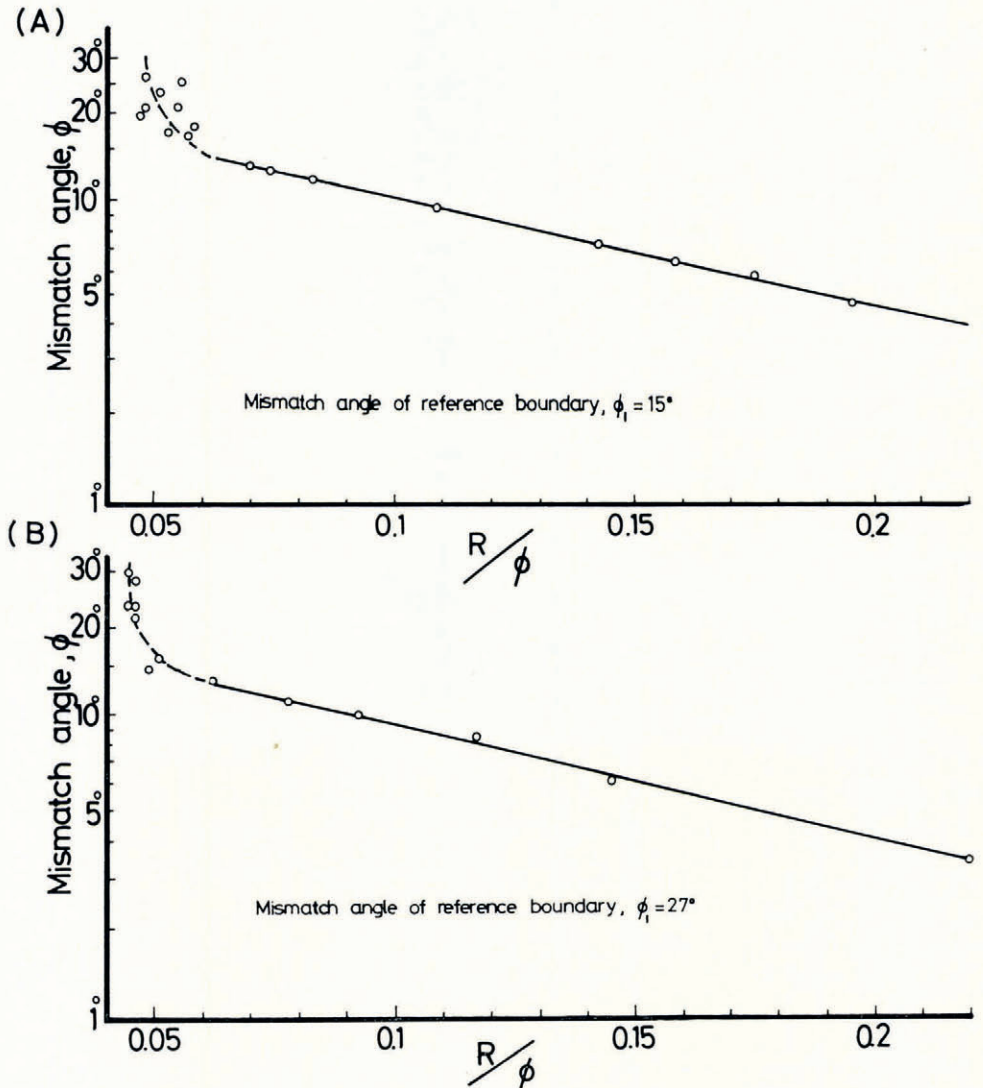

Fig. 8. Plots of R/ϕ versus $\ln \phi$ made from the data obtained in the first type specimen. (A) for $\phi_1 = 15°$, (B) for $\phi_1 = 27°$.

shows the correlation between R/ϕ and $\ln \phi$ for the second type specimens. In this figure, plots were made separately for data obtained from the specimens in which the mismatch angle at the reference boundary was set at 15° and 27°, respectively. A linear relationship was found for the a-axis mismatch angles less than 15°, suggesting that the Read–Shockley Equation may be valid for boundaries tilted within 0° to 15°.

II. Measurement of the solid–vapour grain-boundary groove angle in ice

Experimental procedure

When a polycrystalline ice surface has been exposed to the atmosphere nearly saturated with vapour for a long time, grooves are formed where the grain boundaries meet at the surface. The grooving occurs as a result of the adjustment to equilibrium of the grain-boundary energy γ_{gb} and the surface energy of ice γ_{sv}. If γ_{sv} is isotropic, and γ_{gb} is independent of the boundary orientation and the boundary is exactly normal to the surface, the following relation should be satisfied:

$$\gamma_{gb} = 2\gamma_{sv} \cos(\theta_{sv}/2) \tag{4}$$

where θ_{sv} is the solid–vapour grain-boundary groove angle formed at the root of the groove. If θ_{sv} is measured experimentally and γ_{sv} is known, the value of γ_{gb} is determined. Therefore, in this method, it is very important to make an accurate measurement of θ_{sv}. In metallurgy, the grain-boundary groove angle has been measured by the use of an interference microscope. The interferogram obtained by a monochromatic light allows the angle of the grain-boundary groove to be estimated. However, it may be difficult to have direct observations of the interferogram of a grain boundary groove in ice because of the lower reflectivity of light at the surface of ice. Ketcham and Hobbs (1969) measured the solid–vapour grain-boundary groove angles of ice by the use of the replica method. After making a formvar replica of grain-boundary grooves, they applied silvering to its replicated surface to create the high reflection of the light. According to Kuroiwa and Hamilton (1963), however, the surface of ice is etched by the ethylene dichloride, the solvent of the replica solution. Since it is desirable to measure grain-boundary groove angles of ice without any chemical modifications, we used an extremely thin metallic foil instead of the silvered replica. When a piece of thin brass foil (0.3 μm in thickness) was put carefully on the surface of ice, it adhered tightly on the relief of ice. A slight pressure was applied on the foil surface with clean silk cloth to ensure the adhesion between the foil and ice surface. Figure 9 shows a typical interferogram of a foil that covers grain-boundary grooves. If the grain boundary is not exactly normal to the surface or θ_{sv} is not isotropic, the asymmetric distribution of the interference fringes may be observed in the vicinity of the boundary groove.
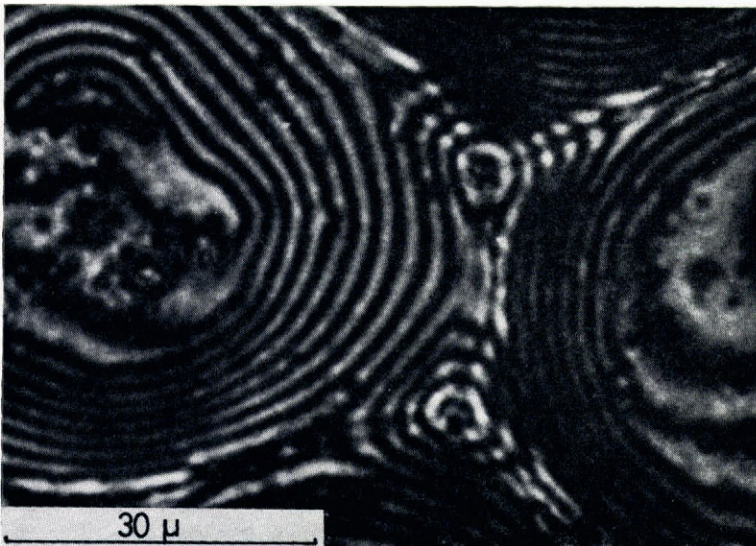

30 μ

Fig. 9. An interferogram observed near foil-covered grain-boundary grooves.

The following procedure (Hilliard and others, 1960) was employed to estimate the angle of grain-boundary grooves in ice. Figure 10(A) shows a typical profile of a foil-covered grain-boundary groove obtained from the interferogram. In this figure, plots $a, b, c, \ldots f$ and $g, h, i, \ldots m$ were made by the measurement of the distance between fringes formed on the foil surface, and the nearest fringes to the grain boundary, f and g, were taken as the origin of the coordinates (X_1, Y_1) and (X_2, Y_2) respectively. The vertical value of Y_1 or Y_2 at X_1 or X_2
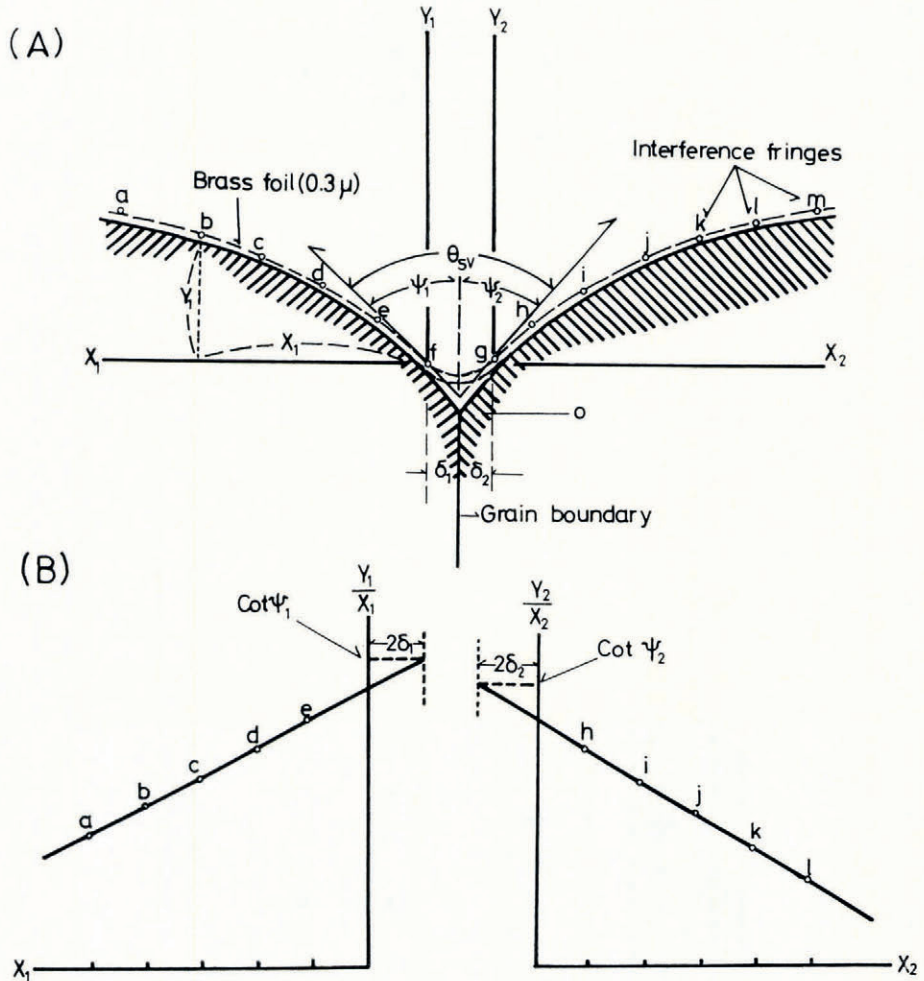

Fig. 10. (A) Profile of a foil-covered grain-boundary groove obtained from interference fringes. (B) Derived plots of Y/X versus X.

was calculated from the number of fringes and the wavelength of the monochromatic light. If we extrapolate the profiles which link $a, b, c, \ldots f$ and $m, l, n, \ldots g$, they will meet at the point o. If ψ_1 and ψ_2 are the angles which the side walls of the groove make with the vertical at the root of the boundary, the angle of groove θ_{sv} is given by

$$\theta_{sv} = \psi_1 + \psi_2. \tag{5}$$

Since the graphic determination of ψ_1 and ψ_2 may include experimental errors due to extrapolation of the profiles, the following procedure was used to estimate ψ_1 and ψ_2.

According to Mullins' theory (1957), the profile of a grain-boundary groove can be expressed by the parabolic formula

$$Y = aX^2 - bX + c, \tag{6}$$

where Y and X are coordinates respectively normal to and parallel to the specimen surface, and a, b, c are constants. Using this equation, if we denote the lateral distance between the origin and the root of the groove as δ_1, the angle ψ_1 will be given by

$$\cot \psi_1 = \{dY_1/dX_1\}_{X_1 = -\delta_1} = a + 2b\delta_1 = \{Y_1/X_1\}_{X_1 = -2\delta_1}, \tag{7}$$

where $c = 0$.

Therefore, if we plot the value of Y_1/X_1 against X_1 measured from the origin, a linear correlation should be found between them. Thus $\cot \psi_1$, and similarly $\cot \psi_2$, can be determined by the construction shown in Figure 10(B).
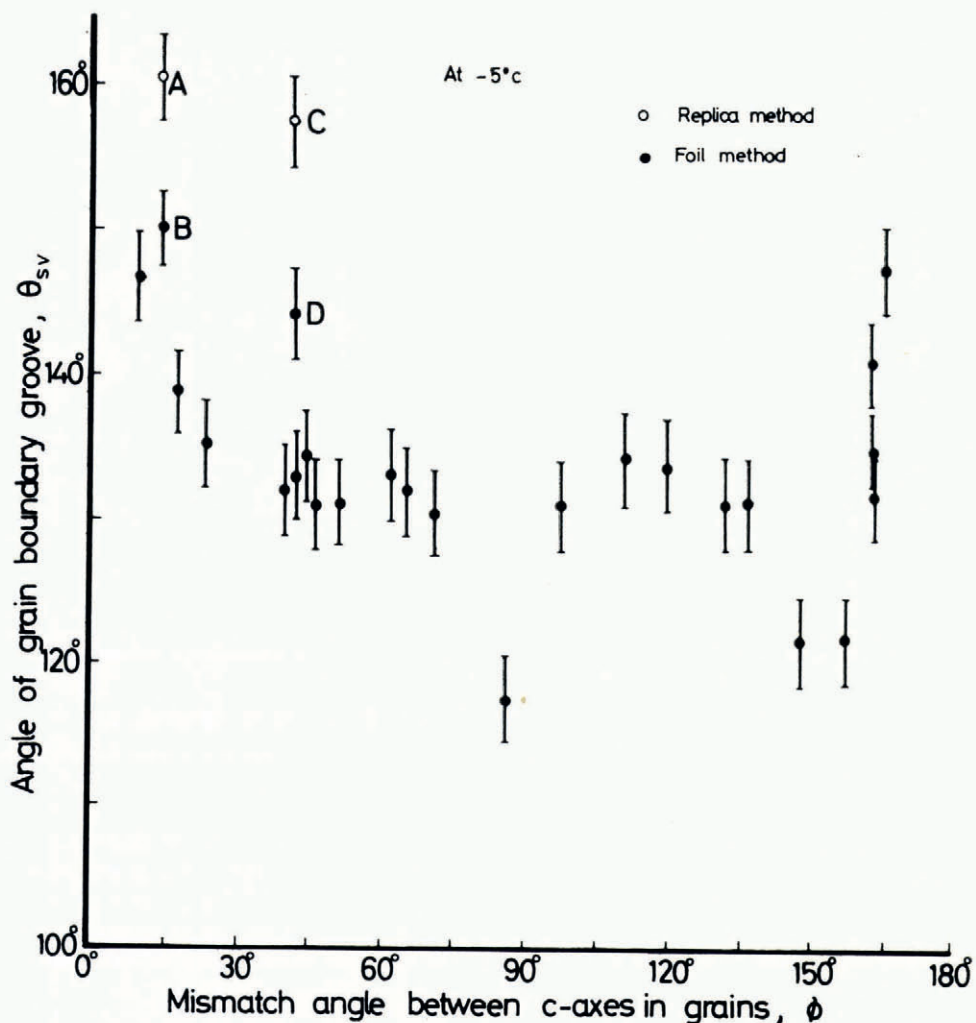

Fig. 11. *Solid–vapour grain-boundary groove angles obtained by both replica (open circle) and foil (solid circle) methods.*

Experimental results

Figure 11 shows a typical result of the solid–vapour grain-boundary groove angle θ_{sv} measured by our foil method. The specimens used in this experiment were prepared at $-5°$ C. The abscissa indicates mismatch angles ϕ made by the *c*-axes in two grains. The accuracy for measuring θ_{sv} was within $5°$ in our method. As seen in this figure, the value of θ_{sv} at first decreased with increasing ϕ and then remained approximately constant in the range between $\phi = 30°$ to $130°$, and then increased again with ϕ.
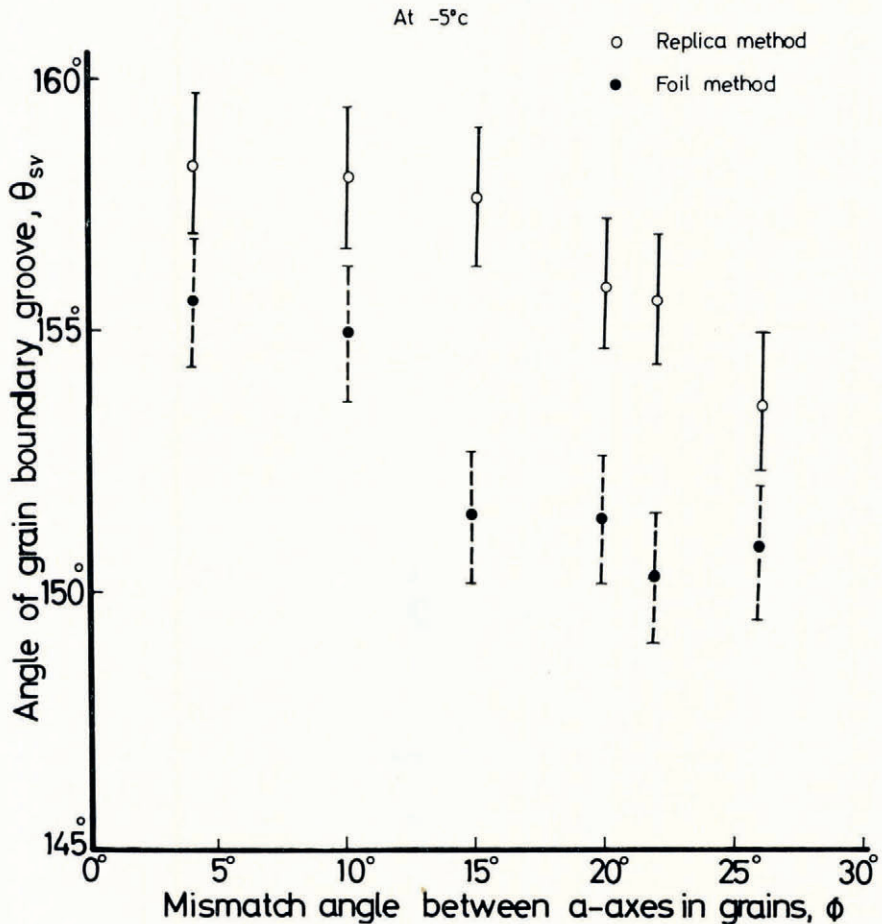

Fig. 12. *Angle of grain-boundary grooves formed on a basal surface. The open and solid circles show data obtained by replica and foil methods respectively.*

It is interesting to compare the value of θ_{sv} measured by our foil method with those measured by the replica method. In order to do this, a half length of a grain-boundary groove was covered with the thin metalic foil and the other half of it was covered with 3% replica solution. After desiccation of the solution, the replica film (approximately 0.1 mm in thickness) was peeled off and the silvering was applied on the replicated surface. In Figure 11, A and B, and also C and D, indicate the value of θ_{sv} measured by the replica and foil method at the same grain boundaries. Apparently, the values of θ_{sv} obtained by the replica method were found to be larger than those measured by the foil method.

Figure 12 shows the experimental values of the angle of grain-boundary grooves formed on basal surfaces of ice. In these specimens, since the c-axes in grains were parallel to each other, ϕ indicated the mismatch angle made by a-axes in two adjoining grains. The solid and open circles represent the values of θ_{sv} measured by the foil and replica methods at the same boundary grooves respectively. It was also found that all data for θ_{sv} obtained by the replica method were larger than those measured by the foil method.

CONCLUDING REMARKS

The relative values of grain-boundary energy in ice were measured as a function of mismatch angles made by the c-axes or a-axes in two neighbouring grains. The relative value of the grain-boundary energy was defined by the ratio of a given boundary energy to a reference boundary energy. The results are shown in Figures 5 and 6. The values of angle shown in the abscissa in Figure 5 indicated only the mismatch angle of the c-axes in two adjoining grains, because, in the first type specimens, it was very difficult to determine the relative orientation of the a-axes in grains owing to the small thickness of the specimen used. Figure 6(A) and (B) shows the value of boundary energy measured at triple boundaries formed on the basal surface as a function of the mismatch angle between the a-axes in grains. In these figures, the angle shown in the abscissa can be considered to be a true mismatch parameter, since the c-axis in each of the individual grains was previously oriented parallel to each other. Figures 7 and 8 indicate that the Read–Shockley equation for grain boundary energy may be valid for grain boundaries tilted within $0°$ and $15°$.

Covering of grain boundary grooves with thin metallic foil allowed interferometry to be applied for the measurement of the angle of grain-boundary grooves in ice θ_{sv}. In our experiments, the value of θ_{sv} obtained by this method was $130°$ to $135°$ for c-axis mismatch angles of $15°$ to $160°$, showing a good agreement with the value of θ_{sv} of unclean grain boundary grooves obtained by Ketcham and Hobbs (1969). The value of θ_{sv} of grain boundaries formed at the basal surface varied with the mismatch angle between the a-axes in grains as shown in Figure 12.

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