EXPERIMENTAL STUDY OF NON-BASAL DISLOCATIONS IN ICE CRYSTALS

By L. Levi, E. M. de Achaval *and* E. Suraski

(Instituto de Física de la Atmósfera, Departamento de Meteorología, Facultad de Ciencias Exactas y Naturales, Buenos Aires, Argentina)

Abstract. Structures produced by chemical etching on the basal plane of ice crystals have been studied and are discussed in terms of non-basal glide features. Slip bands, revealed by parallel rows of etch pits, generally result from a rapidly applied stress. Etch channels were observed relatively rarely in these experiments; they can be interpreted as trails of dislocations moving slowly under the action of local stresses, sometimes to stresses produced during the etching process. Features of the channels indicate that the dislocations emerging on the basal plane are screw dislocations; their Burgers vector was considered by previous authors to be in the direction $\langle 11\bar{2}3\rangle$, gliding on $\{11\bar{2}2\}$ and $\{10\bar{1}0\}$ slip planes. This assumption is inconsistent with the changes of channel direction we observed, for which the $\{01\bar{1}1\}$ and $\{2\bar{4}21\}$ slip planes would have to be considered. As a simpler hypothesis the glide system $\langle 0001\rangle$, $\{10\bar{1}0\}$ and $\langle 0001\rangle$, $\{11\bar{2}0\}$ is proposed.

Résumé. *Étude des dislocations non basales de cristaux de glace.* On étudie les figures produites par corrosion chimique dans le plan basal des cristaux de glace et, en relation avec les résultats obtenus, on discute l'existence de plans de glissement prismatiques ou pyramidales.

On observe que des alignements parallèles de figures de corrosion pyramidales, indiquant des bandes de glissement, sont obtenus généralement par une déformation rapide. Dans les conditions présentes on a obtenu rarement des canaux de corrosion. Ils apparaient seulement dans des régions limitées, probablement sous l'action de tensions locales, et ils peuvent s'interprèter comme les traces de dislocations glissant lentement, quelques fois simultanément avec le processus de corrosion.

Les caractéristiques des canaux indiquent que les dislocations, émergeant dans le plan basal, sont des dislocations vis; le vecteur de Burgers a été considéré par de précédents auteurs, du type $\langle 11\bar{2}3\rangle$, avec les plans de glissement $\{11\bar{2}2\}$ et $\{10\bar{1}0\}$.

Nous montrons que cette supposition n'explique pas les changements de direction observés dans les canaux et qu'on devrait complèter le système en considérant aussi les plans $\{01\bar{1}1\}$ et $\{2\bar{4}21\}$. Comme une hypothèse plus simple nous proposons le système de glissement $\langle 0001\rangle$, $\{10\bar{1}0\}$ et $\langle 0001\rangle$, $\{11\bar{2}0\}$.

Zusammenfassung. *Untersuchung nicht-basaler Versetzungen in Eiskristallen.* Die Arbeit gilt der Untersuchung der chemischen Ätzung an der Basalfläche von Eiskristallen und der Diskussion nicht-basaler Gleiterscheinungen.

Die Ergebnisse lassen daraufschliessen, dass Gleitbänder, kenntlich durch parallele Reihen von Ätznarben, im allgemeinen durch eine schnell einwirkende Spannung hervorgerufen werden. Ätzkanäle sind unter den herrschenden Bedingungen selten zu beobachten; sie können als Spuren von Versetzungen gedeutet werden, die langsam unter der Wirkung örtlicher Spannungen, eventuell hervorgerufen während des Ätzvorganges, vor sich gehen.

Das Aussehen der Kanäle deutet darauf hin, dass die Versetzungen, die von der Basalfläche ausgehen, Schraubencharakter haben; ihr Burgers-Vektor wurde von früheren Autoren dem Typ $\langle 11\bar{2}3\rangle$ zugeschrieben, mit Gleiten auf $\{11\bar{2}2\}$- und $\{10\bar{1}0\}$-Gleitflächen. Wir bemerken, dass diese Annahme nicht die beobachteten Wechsel in der Kanalrichtung erklären könnte und dass $\{01\bar{1}1\}$- und $\{2\bar{4}21\}$-Gleitflächen ebenfalls in Betracht gezogen werden sollten. Als einfachere Hypothese wird das Gleitsystem $\langle 0001\rangle$, $\{10\bar{1}0\}$ und $\langle 0001\rangle$, $\{11\bar{2}0\}$ vorgeschlagen.

Introduction

Recent results indicate that ethylene dichloride is a good etchant for ice crystal surfaces. Three types of etch pits revealing the emergence of dislocations have been observed on different planes. They are hexagonal pyramids on the basal plane, pits elongated in the direction of the *c*-axis on planes containing this direction, and trigonal pyramids on some intermediate planes (Kuroiwa and Hamilton, 1963; Achaval and others, 1964; Bryant and Mason, 1960; Muguruma, 1961, 1963). On the basal plane etch channels, generally in $\langle 10\bar{1}0\rangle$ or $\langle 11\bar{2}0\rangle$ directions have also been observed (Kuroiwa and Hamilton, 1963; Muguruma and Higashi, 1963[b]). They were specifically studied by Muguruma and Higashi (1963[b]) in crystals deformed plastically by bending and by shearing, and they were interpreted as traces of dislocations gliding in slip planes perpendicular or nearly perpendicular to the basal plane. They were considered as proof of the existence of non-basal slip in ice crystals, which it had not been possible to demonstrate by direct study of their plastic deformation (Muguruma and

https://doi.org/10.3189/S0022143000018682 Published online by Cambridge University Press

Higashi, 1963[a], [b]). The formation of etch-pit rows in the same crystallographic directions was considered by these authors as a more unusual feature, only observed in localized regions of their crystals. In the only example they give, various etch-pit patterns are formed in different directions in the same small area; they were interpreted as slip bands in $\langle 10\bar{1}0 \rangle$ directions and as the result of cross-glide multiplication in $\langle 11\bar{2}0 \rangle$ directions.

The present investigation was carried out almost simultaneously with most recent of these other investigations. It provides some complementary information which leads to further discussion of the previous conclusions.

Experimental Procedure

The samples were grown in "Pyrex" glass tubes about 3·5 cm. in diameter, their axis being parallel to the temperature gradient. Distilled water of about 10^{-6} ohm^{-1} cm.$^{-1}$ was used. The resulting specimens were usually single crystals, though sometimes two or three crystals, and varied in length from 3 to 6 cm. The orientation of the crystals was determined using the method of Higuchi (1958). The *c*-axis and, usually, one of the *a*-axes were found to lie in a plane perpendicular to the temperature gradient.

A smooth surface nearly parallel to the basal plane was prepared on the ice rod and the thermal etching process was repeated. The resulting surface then had a 2 per cent solution of formvar in ethylene dichloride applied to it, and the resulting chemical etching inside the large thermal etch pits was studied using the replica films by optical microscopy.

Some samples were plastically deformed in compression using a small press adjusted manually. The compression was generally applied for a few seconds; the strain was measured under the microscope.

The samples were stored and handled at about $-15°$C. in a cold chamber of average relative humidity about 50 per cent.

Results

Etch-pit patterns

Typical etch pits with hexagonal symmetry were observed on the basal plane. When the crystals had been plastically deformed, slip bands generally appeared, marked by sets of parallel rows of pits almost homogeneously distributed over large regions of the crystals (Achaval and others, 1964) as shown in Figure 1. The direction of the stress, marked by the arrow, was nearly parallel to the axis of the rod. The slip bands are formed in a $\langle 10\bar{1}0 \rangle$ direction making an angle of about 60 degrees with the stress axis. The strain was about 3 per cent. The pit rows in Figure 2 run in a $\langle 11\bar{2}0 \rangle$ direction, which in this case is nearly perpendicular to the applied stress. The strain was 1 per cent. In this case the etch features were formed inside a large thermal pit whose surfaces formed various different angles with the basal plane. An inclined section of rows of dislocations can be seen on a surface forming an angle of less than 60 degrees with the corresponding slip planes; the elongated etch pits are parallel to the projection of the *c*-axis on this surface.

Ordered patterns of etch pits were also frequently observed in our crystals without the application of an external stress, but in this case the rows were approximately parallel to the direction of growth (Fig. 3). Figures 3 and 1 were obtained on the same crystal respectively before and after straining; the results are similar but the direction of the rows of etch pits has been changed by 60 degrees after straining. These results indicate that the stresses produced during crystal growth may be enough to originate non-basal glide. If we suppose these stresses to be related to the different expansion coefficients of ice and glass, and if we consider a temperature variation during the process between 0° and $-20°$C., a maximum radial strain of 0·1 per cent can be deduced.

The density of dislocations has been determined in various samples and an average value of 2×10^6 cm.$^{-2}$ was found without any difference between stressed and unstressed samples. The distance between etch pit rows was about 20μ.

Etch channels

Kuroiwa and Hamilton (1963) observed the formation of etch channels in crystals etched and stressed at the same time. They considered them to be the result of direct etching on moving dislocations. In some cases the channels had a tapering shape, which they related to a

Fig. 1. Rows of etch pits in a stressed crystal. Stress axis in direction of arrow ($\times 200$)

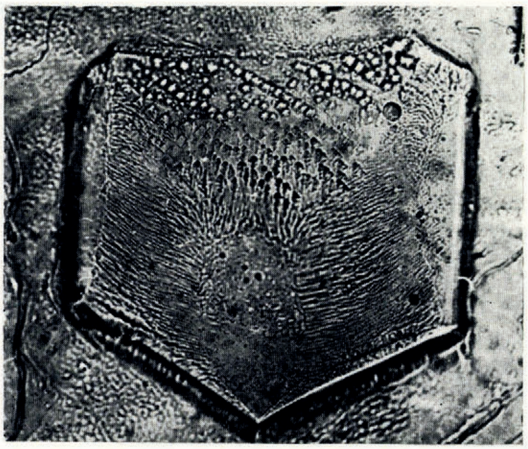

Fig. 2. Inclined section of rows of etch pits in a stressed crystal ($\times 150$)

reduction in dislocation velocity. Muguruma and Higashi (1963[b]) obtained a high channel density in their crystals, which were slowly deformed by bending and by shearing—a shear stress of 2 kg.cm.$^{-2}$ applied for 24 hr. at -5°C. produced a 3 per cent deformation and a channel density of 10^5 cm.$^{-2}$. Their crystals were thermally etched by Higuchi's technique and chemically etched about 24 hr. after the stress had been removed. They interpreted the channels as being due to trails of defects left behind by moving dislocations, which etched easily because of the consequent impurity segregation. They observed that channels were generally formed of branches in $\langle 10\bar{1}0\rangle$ and $\langle 11\bar{2}0\rangle$ directions, the former being thinner and longer, the latter generally short and of tapering shape.

In our case channels were seldom observed, but a relatively high channel density was revealed in a region of one sample formed near the bottom of the glass tube. This sample had not been stressed externally. Various examples are shown in Figures 4 to 8, where some

Fig. 3. Rows of etch pits formed without external stressing. Growth direction shown by arrow ($\times$ *120*)

differences from Muguruma and Higashi's results can be seen. Tapering channels predominate in Figure 4, and run in both $\langle 10\bar{1}0\rangle$ and $\langle 11\bar{2}0\rangle$ directions. They are formed near the edge of a large thermal pit and approximately follow the slope of the surface, their thinner end pointing down-slope. Figure 5 shows several non-tapering channels in a $\langle 11\bar{2}0\rangle$ direction; they join together two groups of hexagonal pits one of which is of high density. Figure 6 shows channels forming more complex patterns; they seem to be deflected in the vicinity of an etch pit or of another channel. In Figure 7 two channels seem to begin simultaneously at the left of the photograph, they turn around an hexagonal pit in nearly parallel paths and then separate into different directions. One of them comes across another pair of pits and turns again in order to pass along the narrow space between them. In Figure 8 channels in $\langle 11\bar{2}0\rangle$ directions predominate, radiating from a centre of high dislocation density. They are relatively wide but not strongly tapering. They generally end in small hexagonal pits. We have observed similar channels in some polycrystalline samples, both stressed and unstressed.

These results show that no rigid distinction between $\langle 11\bar{2}0\rangle$ tapering channels and $\langle 10\bar{1}0\rangle$ non-tapering channels can be established; instead a relationship evidently exists between both types of channels and between the channels and hexagonal etch pits, indicating a common origin for these phenomena.

Discussion

From the experimental evidence now available it is possible to relate some of the various features produced by etching on the basal plane to the different experimental conditions. Crystals strained by a rapidly applied external stress usually show etch pits arranged in parallel rows, the direction of which is clearly related to the stress axis. On the other hand previous work had shown that etch channels predominate in ice crystals slowly deformed by a stress applied for a period of several hours, and these channels show a complicated pattern which cannot be easily related to the direction of the applied stress. In our experiments

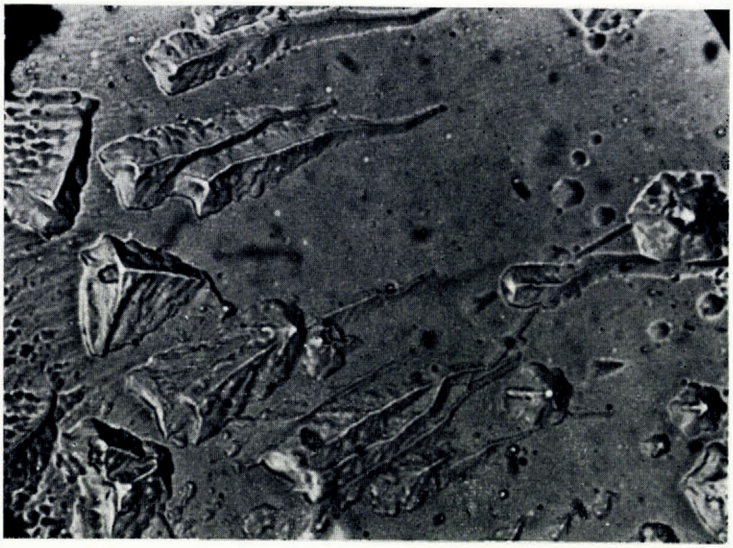

Fig. 4. Tapering etch channels in $\langle 11\bar{2}0\rangle$ and $\langle 10\bar{1}0\rangle$ directions ($\times 1{,}000$)

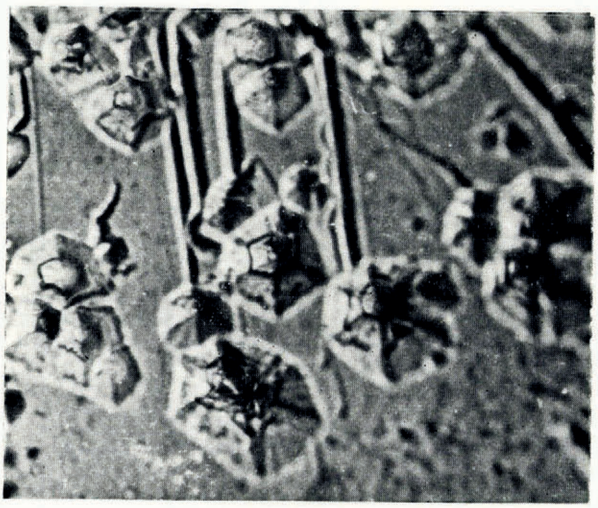

Fig. 5. Non-tapering channels in $\langle 11\bar{2}0\rangle$ direction ($\times 1{,}000$)

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Fig. 6. Channels deflected in the vicinity of etch pits ($\times 500$)

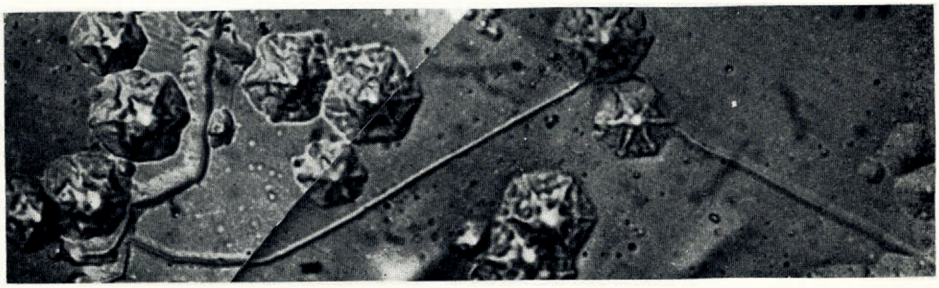

Fig. 7. Channels deflected in the vicinity of etch pits ($\times 1{,}000$)

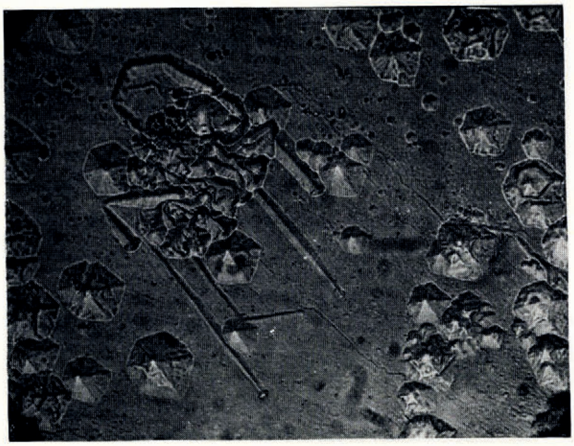

Fig. 8. Channels radiating from a centre of deformation ($\times 500$)

https://doi.org/10.3189/S0022143000018682 Published online by Cambridge University Press

channels were mainly obtained in regions where no common direction prevails either for etch channels or for rows of etch pits. Consequently local stresses are probably an important factor in the straining of these regions.

Surface conditions seem to have some influence on the channels; in Figure 4 their direction is related to the slope of the ice surface, while in Figures 6 and 7 the deflection of channels has probably been determined by the surface modifications around the chemical etch pits and not by direct interaction between dislocations, for the minimum distance from the channel to the centre of the pit is usually several microns. This behaviour indicates that the dislocations giving rise to the channels have moved during the development of chemical etching, and so it may be inferred that channels are easily etched simultaneously with, or immediately after, the movement of their dislocations. This result is in accordance with the observations of Kuroiwa and Hamilton (1963), whose channels were etched at the same time as the stress was being applied. Thus the channel distribution in the experiments of Muguruma and Higashi (1963[b]) could also be interpreted as revealing slow dislocation movement taking place after the removal of the stress up to the time of the thermal or chemical etching.

However, the possibility cannot be excluded that the channels may be etched some time after the glide of the dislocations, and here some analogy probably exists between these channels in ice and the trails previously observed in silicon by Dash (1958) and in zinc and cadmium by Price (1960). These trails have been interpreted as lines of defects left behind by the non-conservative motion of jogs formed in gliding screw dislocations. Considering the similarity in structure between ice, zinc and cadmium (all three being hexagonal in the D^4_{6H} group), Muguruma and Higashi (1963[b]) suppose that the same type of screw dislocations considered by Price, with Burgers vector $\frac{1}{3}\langle 11\bar{2}3\rangle$, would be responsible for the features observed in ice, for which they assume the glide systems $\langle 11\bar{2}3\rangle\{11\bar{2}2\}$ and $\langle 11\bar{2}3\rangle\{10\bar{1}0\}$. They also attempt to use this to explain the tapering shape of their $\langle 11\bar{2}0\rangle$ channels; they consider that a $\langle 11\bar{2}3\rangle$ dislocation gliding in a $\{10\bar{1}0\}$ plane would leave behind a trail along a $\langle 11\bar{2}2\rangle$ direction, which is inclined to basal plane. This trail would emerge progressively at the surface during the evaporation process preceding the chemical etching, and so the etch would be deeper at the place where it first emerged.

From our experiments we must conclude that if $\langle 11\bar{2}3\rangle$ dislocations are responsible for the patterns formed by the channels in ice, it is necessary to have a more complex system of slip planes. As can be seen in Figures 4 to 8, different branches of a channel generally form angles of 30° (or 150°), 60° (or 120°) or, in a few cases, 90° with each other. The corresponding slip planes for a dislocation originally gliding in the $(11\bar{2}2)$ plane are shown in Figure 9. In Figure 9a the deflected channel is along $[\bar{2}110]$ and the corresponding slip plane is $(01\bar{1}1)$; in Figure 9b the deflected channel is along $[10\bar{1}0]$ and the slip plane is $(2\bar{4}21)$, while in Figure 9c they are respectively $[11\bar{2}0]$ and $(1\bar{1}00)$. All trails apart from the initial one would be inclined to the basal plane with increasing slope from Figure 9a to Figure 9c. Only the last case belongs completely to the glide systems proposed by Muguruma and Higashi, so according to these authors' hypothesis only channels branching at right angles should be observed, the $\langle 11\bar{2}0\rangle$ branches being tapering. However, their own photographs only show channels branching at 30° (or 150°) and 60° (or 120°). In our experiments two cases of channels forming perpendicular branches were observed, marked A and B in Figure 6. None of these branches was tapering. We conclude that if non-basal glide in ice crystals is due to the movement of $\langle 11\bar{2}3\rangle$ dislocations, the glide systems proposed by Muguruma and Higashi should be supplemented by the other slip planes shown in Figure 9. The channels more developed in length being mainly formed by branches in $\langle 10\bar{1}0\rangle$ directions at 60° (or 120°) to each other, both $\{11\bar{2}2\}$ and $\{2\bar{4}21\}$ should be considered as principal slip planes.

On the other hand, we have shown in Figure 2 that, when inclined sections of dislocation lines are observed, they appear to be parallel to the projection of the *c*-axis (see also figure 11 in Kuroiwa and Hamilton (1963)). Thus we may assume for ice the much simpler slip systems $\langle 0001\rangle\{10\bar{1}0\}$, $\langle 0001\rangle\{11\bar{2}0\}$. We also notice that the lattice vector is shorter in the $\langle 0001\rangle$ direction than in the $\langle 11\bar{2}3\rangle$ direction. Also it is not obviously justifiable to generalize the Burgers vector accepted for the hexagonal close-packed structure of zinc and cadmium to the more complicated lattice of ice with its tetrahedral arrangement of H_2O molecules. Finally it should be noted that neither the systems proposed here nor those proposed by Muguruma and Higashi as modified above can explain properly the tapering shape of some channels by the inclination of trails to the basal plane. For our systems all the trails should lie

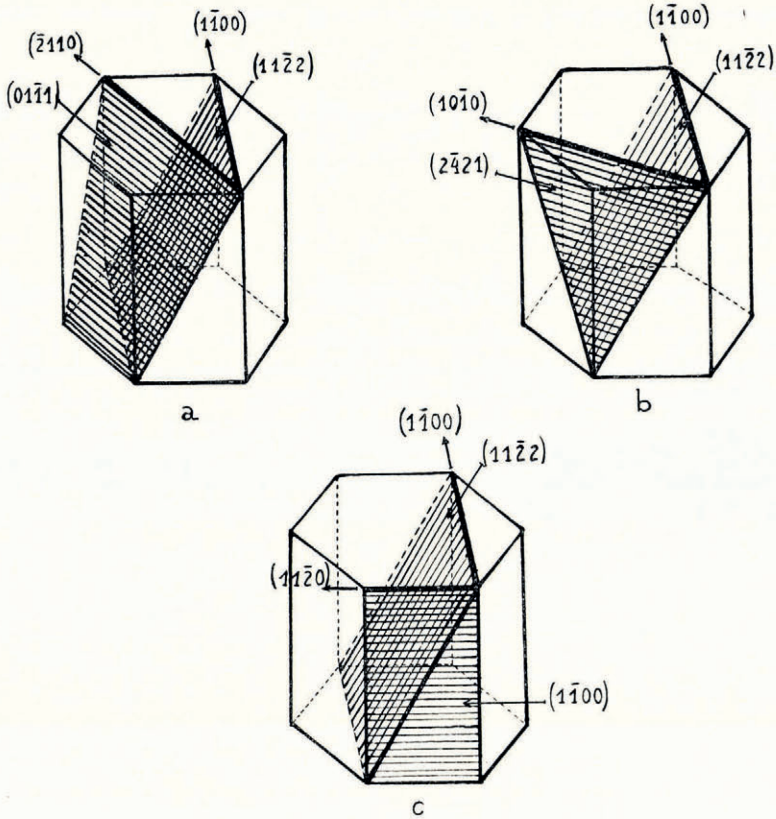

Fig. 9. Possible glide planes for a $\langle 11\bar{2}3\rangle$ screw dislocation

in the basal plane, while for Muguruma and Higashi's tapering should be a very general feature. Accordingly tapering must be determined by some other cause such as changes in the dislocation velocity. The research on the behaviour of dislocations in ice is being continued in this Institute to obtain more definite information about these matters.

Acknowledgements

The authors are grateful to Dr. A. Grinberg for comments on the paper. L. Levi and E. Suraski acknowledge the support they have received from the Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina).

MS. received 10 September 1964

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