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Structure of sodium chloride cleavage surfaces etched in vacuum at moderate temperature

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ABSTRACT

The structure of NaCl cleavage surfaces subjected to evaporation in vacuum at temperatures between 100° to 300°C has been studied by examination of gold-decorated replicas in the electron microscope.

The effect of bi-atomic step splitting and random formation of surface depressions is interpreted, assuming a vacancy cluster nucleation process. The phenomenon is correlated with the similar formation of impurity clusters observed by previous authors on the surface of thermally treated doped crystals.

It is noted that, though split steps largely prevail on thermally etched surfaces, showing that mono-atomic steps rarely exist, this fact does not signify that $a/2\langle 011\rangle$ dislocation loops do not form in front of the crack. Such loops left behind by cleavage may change into half-loops. In these circumstances the electric forces associated with the surface emergence of the half-loops and the charged kinks existing along correlated steps combine to restore electric equilibrium and annihilate the steps generated on the surface.

§ 1. INTRODUCTION

Previous authors (Levi 1973, Bassett and Yacamán 1976, Yacamán and Ocaña 1977) have shown that sub-microscopic cleavage and slip steps, revealed by gold decoration (Bassett 1958) on the (001) surfaces of alkali-halide crystals, may split, after slow evaporation in vacuum at moderate temperature, into two smaller steps. This has been interpreted by assuming that the simplest steps appearing on the cleavage surfaces of these crystals are usually bi-atomic rather than mono-atomic.

Yacamán and Ocaña (1977) also suggest a possible correlation between the bi-atomic nature of the steps observed after cleavage and a similar result obtained by Bethge and Keller (1974) in their studies of such surfaces etched by evaporation at high temperature. These authors found that steps emanating from a multiple cleavage step were annihilated by interaction with two mono-atomic steps of an evaporation spiral, so that they had to be considered bi-atomic. However, the effect observed by Bethge and Keller (1974) was determined by the kinetics of the evaporation process at high temperature,

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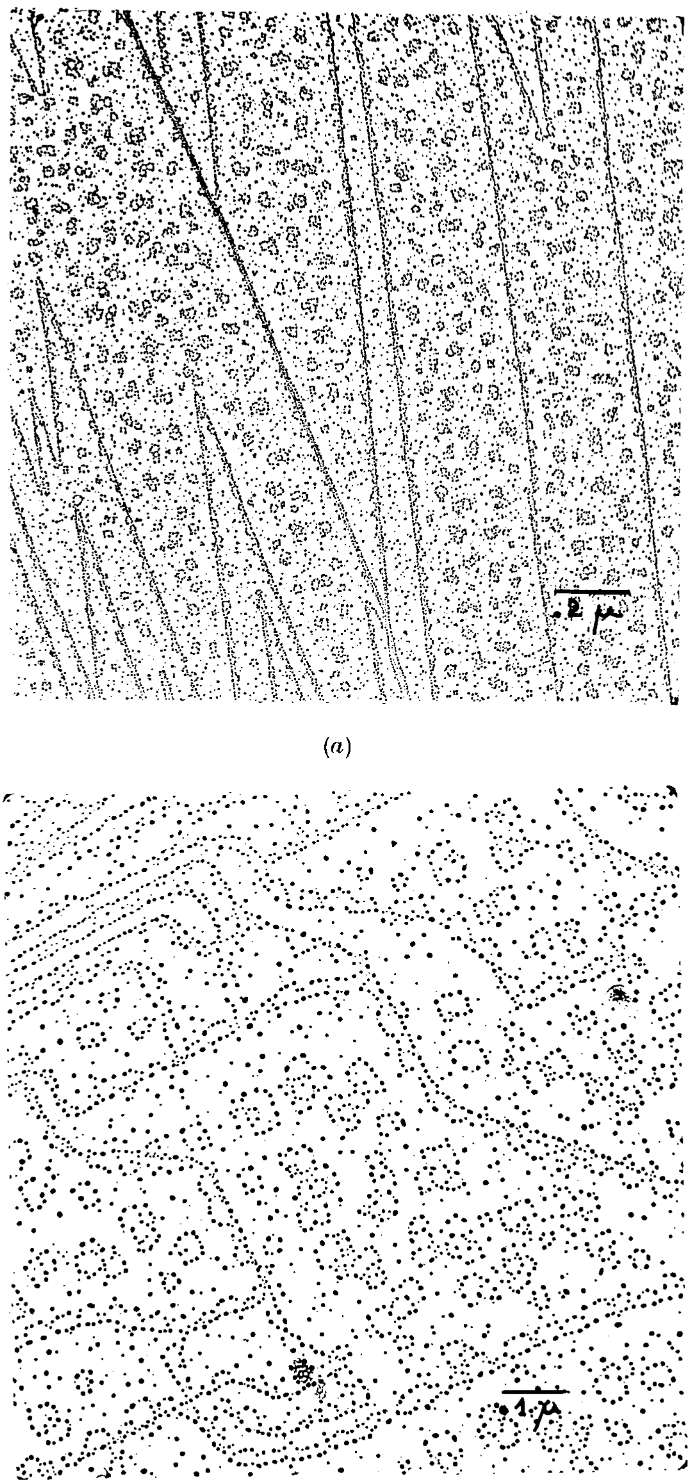
Fig. 1



(b)

Split steps and depressions on the surface of crystals of the first batch heated in vacuum at 200°C for 1 hour. (*a*) Longitudinal steps and V-patterns ; (*b*) higher enlargement of a similar surface structure with steps running in different directions.

while bi-atomic V-steps and similar structures were apparently formed during or immediately after cleavage at ambient temperature, where the step motion on the surface may be considered negligible.

In the present work these considerations have been taken into account and the structure of cleavage surfaces of NaCl crystals, heated in vacuum so that they showed the first evidences of slow evaporation, have been analysed, in order to study the mechanism of step splitting and the process which may be responsible for the generation of bi-atomic steps on such crystal surfaces.

§ 2. EXPERIMENTAL METHODS AND RESULTS

The samples studied were obtained from different batches of nominally pure NaCl crystals, supplied by Hilger & Watts. The residual impurity content of the crystals was not altogether negligible, as was shown by the results of the chemical analysis provided by the manufacturer for samples of the second batch. The concentration of elements such as Fe, Pb, Ba and Ca reached values of the order of a few 10 p.p.m.

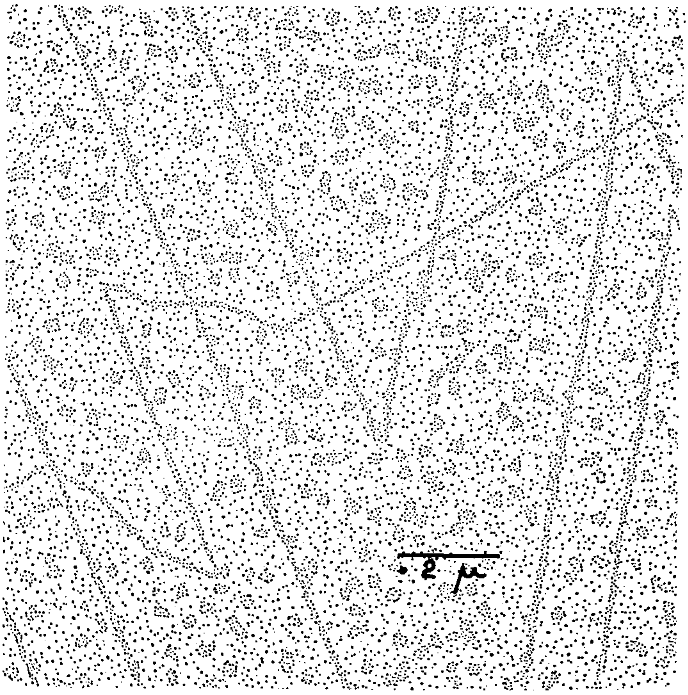
The samples were cleaved in dry air and evaporated in vacuum (10^{-5} torr) at temperatures varying from 100° to 300°C. Gold-decorated replicas of the surfaces following this treatment were subsequently obtained by the method described by Bassett (1958) and studied in the electron microscope. A few crystals were γ-irradiated for periods of several weeks before cleavage.

Figures 1 (*a*) and (*b*) show, in different magnifications, the surface structure of crystals of the first batch, obtained after evaporation for about one hour in vacuum at 200°C. V-steps running approximately in the crack direction prevail in fig. 1 (*a*), whereas transverse and longitudinal steps may be seen in fig. 1 (*b*). In both cases steps are split and vacancy clusters or depressions are formed on the flat surfaces. Similar modifications of the surface structure were observed on crystals of the second batch, though the temperature during evaporation had to be increased up to 250°–300°C. An example of the results obtained in such samples after evaporation in vacuum for one hour at 270°C is given in fig. 2. Here, V-steps, approximately longitudinal with respect to the crack direction, and a transverse slip step, showing successive glide and cross-glide segments, present the same split structure.

It may be noted that in this case the concentration of Au nuclei formed by decoration along split steps and inside depressions created by thermal etching on flat surfaces is higher than that existing in the surrounding zones, where the surface was not modified by the thermal treatment. This effect, which is probably caused by the presence of impurities (Bassett and Yacamán 1976), will be analysed in the next section.

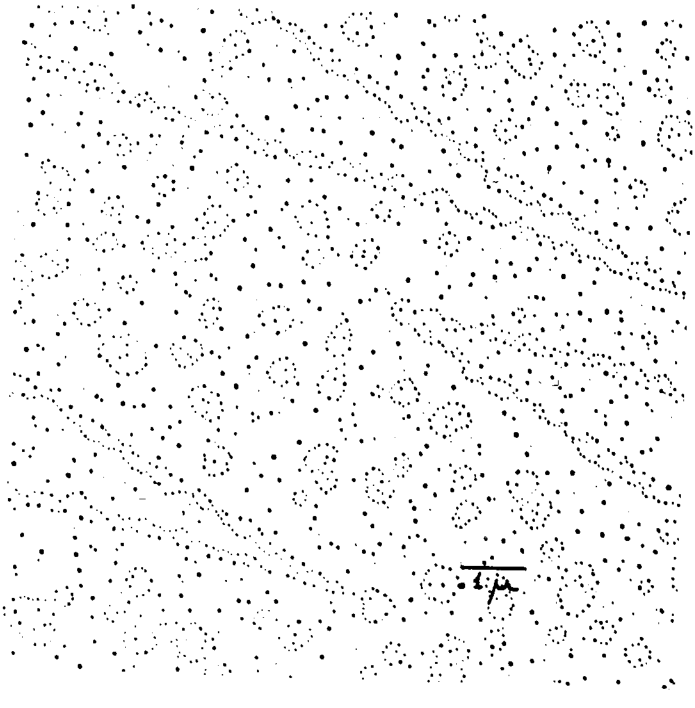
Figure 3 shows that, when γ-irradiated crystals of the first batch were used, steps already appeared split and depressions were formed on the flat surfaces after heating the sample for one hour in vacuum at 120°C. The effect of irradiation was less marked on the surfaces of crystals of the second batch, which, even after 2–3 months storage in the γ-cell, had to be warmed up to about 250°C for one hour in vacuum in order to obtain the first evidence of thermal etching.

Fig. 2



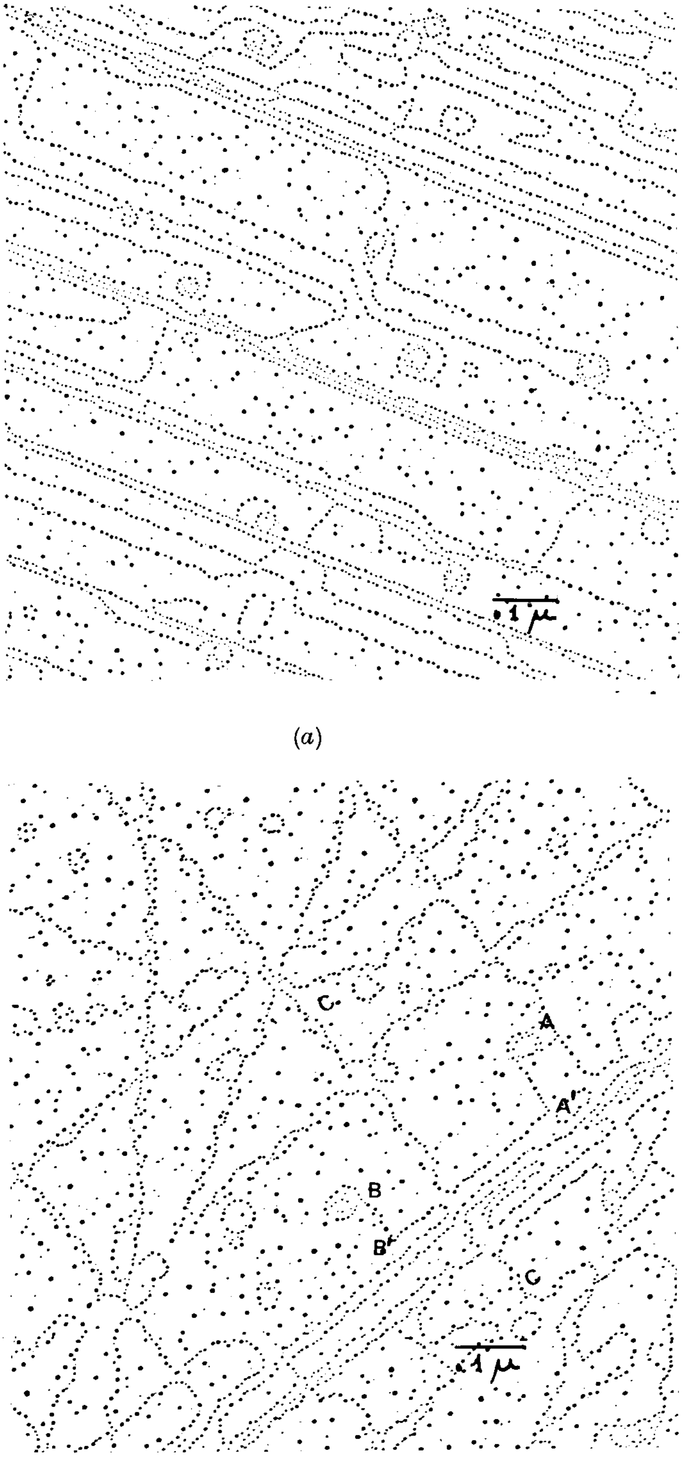
Split steps and depressions on the surface of a crystal of the second batch, heated in vacuum at 270°C for 1 hour.

Fig. 3



Split steps and depressions on the surface of a γ-irradiated crystal of the first batch after heating in vacuum at 120°C.

Fig. 4



Steps formed by a transverse slip band on the surface of a γ-irradiated crystal of the first batch after thermal etching at 120°C for 1 hour. (*a*) Etching effects at several dislocation emergences ; (*b*) the emergences of a half-loop.

Figures 4 (*a*) and (*b*) were obtained from the same sample as that of fig. 3, but represent a zone characterized by the presence of a slip band, transverse with respect to the crack direction. In this case, the interaction during evaporation of the steps nearest to the slip band hinders the splitting. However, the effects of evaporation are shown in fig. 4 (*b*) by the splitting of some isolated steps and, in both figures, by the formation at the end of transverse steps of a few spiral turns. These represent the first evidence of thermal etching occurring around points of emergence of dislocations.

This result is interesting, because in these conditions the points of emergence of dislocation half-loops, left under the surface by the crack, are revealed simultaneously with the steps generated by the dislocation motion probably occurring during cleavage immediately behind the crack tip. Thus, the two spirals of opposite sign, marked A and B in fig. 4 (*b*), may be considered to represent the emergences of a small half-loop which had glided and then cross-glided, forming the slip step A′B′ and the cross-slip steps A′A and B′B. Here, the discontinuity formed by evaporation at the intersection of the transverse step A′B′ with the longitudinal one CC shows that both steps are the same height. It may be concluded that both these intersecting steps were bi-atomic and the Burgers vector of the dislocation half-loop emerging at A and B was $\mathbf{a}\langle 001\rangle$.

Figures 5 (*a*) and (*b*) give examples of step structures obtained on irradiated samples of the first batch which were thermally etched in vacuum at 150°C for only half an hour. Owing to the short evaporation time, steps are not split and depressions may not be seen on the flat surfaces. However, small circular features formed at the ends of the transverse slip steps or of the correlated cross-slip segments, and marked A, B, C and D in fig. 5 (*a*), indicate the existence of dislocation emergences which were just beginning to be etched. In this figure the emergences A and B correspond to a half-loop that had glided and cross-glided in a manner similar to that of the half-loop shown in fig. 4 (*b*). Here a step discontinuity may be seen at B′, where a longitudinal step intersects the trace AA′B′B of the half-loop. Similar discontinuities may be seen in fig. 5 (*b*) where several V-steps are intersected by a transverse one. Taking into account the analysis of fig. 4 (*b*), it may be concluded that all the steps are bi-atomic and the Burgers vector of the dislocations emerging in fig. 5 (*a*) is $\mathbf{a}\langle 001\rangle$.

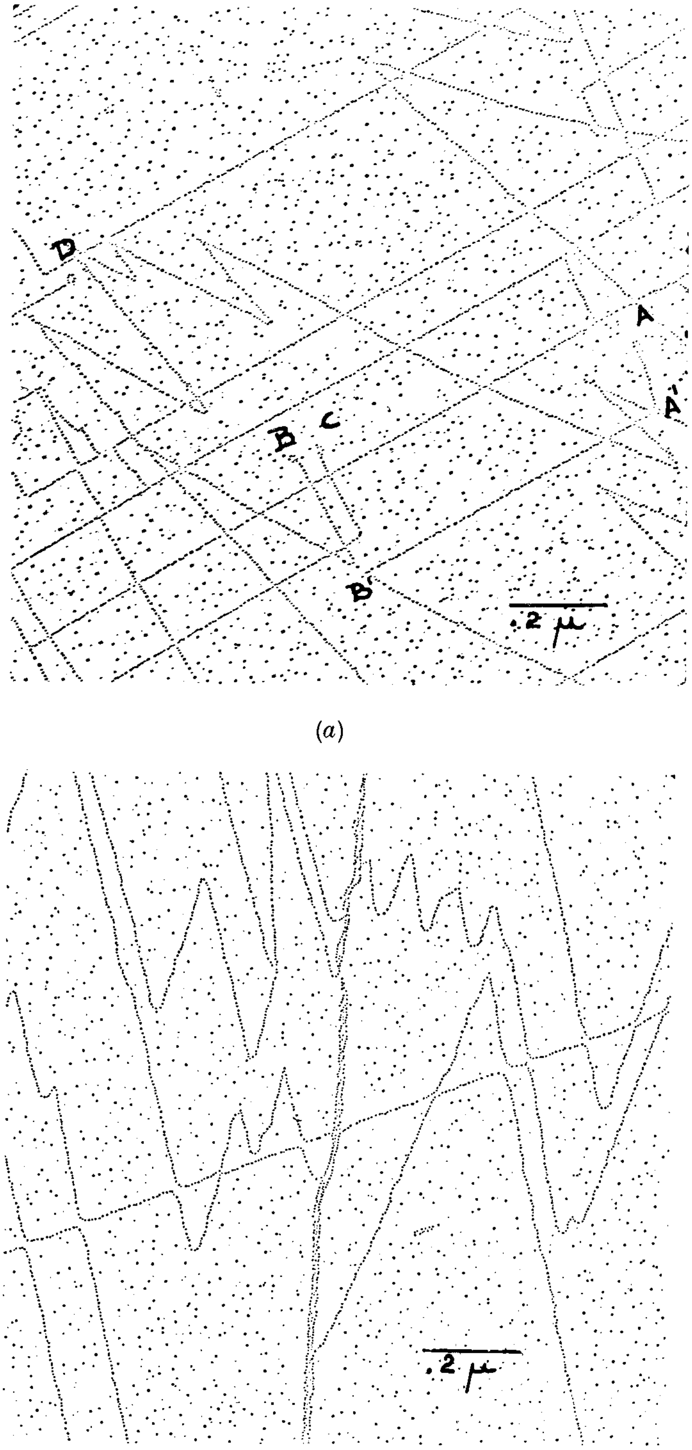
On the contrary, we show in fig. 6 an exceptional case where a few steps, running approximately in the crack direction, do not appear split, though their lines are made irregular by evaporation. It may also be seen that, when these un-split steps are intersected by split ones in A, B, C and D, they only interact with the higher half of the latter, whereas the weakly decorated lower half of the same steps remains continuous. It may be concluded that the un-split steps were mono-atomic, so that they were probably cleavage steps generated by the interaction of the crack tip with dislocations having $\mathbf{a}/2\langle 011\rangle$ Burgers vector.

§ 3. Discussion

3.1. *Process of step splitting and formation of depressions on the surface*

Comparison of the different surface structures just described shows that the effects of step splitting and of vacancy clustering on the flat surfaces are

Fig. 5

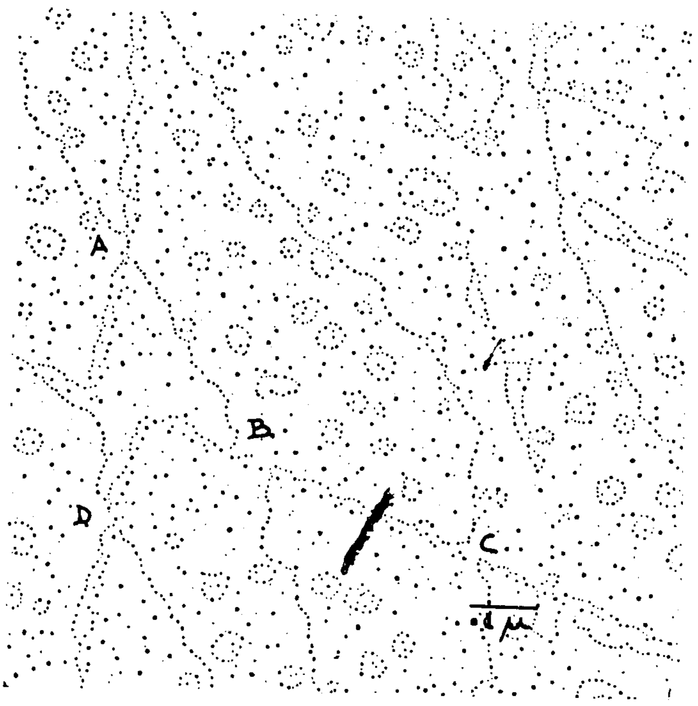


(*a*)

(*b*)

Surface of γ-irradiated crystals of the first batch after heating in vacuum at 150°C for ½ hour. (*a*) First evidence of thermal etching at dislocation emergences; (*b*) effects of evaporation at longitudinal-transverse step intersections.

Fig. 6



Some non-split, mono-atomic steps.

related phenomena. They never appear independently on slowly evaporated surfaces, and, when present, they also show a similar development. These observations suggest that both of these effects are produced by the same process of vacancy cluster nucleation, occurring on the uppermost lattice plane of the surface of the crystal. Such a process would give place to a random distribution of depressions on the flat surfaces, where these have been observed with a density of about 2×10^{10} cm^{-2} (i.e. with a linear density of about $1{\cdot}5 \times 10^{5}$ cm^{-1}).

The rate of nucleation of vacancy clusters should be enhanced along the step edges, forming kinks of mono-atomic height, distributed along the steps with a linear density about twice the value of that for the flat zones of the surface. For bi-atomic or poly-atomic steps this effect can initiate the process of splitting, which should be completed when such kinks merge, because their lateral growth forms continuous though usually irregular mono-atomic steps separated from the lower part of the initial step by a distance comparable to the depression radius.

This phenomenon of thermal etching may now be compared with a similar effect observed by Bassett and Yacamán (1976) on the surfaces of NaCl crystals doped with Mn^{2+} and heated for several hours in vacuum at about 250°–300°C. The above-mentioned authors noted that, during the heat treatment of the samples, the impurity diffused towards the surface where it precipitated along split steps and formed randomly distributed clusters on flat zones. The distribution of these impurity clusters was very similar to that of the surface depressions observed in thermally etched crystals studied in the present work. It may be noted that the latter crystals contained a significant impurity concentration, which could probably initiate the effect observed by Bassett and Yacamán (1976). This effect appears to be partially evident with crystals of the second batch, which had to be heated in vacuum up to 250°–300°C in order to obtain the phenomenon of step splitting. For instance, the presence of impurities was probably responsible for the effect shown in fig. 2, where the density of the Au nuclei formed by decoration was higher inside depressions and along split steps than on the surrounding surface. According to a recent observation of Yacamán and Hirth (1976), such a larger density of small Au nuclei is formed by decoration on the surface zones which contain a larger concentration of impurities.

However, the results obtained here using crystals of the first batch, where the etching effects were obtained at lower temperatures, indicate that the concentration of Au nuclei is not always markedly higher inside depressions and along split steps than on the surrounding surfaces. This fact suggests that the observed surface structure primarily depends on the nucleation of vacancy clusters on the surface, as we have previously assumed. Thus, the presence of impurities would play only a secondary rôle in the phenomenon, determined by the tendency of foreign ions to migrate towards steps and vacancy clusters where they would accumulate, replacing vacancies inside depressions and changing the latter into impurity clusters.

This interpretation of the phenomenon is also supported by the lowering of the etching temperature observed for irradiated crystals of the first batch, where structures of the type shown in figs. 3 and 4 were obtained by carrying out the thermal treatment of the samples at temperatures near 100°C.

Since, according to Hobbs, Hughes and Pooley (1973), defect clusters created by irradiation of alkali-halide crystals are formed by interstitials only, vacancies created at the same time in the irradiated lattice could be assumed to diffuse preferentially towards the surface, increasing the rate of step splitting and of depression nucleation and enhancing the etching effects at the dislocation emergences.

3.2. *Step height and Burgers vector of related dislocations*

As observed by Yacamán and Ocaña (1977), when ionic crystals are cleaved, dislocation loops with $\mathbf{a}/2\langle 011\rangle$ Burgers vector would be expected to prevail in the stressed material existing in front of the crack because they are associated with a lower energy than dislocation loops with $\mathbf{a}\langle 001\rangle$ Burgers vector. Thus, when the crack tip intersects these dislocations, mono-atomic steps have to be created on the cleavage surfaces. However, their presence would entail the formation of extra charges on each half of the cleaved material, owing to the charged kinks usually existing along such steps. Consequently, Yacamán and Ocaña (1977) suggested that the absence of such steps could be correlated with some process of charge rearrangement, which would take place on the cleavage surfaces in order to restore electric equilibrium. On the other hand, the presence on the same surfaces of bi-atomic steps could be explained by taking into account the fact that double kinks in these steps are electrically neutral.

However, we have shown in fig. 6 that cleavage surfaces are not completely free of mono-atomic steps. Furthermore, the phenomenon of step splitting itself does not only confirm that such steps may exist but also that, during slow evaporation in vacuum, bi-atomic steps are not stable and change into pairs of mono-atomic steps. Therefore it seems that the almost total absence of mono-atomic steps formed by cleavage on the surfaces of the crystals would be more likely correlated with processes that depend on the step dislocation interaction occurring during cleavage than on some subsequent effect of charge rearrangement.

Taking into account these observations, some processes that could be responsible for the observed step structure of NaCl cleavage surfaces will be analysed, considering the cases of longitudinal and transverse steps separately.

(*a*) *Longitudinal steps*

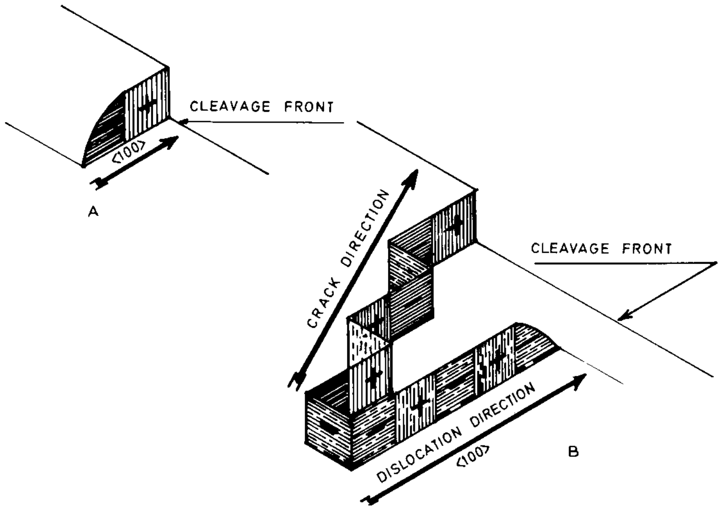
Longitudinal cleavage and slip steps of opposite sign have been shown to form when the first side of a dislocation loop, created in front of the crack, is intersected by the crack (Robins, Rhodin and Gerlach 1966, Burns and Webb 1970, Levi 1973). In fact, the kink formed on the tip of the advancing crack caused by the intersection of the latter with the screw component of such a dislocation, would generate a cleavage step, while the intersected dislocation, subsequently moving out of the material behind the crack tip, would generate a slip step. The formation of such steps evidently requires that the path of the dislocation emergence and that of the kink on the crack tip differ from each other. According to the results discussed here this would occur for the electrically neutral emergences of the intersected loops with $\mathbf{a}\langle 001\rangle$ Burgers vector and for the corresponding kinks on the crack tip that generate bi-atomic V-steps.

The absence of similar mono-atomic patterns may now be justified by observing that, when the crack intersects a screw dislocation with $\mathbf{a}/2\langle 011\rangle$ Burgers vector, a pair of kinks carrying electric charges of opposite sign and belonging to matching cleavage surfaces would be created on the crack tip. Thus, if, during crack propagation, the intersected dislocation remained in a fixed position, the electric charges carried by the kinks, which alternate their sign, would successively be opposite or equal to those existing at the corresponding dislocation emergences, so that, on average, extra electric charges would exist on the surfaces. On the contrary, electric equilibrium would be nearly restored if the emergences of the newly intersected dislocation advanced with cleavage, following the same path of the kink on the crack tip at such a distance that the kink and the dislocation emergence would always carry electric charges of opposite sign. Such a configuration is shown for instance, in fig. 7 (*a*), where the kink on the crack tip and the dislocation emergence are assumed to advance together with a separation of one ionic distance. It may easily be seen that under these conditions neither cleavage nor slip steps would be left permanently on the surface.

Finally, when the second side of the loop is also intersected by the crack, the kink on the crack tip would be annihilated and the loop would pop out from the material, leaving no trace of its previous existence in the crack front.

An objection to this interpretation of the absence of mono-atomic V-steps could arise from the observation that, when the crack advances in a direction

Fig. 7



(A) The emergence of a dislocation with $\mathbf{a}/2\langle 011\rangle$ Burgers vector is assumed to follow the kink it has formed on the crack tip ; no step is left on the surface ; (B) electric charges distributed along steps, if a mono-atomic V-pattern were formed.

that is not a rational crystallographic direction, the dislocation emergences would have to glide and cross-glide behind it in order to follow the corresponding kink on the crack tip. However, this assumption may be justified by taking into account previous observations on the V-pattern structure (Levi 1973), which have shown that the slip steps forming one of the arms of these bi-atomic patterns frequently follow irrational crystallographic directions. This result indicates that small dislocation loops formed near the cleavage plane and partially intersected by the crack may cross-slip easily when they advance with the tip.

For comparison with the configuration shown by fig. 7 (*a*), we also represent in fig. 7 (*b*) a mono-atomic V-pattern, as it would have formed behind a cleavage front advancing in an irrational direction, if the first side of the dislocation loop with $\mathbf{a}/2\langle 011\rangle$ Burgers vector, intersected by the crack tip, would only be able to glide in the $\langle 001\rangle$ direction. It may be seen that in this case a high density of extra charges would be created at the V-vertex, making this configuration rather improbable.

Finally, it must be noted that the previous analysis is convenient only for dislocation loops that may pop out from the material after being intersected by the crack. Thus, it may not be applied to the behaviour of dislocations with $\mathbf{a}/2\langle 011\rangle$ Burgers vector which belong to the dislocation net existing in the crystal before cleavage. In such cases, when the dislocation is intersected by the crack, the emergence formed on the cleavage plane would remain clamped at some point of the latter, so that a cleavage mono-atomic step of the type shown in fig. 6 would be formed by the corresponding kink on the advancing crack tip. However, since the density of screw dislocations belonging to the net and intersecting the cleavage plane is very low with respect to that of dislocation loops created by the crack, such mono-atomic steps would be rarely revealed by the surface analysis, in agreement with the experimental results.

(*b*) *Transverse steps*

The mechanism just considered to explain the mutual annihilation of mono-atomic cleavage and slip steps, both longitudinal with respect to cleavage, may not be applied without modification to justify the similar absence of mono-atomic transverse slip steps. In effect we have to take into account that the bi-atomic transverse slip steps frequently observed on the cleavage surfaces were formed by dislocation loops that had broken the surface behind the crack tip and remained afterwards, as half-loops, inside the cleaved material. This may be derived from the analysis of the step structure in figs. 4 and 5 which show : (1) the absence of longitudinal cleavage steps starting from the transverse slip bands indicating that the corresponding dislocations with $\mathbf{a}\langle 001\rangle$ Burgers vector had not been intersected by the crack tip ; (2) the etching effects occurring at the step ends, which indicate that the dislocations under consideration still remained inside the material after the thermal treatment of the samples.

If may now be noted that, if the Burgers vector of a loop that has broken the surface behind the crack tip was $\mathbf{a}/2\langle 001\rangle$, the dislocation emergences appearing at the ends of the step formed on the surface would carry electric charges of opposite sign. Therefore, owing to the electric field created by these charges and possibly also by charged kinks distributed along the mono-atomic step that joins the corresponding emergences, the half-loop would not be stable. Instead of expanding behind the crack front, the half-loop would consequently contract or pop out from the surface, annihilating at the same time the step formed when the loop had initially broken the surface.

Thus, dislocation half loops with $\mathbf{a}\langle 001\rangle$ Burgers vector, which do not carry electric charges at their emergences, would be the only ones that could remain inside the material at the end of cleavage.

§ 4. CONCLUSIONS

It follows from the previous discussion that the slow phenomenon of thermal etching occurring in vacuum on NaCl crystal surfaces, heated at temperatures ~300°C, is mainly a consequence of a process of vacancy cluster nucleation and growth taking place on the surface. These clusters would usually consist of depressions enclosed by mono-atomic steps, so that their nucleation along the edges of bi-atomic steps previously existing on the surface would determine their splitting.

On the other hand, the large number of split steps observed on cleavage surfaces after the thermal treatment of the samples is interesting, because it shows the prevailing bi-atomic structure of such steps. According to the present interpretation of the phenomenon, the usual absence of mono-atomic steps observed on the cleavage surfaces depends on a process of step-dislocation annihilation occurring for half-loops with $\mathbf{a}/2\langle 001\rangle$ Burgers vector, intersected by the crack.

It may be noted, in conclusion, that the instability of half-loops with this Burgers vector, as revealed by the step structure after cleavage, is probably an inherent property of such dislocations in ionic crystals that does not depend on the special process of crack propagation. It would be worth verifying whether the prevalence of bi-atomic steps is in fact a general characteristic of such crystal surfaces, independently of the mechanism that has generated the plastic deformation of the samples.

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