CAVITY FORMATION IN NITRATE-DOPED ALKALI HALIDES*

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Cavities filled with a gaseous product were formed in nitrate-doped alkali halide crystals after anneal in a hydrogen atmosphere.

These experiments show that the gaseous products of a chemical reaction in a solid, precipitate along dislocations if enough activation is present to allow diffusion.

Diffusion is facilitated by the formation of small agglomerates consisting of a few gas molecules and a number of vacancies.

LA FORMATION DE CAVITES DANS LES HALOGENURES ALCALINS DOPES AU NITRATE

Des cavités, renfermant un produit gazeux, ont été formées dans des cristaux d'halogénures alcalins dopés au nitrate après un recuit en atmosphère d'hydrogène.

Ces expériences montrent que les produits gazeux résultant d'une réaction chimique dans un solide, précipitent le long des dislocations si l'activation existante est suffisante pour permettre la diffusion.

La diffusion est facilitée par la formation de petits agglomérés composés de quelques molécules de gaz et d'un certain nombre de lacunes.

HOHLRAUMBILDUNG IN ALKALI-HALOGENIDEN MIT NITRATZUSATZ

In Alkalihalogenid-Kristallen mit zugesetztem Nitrat werden nach Glühen in einer Wasserstoffatmosphäre gasgefüllte Hohlräume gebildet.

Die Experimente zeigen, dass die gasförmigen Reaktionsprodukte einer chemischen Reaktion in einem Festkörper sich entlang von Versetzungen ausscheiden, wenen genügend Aktivierung vorhanden ist, um Diffusion zu ermöglichen.

Die Diffusion wird erleichtert durch die Bildung von kleinen Agglomeraten aus einigen Gasmolekülen und einer Anzahl von Leerstellen.

It has been shown in this laboratory that dislocations can be decorated in silver activated alkalihalide crystals by annealing them in hydrogen.$^{(1)}$ The decorating particles are silver, but, in a few cases, it was observed that cavities also developed along the dislocation lines. This could be traced back to a contamination of the silver salt with the corresponding nitrate. A systematic study of this phenomenon was made, and the following crystals were studied:

(a) KCl + 0.75% AgCl containing traces of $AgNO_3$.
(b) KBr + 0.75% AgBr containing traces of $AgNO_3$.
(c) KCl + 0.75% Ag_2O.
(d) KCl + 0.90% $AgNO_3$.
(e) KCl + 0.70% KNO_3.

The crystals were grown in the laboratory by the Czochralski method. The indicated additions are weight percentages added to the melt; they are chosen to correspond to an addition of 0.75% AgCl.

DECORATION EFFECTS

(i) *After hydrogen anneal*

Cleavage parallelepipeds of all crystals were annealed for 2 hr at some 750°C in oxygen-free hydrogen and then cooled slowly. After this treatment the dislocations were decorated in crystals *a*, *b*, *c* and *d* by silver particles, visible by ultramicroscopy. In *a*, *b*, *d* and *e*, cubic cavities, centered on the dislocation lines and bounded by (100) faces or sometimes by a combination of (100) and (110) faces, were found. In most cases (crystal *e* excepted) a silver speck can be observed in them. The cavities can be observed as well in transmission as in ultramicroscopy. Fig. 1, taken in ultra microscopy, reproduces an example from which it is evident that they are on dislocations. With a sufficient concentration of cavities, one obtains a decoration consisting of a *quasi*-continuous channel, as visible in Fig. 2. This was practically always so for crystal *e*.

Although the silver decoration is of course absent in the latter case, it is evident that the cavities are on dislocations. They are very often elongated in the direction of the dislocation line, which of course favours the formation of channels; their surfaces are sometimes visibly stepped. The concentration of

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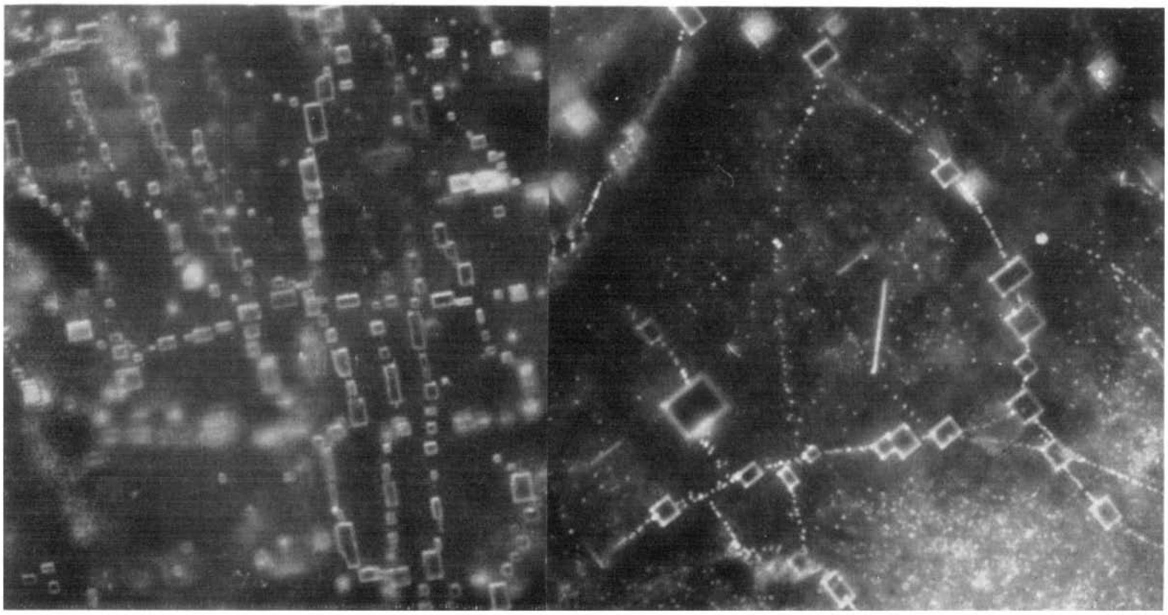

Fig. 1. Cavities along dislocation lines in silver nitrate doped KCl crystals, after thermal treatment in hydrogen. ×675.

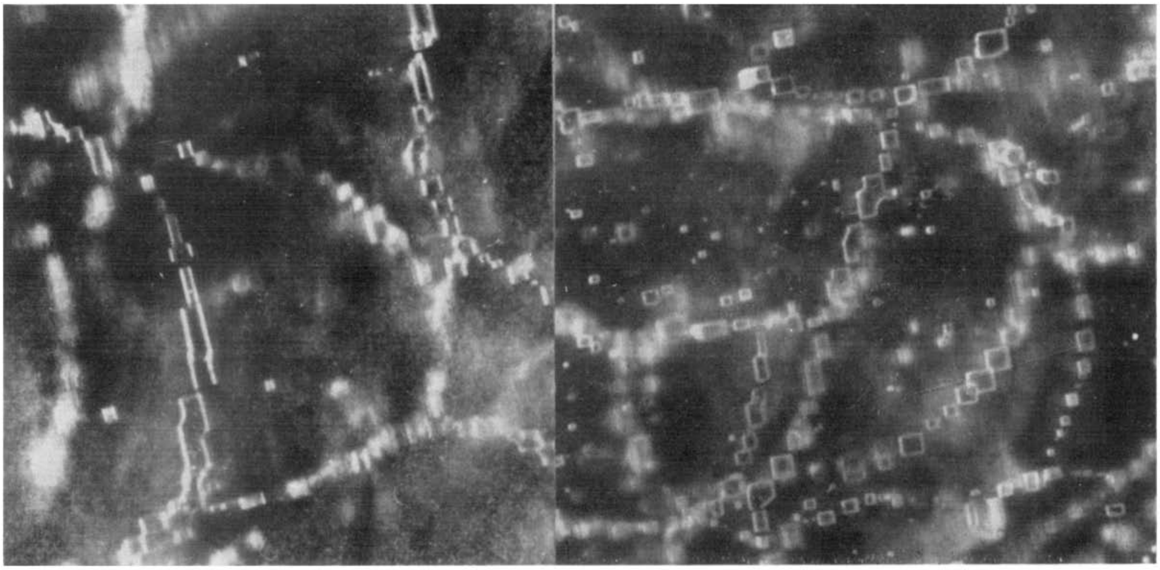

Fig. 2. *Quasi*-continuous channels along dislocation lines due to high concentration of cavities in KNO_3–doped KCl. ×600.

cavities is largest in the neighbourhood of the surface which has been in contact with the hydrogen; the central part of the crystal remains practically clear.

To study the nature of these cavities, a crystal fragment was dissolved in water under the microscope. Every time the dissolution front reached a cavity, a gas bubble two or three times larger than the cavity escaped. This means that the cavities are filled with gas under a pressure of a few atmospheres. The gas is practically insoluble in water. Quenching the crystal results in a higher pressure, but a somewhat smaller cavity size. A very long anneal of 24 hr, produced larger cavities containing gas under a lower pressure; the zone containing a large concentration of cavities extends further in the crystal.

(ii) *After additive coloration*

In order to obtain indications of the role of the hydrogen in the process described in the previous paragraph, the crystals were coloured additively with

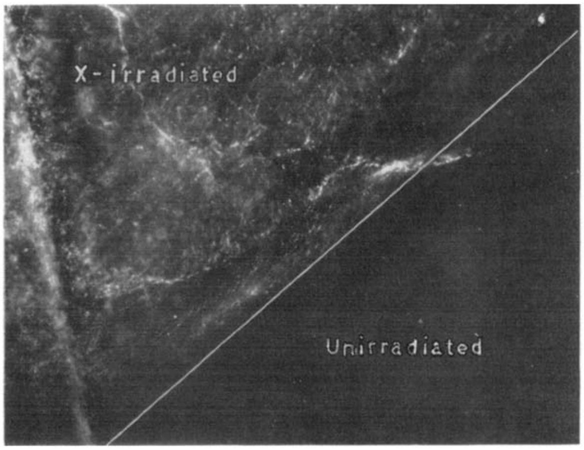

Fig. 3. Boundary zone between the non-irradiated and irradiated parts of a silver nitrate doped KCl crystal.

potassium metal by the Rexer method. The same results were obtained. This indicates that the hydrogen probably plays the same role as the potassium metal, i.e. supplies electrons and forms HCl at the surface, just as KCl is formed when potassium is used. As no closed vessel is needed for the Rexer method, this excludes the possibility that the small amount of hydrogen which could be dissolved in the potassium has played a role in the process.

(iii) *After irradiation and anneal*

It has been reported that specks can be observed in silver activated alkalihalide crystals after an intense X-ray irradiation.(2) Although experiments were performed under variable circumstances, we never could reproduce this effect when pure silver chloride was added to the melt. The effect of temperature, of irradiation time and of silver concentration was tried out, all with negative results.

On the other hand, it is known that $NaNO_3$ decomposes partially when it is irradiated with ionizing radiation of sufficient energy, and that gas pockets are formed on subsequent anneal.(3) It was therefore worthwhile to try to see if similar treatments of silver nitrate doped crystals would produce specks, release gas, or both; and, if so, whether the pockets would develop along dislocation lines. Both X- and γ-rays were used in these experiments.

When the added silver chloride was contaminated with $AgNO_3$, or when the crystals were doped with $AgNO_3$, the as-grown crystals contained already very small silver specks. Their size and number is markedly affected by an X-ray irradiation (copper tube, 40 kV, 20 mA) followed by an anneal. Fig. 3 illustrates this effect. It shows the boundary zone between the non-irradiated and irradiated parts of such a crystal which was X-rayed partly covered by a lead screen. The crystal was heated to 600°C immediately after irradiation. An anneal prior to irradiation, even at higher temperatures, has no effect at all. The decoration in this case is also due to cavities filled with gas and covered with silver. Crystals irradiated in the pile at Mol ($\sim 10^{17}$ neutrons/cm^2), are heavily coloured. The F-bands are bleached when they are exposed to daylight and after an anneal at 600°C the decoration is extremely dense. This decoration is also due to cavities filled with gas and some small silver specks. Crystals irradiated with high energy γ-rays produced by fission products are not coloured and show no special decoration when they are annealed.

ABSORPTION MEASUREMENTS

(i) *Infra-red*

As $AgNO_3$ decomposes in air at temperatures (+450°C) well below the melting point of KCl, it is important to know which groups are incorporated into the crystals. Therefore, absorption measurements were performed in the infra-red region. A Beckman recording spectrophotometer was used. Similar measurements have already been performed by Maslakowez(4) who examined alkalihalide crystals doped with the corresponding alkalinitrite and nitrate, and found two absorption peaks respectively at 1420 cm^{-1} (7.22–7.26 μ) and 1250 cm^{-1} (7.85–8 μ). The first one was attributed to the nitrate group, the other to nitrite ions. The relative intensities of the peaks depends on the melting point of the alkalihalide. Maslakowez therefore postulated that an equilibrium was formed in the melt between nitrite and nitrate groups through oxygen release of the latter ion. Our measurements of the untreated crystals are shown in Fig. 4. More than two peaks were observed, specimens doped with $AgNO_3$ and KNO_3 having the same absorption spectrum. The absorption maxima shift to shorter wavelength as the lattice parameter decreases. This is shown in Table 1 for the two most intense peaks.

Slices taken from the surface region and from the central part of hydrogen treated specimens were also examined. In the first, which contain a high concentration of cavities the NO_3 and NO_2 peaks are no longer present; in the second, containing far less

TABLE 1.

Crystal	Lattice parameter (Å)	max 1 (μ)	max 2 (μ)
KBr	6.59	7.80	7.22
KCl	6.28	7.77	7.14
NaCl	5.63	7.66	6.99

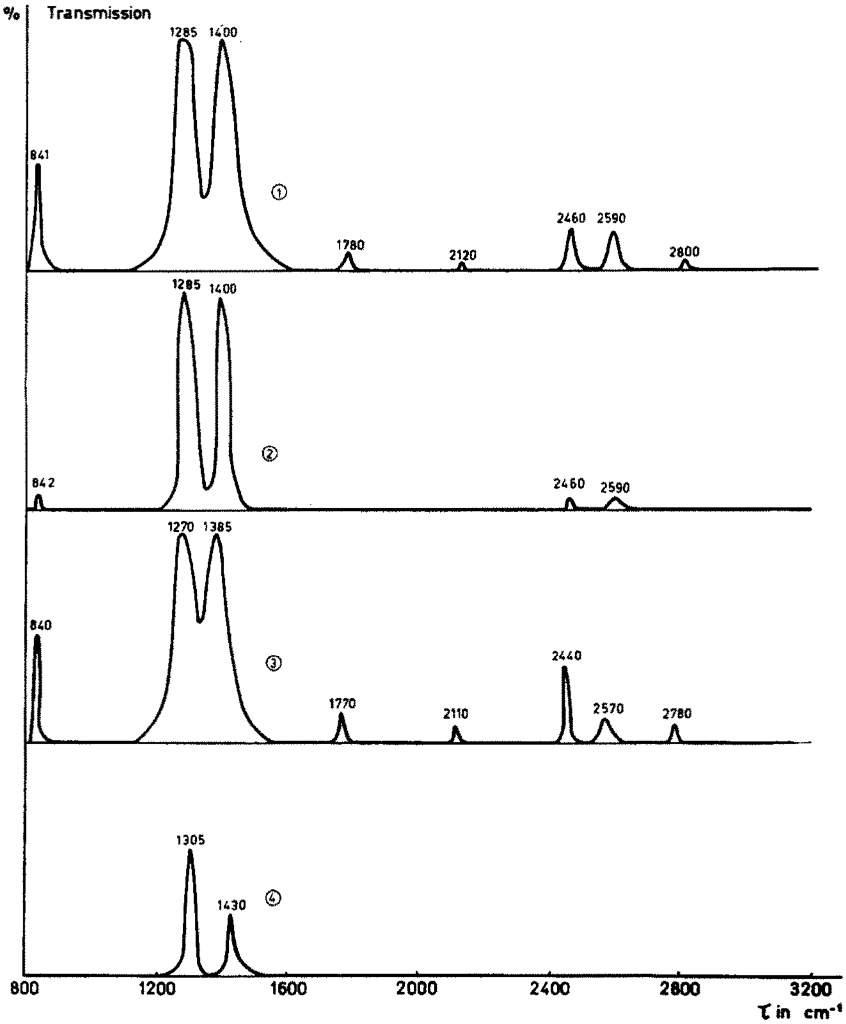

FIG. 4. i-r spectra
(1) KCl + KNO_3 $d = 3.14$ mm
(2) KCl + $AgNO_3$ $d = 0.97$ mm
(3) KBr + $AgNO_3$ $d = 2.26$ mm
(4) NaCl + $AgNO_3$ $d = 1.66$ mm

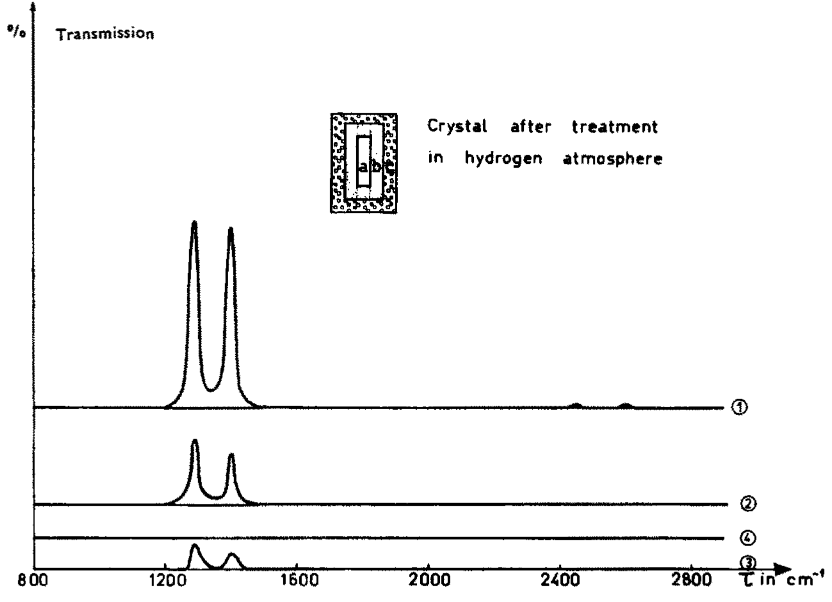

FIG. 5. i-r spectra from a KCl + $AgNO_3$ crystal: (1) untreated specimen; (2) (3) (4) After treatment in hydrogen atmosphere. The curves correspond respectively to sections *a*, *b*, and *c* of the crystal.

cavities, they are strongly reduced as shown in Fig. 5.

This indicates that the oxygen–nitrogen groups are at the origin of the gaseous products which fill the cavities after the indicated treatment. The latter however do not show up in the infra-red diagrams.

(ii) *Visible and u-v absorption measurements*

The absorption spectra of irradiated and uncoloured alkali halide crystals doped with Ag^+, NO_2^- and NO_3^- have been extensively studied by several authors.(5,6,7) In order to follow the evolution occurring during the hydrogen treatment of such crystals, we have extended such measurements to crystals doped with nitrate-contaminated silver chloride, silver nitrate, silver oxide and potassium nitrate. The quantities of these impurities added to the melt was calculated to correspond to 0.75 wt. % of pure silver chloride, which allows comparison with crystals doped with the same amount of AgCl.

The absorption measurements were performed with a Beckman spectrophotometer D.U. The specimens were coloured by X-rays originating from a tube with a copper target operating at 40 kV and 20 mA. In all experiments the crystals were at a distance of 6 cm from the window. X-rayed crystals were measured immediately after irradiation.

(a) *Untreated crystals.* Table 2 summarizes the relative intensities of the different absorption bands. In accordance with earlier investigations the silver ion bands are found in all crystals containing this ion. This 2150 band is more pronounced when the AgCl is contaminated with $AgNO_3$, owing to overlapping of a nitrate ion band. KCl crystals containing 0.75% of KNO_3 show a small peak at 3600 Å and a very intense one at 2150 Å, whilst the band at 2900 Å observed by Maslakowez does not seem to be present. The same bands were also observed in KBr and KCl crystals containing 0.75% $AgNO_3$, whilst NaCl doped with $AgNO_3$ only has the intense band at 2150 Å (Fig. 6).

The bands at 2150 Å and 3600 Å in KBr–$AgNO_3$

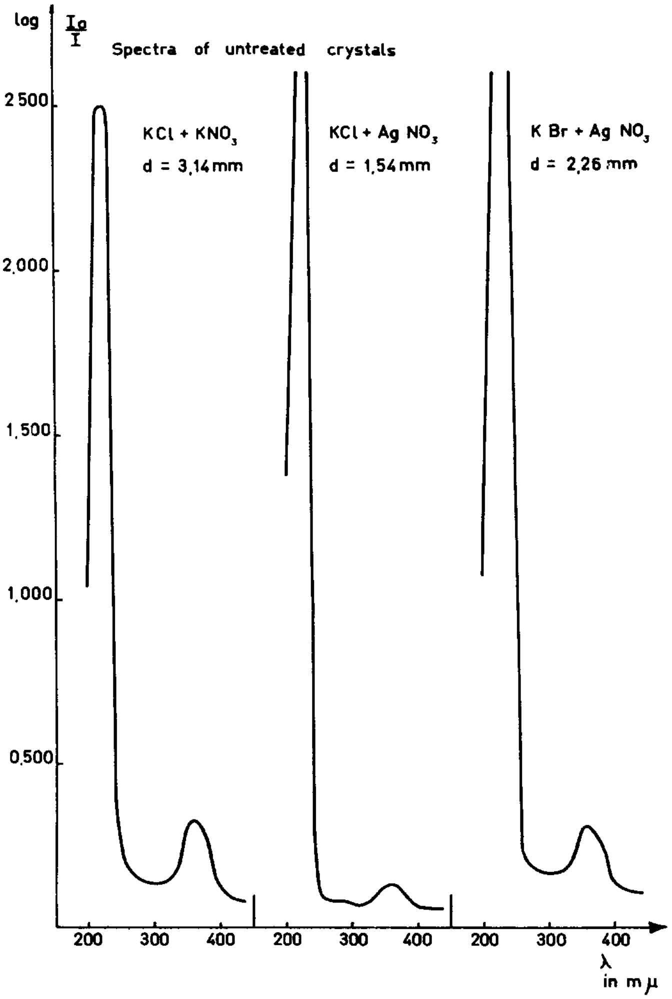

FIG. 6. u-v spectra of untreated nitrate-doped KCl and KBr crystals.

TABLE 2.

	λ in Å	Half width (Å)	log I_0/I	λ in Å	Half width	log I_0/I
KCl + AgCl pure	2150	25	1.6	—	—	—
KCl + AgCl imp.	2150	30	1.9	—	—	—
KCl + Ag_2O	2150	25	1.7	—	—	—
KCl + $AgNO_3$	2150	35	2.6	3600	50	0.11
KBr + $AgNO_3$	2150	50	2.6	3600	50	0.2
NaCl + $AgNO_3$	2150	30	2.6	—	—	—
KCl + KNO_3	2150	30	2.6	3600	50	0.17

crystals are more intense and very broad in comparison with those observed in KCl–$AgNO_3$ and KCl–KNO_3 samples.

The KCl–Ag_2O crystals only have a small band at 2150 Å which must be ascribed to the silver ions.

(b) *Coloured crystals.* In all the irradiated silver activated crystals the characteristic X-ray induced A, B, C, D, E-bands are present. Their relative intensity was affected by the different added negative ions: the F-band is reduced in comparison with the others: the A-band is more intense. This is illustrated in Fig. 7 and Table 3 in which the absorption peaks of two specimens, one containing AgCl contaminated with $AgNO_3$, the other pure AgCl, are compared. Both specimens were irradiated for 7 hr in identical conditions, and have nearly the same thickness *d*. The B-band is very intense with respect to the others in crystals doped with pure $AgNO_3$. In the early stages of the irradiation, the E-band is prominent and grows more rapidly than the A, B, C and D-bands. This is reversed after a certain time, E reaches a saturation value while B, being the most intense, and also C and D continue to grow steadily (Fig. 8). The E-band is always less intense in nitrate doped crystals than in those to which pure silver chloride was added.

When the coloured crystals are irradiated in the F-band, the B and A-bands increase. Even when kept in the dark for several hours, the F-band decreases while the A and B-bands become more intense (Fig. 9).

All crystals, except those of KCl doped with pure $AgNO_3$, are fully bleached thermally when heated up to 600°C. In the latter the A-band is unaltered, the B and D-bands are partly bleached and an intense colloid band at 4350 Å which overlaps the E-band is present. The same colloid band is also present in hydrogen-treated silver-activated halides, and its maximum shifts somewhat according to the duration of the anneal and rate of cooling (Fig. 10). The coloured crystals doped with KNO_3 showed some special features. Next to the F-band, strong bands at 2100 Å and 3600 Å are present as well, and a shoulder at 2750 Å is observed. When the irradiation is prolonged a broad band develops overlapping those originally situated at 3250 and 3600 Å (Fig. 11). The 3250 Å absorption is also found in specimens treated in a hydrogen atmosphere, and in this case no trace is found of the absorption at 3600 Å.

TABLE 3.

Absorption bands	KCl + $AgCl_{pure}$ d = 1.14 mm	KCl + $AgCl_{AgNO_3}$ d = 1.16 mm
	log I_0/I	
2200 A	1.65	2.6
2900 B	0.69	0.88
3500 C, D	0.56	0.61
4350 E	0.64	0.59
5600 F	1.66	1.13

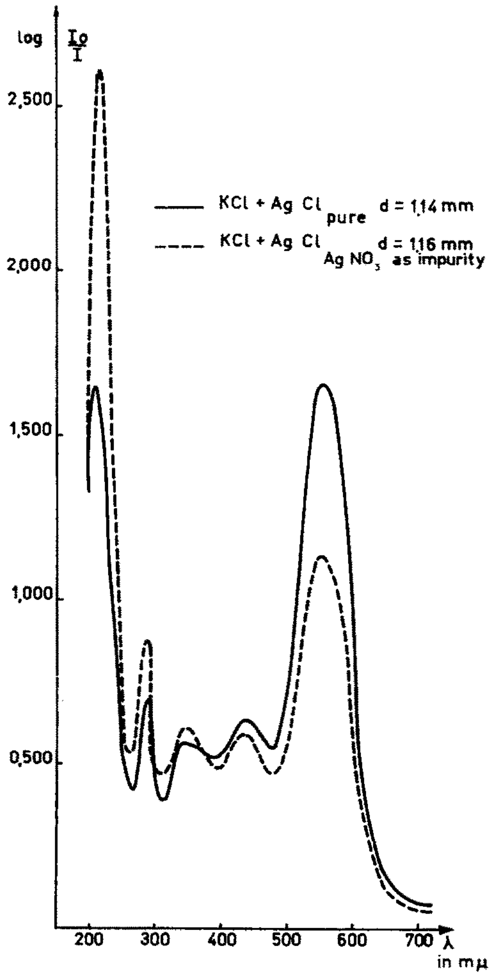

FIG. 7. Spectra of different silver-activated KCl crystals, respectively doped with pure AgCl, and AgCl with $AgNO_3$ as impurity.

THE NATURE OF THE GASEOUS PRODUCT

Attempts were made to determine the nature of the

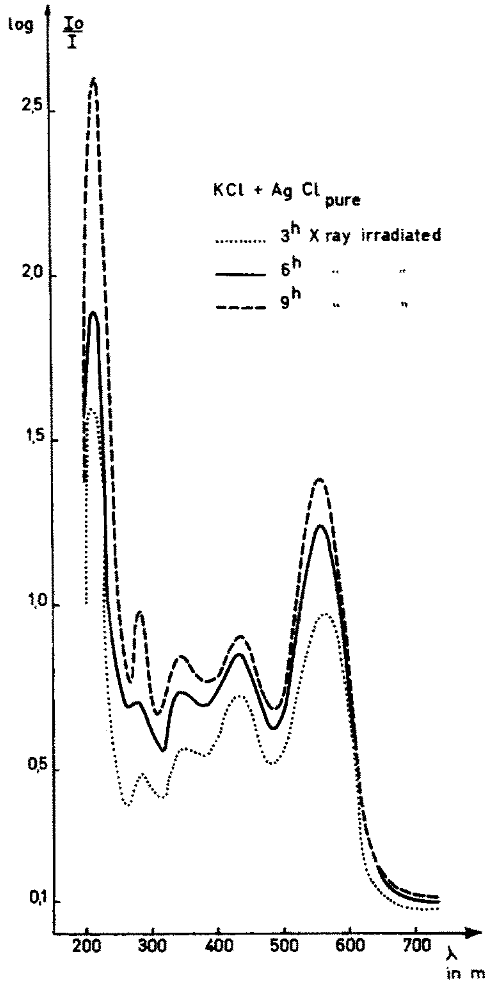

FIG. 8. Relative intensity of the absorption bands in KCl + pure AgCl after different irradiation times.

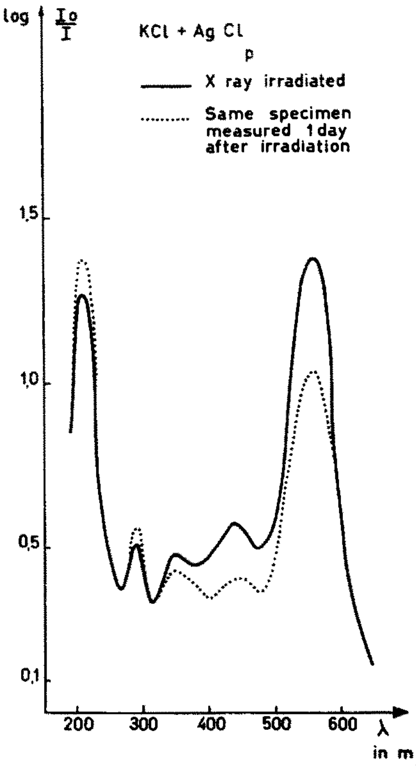

FIG. 9. Influence of bleaching of the F-band in the dark, on the A and B-bands.

gaseous product which was found to be a mixture of oxygen and nitrogen. This conclusion is based on the following experiments:

(i) the gas results from the decomposition of NO_3^- and NO_2^- groups.

(ii) as already stated no reaction between the gas and water could be detected.

(iii) when a quantity of crystals containing cavities are dissolved in gas-free distilled water, the escaping bubbles can be trapped in a test tube where they assemble to a volume of several cm^3. When white phosphorus is brought under water into contact with this gas, white fumes soluble in water develop, but only part of the gas reacts.

(iv) when a crystal doped with $AgNO_3$ is sealed in an evacuated tube and irradiated, it was proved by mass spectroscopy that oxygen and nitrogen were formed. Attempts to examine by mass spectroscopy a bubble captured from dissolved crystals failed.

If we consider the starting and end products we can write the reaction chemically as follows:

$$2Ag^+ + 2NO_3^- \rightarrow 2Ag^0 + N_2 + 3O_2$$

It is however clear that some intermediate stage occurs: as written the reaction only involves a transfer of the electron of the NO_3^- group to the Ag^+. Experimentally it is found that no cavities are formed by a heat treatment alone, even if silver specks are already present; it is necessary to heat the crystals in hydrogen or alkali metal vapour. This means that the surface reaction

$$[H_2 + 2KCl \rightarrow 2HCl + 2K^+ + 2e + 2\square^-]$$

i.e. the electron, the vacancy or both, are essential for the decomposition of the NO_3^- groups and subsequent cavity formation. As the information so far available only permits highly speculative considerations about the details of this reaction, we will not attempt to go into further details. Two points may be noted. First it looks as if clustering of the NO_3^- is also necessary, because the formation of single oxygen atoms does not seem very probable. Secondly volume considerations equally favour such a hypothesis. A NO_3^- group can

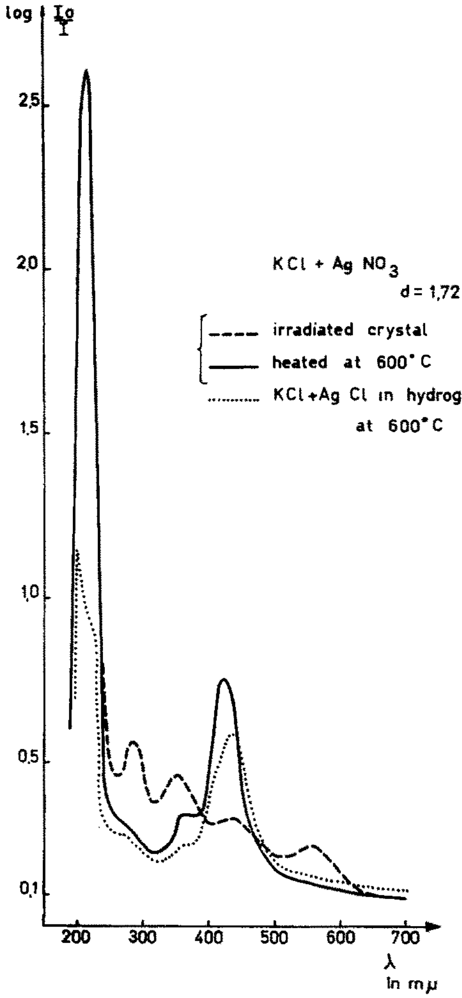

FIG. 10. Formation of the silver colloid band after heat treatment.

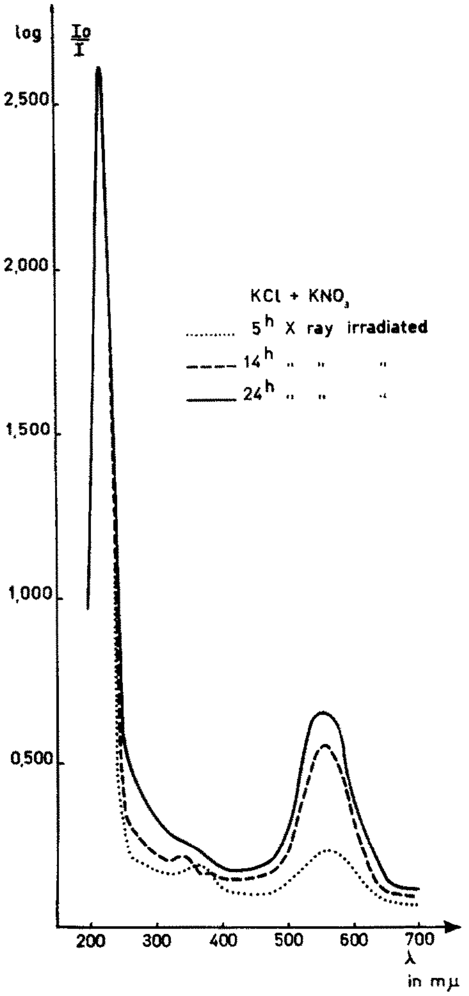

FIG. 11. Absorption spectra of KNO$_3$-doped KCl crystals after different irradiation times.

easily replace a Cl$^-$ ion in KCl. Decomposition of a single group would produce four atoms, or one molecule and three atoms, which would produce a severe hydrostatic pressure if confined to the same volume. Clustering can reduce this considerably, e.g. two neighbouring NO$_3^-$ groups produce four molecules. This view is supported by the experiments with crystals doped with KNO$_3$ in which cavities develop along dislocation lines without the "help" of silver specks.

MECHANISM FOR THE FORMATION AND GROWTH OF THE CAVITIES

Ultramicroscopic examination of the as-grown crystals of the type *a*, *b*, *c*, *d* revealed that they already contained small specks, resulting from the thermal decomposition of the silver nitrate during the growth process. As it was found that most of the cavities contained a silver speck, we must consider the possibility that they are preferentially nucleated around them. This would lower considerably the activation energy for the formation of a cavity. This idea was already put forward by Seitz(8) in an attempt to explain the formation of porosity in Kirkendall experiments. It was suggested on that occasion that small impurity particles were responsible for the nucleation of pores, as this would considerably diminish the required degree of supersaturation of vacancies with respect to a perfect crystal.

To see whether this was the case, or whether the cavities nucleated directly at dislocations, the following experiments were performed.

A crystal was bent, slightly annealed and then treated in hydrogen. It was found that although the newly formed dislocations were decorated with silver, cavities had only developed along "old" dislocation lines, i.e. on pre-existing specks.

When the bent crystal was well annealed at a temperature close to the melting point, and allowed to cool slowly, specks were present along the polygonisation boundaries, and cavities developed around them when the crystals were hydrogen treated.

These experiments indicate that the silver precipitates more readily than the NO_3^- reduction products. This is due, in our view, to the greater mobility of the Ag^+ ion. In the first experiments no cavities were formed along the newly formed dislocation lines because the temperature and time of anneal had not been sufficient to allow movement of a sufficient number of NO_3^- groups towards them.

We imagine the process of the formation and growth of a cavity in the following way. As soon as a small number of gas molecules succeed in agglomerating, they form a center of hydrostatic vacancies. The resulting small agglomerate (let us call it a "micro-cavity") of gas and vacancies has now the ability of rapid diffusion, as this implies only transfer of material from one wall of the "micro-cavity" to the other. As a consequence these micro-cavities will agglomerate, the larger ones growing at the expense of the smaller ones. Agglomeration will mainly take place at the dislocation lines as there is also elastic interaction between the stress field of the micro-cavity and that of the dislocation. This results in the formation of the larger cavities along dislocations.

The gas in this cavity may still be under high pressure, and it will then as a consequence attract vacancies, which will allow the cavity to expand and release the pressure. More gas can now be accommodated. There is then a balance between gas pressure and flow of vacancies towards the cavity.

The growth of a cavity centered on a dislocation probably takes place according to a mechanism similar to that considered by Frank for the growth of dislocated crystals. Consider the cavity centered on a dislocation with screw character, as represented in very schematic fashion in Fig. 12.

It is now clear that growth of the cavity i.e. removal of material from the crystal, will occur preferentially along the steps *AB* and *CD*. Stated in another, equivalent way: vacancies will precipitate along the steps *AB* and *CD* (this process will even be favoured by diffusion along the dislocation line). As a result the steps *AB* and *CD* wind up into a spiral and the situation shown in Fig. 9 follows. The side faces, in which no dislocations emerge, will either grow slowly or not at all at the final stage of the growth process.

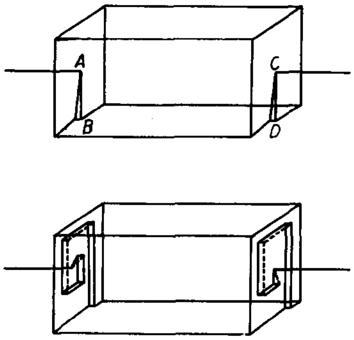

FIG. 12. Schematic view of the cavity formation along screw dislocations.

This explains why the cavities are very often elongated in the direction of the dislocation line, and why faces of the cavity are stepped.

As a consequence of its line tension, the dislocation line will in many cases end at a corner of the cavity.

It is clear that as soon as vacancies precipitate, new vacancies will be produced to maintain the equilibrium concentration. The density of the crystal will be considerably lower in the regions containing cavities. In order to verify this, Dr. Spaepen of the C.S.K. at Mol (Belgium) kindly performed density measurements. The following results were obtained:

Specimen	Density at 15.26°C (g/ml)
Pure KCl	1.98970 ± 0.00002
$KCl + AgNO_3 + H_2$ (bulk)	1.98935 ± 0.00002
$KCl + AgNO_3 + H_2$ (near surface)	1.97610 ± 0.00005
$KCl + AgCl + AgNO_3$ as impurity $+ H_2$ (bulk)	1.98971 ± 0.00002
$KCl + AgCl + AgNO_3$ as impurity $+ H_2$ (near surface)	1.98948 ± 0.00002
$KCl + AgCl + AgNO_3$ as impurity	1.99013 ± 0.00002
$KCl + KNO_3$	1.98931 ± 0.00002
$KCl + Ag_2O$	1.98959 ± 0.00002

This proves beyond doubt that a considerable expansion of the crystals takes place.

DISCUSSION

These experiments illustrate that the gaseous products of a chemical reaction in a solid precipitate along dislocations, if enough thermal activation is present to allow diffusion. The precipitation is made easier still at already existing specks.

One can draw a close analogy between the phenomena described here and the process of hydrogen embrittlement observed in copper (containing copper oxide) for instance. In both cases, a gaseous product is formed (in the latter case water vapour). From our observations it is reasonable to assume that in copper also the cavities will form on dislocations and pin them, thus causing the observed embrittlement. Also, in the case of copper the presence of particles of oxide or of another impurity will certainly favour the formation of cavities.

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