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TEMPERATURE INFLUENCE ON THE POLYGONIZATION PHENOMENON INDUCED ON NaCl SURFACES BOMBARDED WITH ELECTRONS AND ILLUMINATED (*)

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Résumé. — Dans de précédentes études sur la polygonisation des surfaces des halogénures alcalins bombardées par des électrons de moyenne énergie (44 keV) et ensuite illuminées, on avait démontré que la transformation des centres colorés introduits par l'irradiation produit une modification locale du potentiel cristallin, ce qui permet aux dislocations chargées de se déplacer en laissant derrière elles des lacunes.

On présente de nouveaux résultats concernant le développement du phénomène de polygonisation sur des cristaux chauffés à différentes températures, depuis la température ambiante jusqu'à 350 °C, au cours de leur bombardement électronique. Ces études ont été reliées aux mesures au spectrophotomètre avant et après l'illumination des cristaux.

Abstract. — Previous studies of the polygonization phenomenon of alkali halide surfaces bombarded with medium energy electrons (44 keV) and subsequently illuminated have been made [1, 2]. One has shown that the transformation of the colour centres induced by irradiation produces a local modification of the crystal potential, which allows charged dislocations to move, leaving vacancies behind.

New results are presented concerning the polygonization phenomenon in crystals heated at different temperatures from ambient to 350 °C during their electron bombardment, and the studies were correlated with spectrophotometer measurements before and after the crystal illumination.

1. Introduction. — As was already shown in some previous papers [1, 2], medium-energy electron bombardment and subsequent illumination with white light could produce a surface polygonization phenomenon, which consists of a modification in time of the crystal surface microtopography until an equilibrium state is attained, and consequently a polygonal network is formed. Some other experiments have demonstrated that similar processes can occur on alkali halides by vacuum deposition or sputtering of thin films [3, 4, 5, 6], or by irradiation in high vacuum with u. v. light or low energy electrons [7].

From all this experiments it appears very important the fact that the polygonization effect can develop only after the illumination of the previously bombarded surfaces of alkali halides in a thin layer, in which colour centres were introduced. No polygonization lines were observed after thermal annealing in dark-

ness of electron bombarded crystals [8, 2], or if the crystal were γ or X-irradiated so that the bulk became coloured [9].

White light plays a major role on starting and formation of polygonization patterns. By the optical transformation of colour centre (especially the F-centres) a local modification of the microcrystallin potential appears, which might unpin some of the charged dislocations and allow them to move, leaving vacancies behind [10]. At the same time, free vacancies and atoms on the crystal surface migrate to produce clusters or to accumulate at dislocations or vacancy tracks introduced by the dislocation motion. All these processes of surface migration continue to take place until a new equilibrium is attained.

So, taking into account the fact that the polygonization phenomenon is a result of a photomechanical effect [11], it appears important to decide which defects contribute in the illumination stage to the process, and why thermal annealing of colour centres in darkness do not enable such an effect.

To this end, NaCl crystals cleaved from the same block were irradiated with medium energy electrons

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in darkness, at different temperatures between ambient and 350 °C, and subsequently illuminated with white light. Optical absorption measurements were done on each crystal before and after illumination. Microscope observations of the polygonization phenomenon were then correlated with the spectrophotometer measurements.

2. Experimental. — Pure single crystals of NaCl freshly cleaved in air were irradiated in darkness with 44 keV electrons at a current density of about $2 \times 10^{-4} \text{ A cm}^{-1}$. The crystals were heated to different temperatures from ambient to 350 °C during their bombardment, in a furnace fitted to the specimen holder. Temperature was measured to $\pm 5 \text{ °C}$ with a chromel-alumel thermocouple. After bombardment the crystals were kept in darkness in the irradiation chamber for at least 24 h to allow defects to relax. Still in darkness, they were transferred to the spectrophotometer, and absorption spectra were measured at room temperature over the wavelength range 250 to 900 nm. Then the crystals were illuminated with white light and optical microscope studies were made in time to observe the appearance and development of the polygonization phenomenon. After 10 days' illumination, new spectrophotometer measurements were done in the same conditions.

3. Results and discussions. — **3.1 OPTICAL ABSORPTION.** — As it was shown, the relative strength of the optical absorption bands varies with the dose rates [12, 13, 14], and with the impurity concentrations in the crystals [15, 16]. To avoid this all the crystals were cleaved from the same block and irradiated at the same dose rate, in darkness. The only varying parameter was their temperatures during irradiation.

Figure 1 gives the optical absorption bands of eight crystals irradiated at different temperatures from room temperature to 350 °C. Curve 1 represents a typical absorption spectrum for a room-temperature-irradiated crystal showing the characteristic F, R, M and N bands (the R and N peaks are barely resolved). Curve 2, taken on a crystal heated at 45 °C during the electron bombardment, shows an increasing concentration of long-wavelength aggregate centres, at the expense of the F-centres. Thus by raising the temperature the mobility of the vacancies is increased and they can coagulate, forming aggregate centres. The F-centre glow peak decreases on account of the temperature dependence of the F-band formation in alkali halides [17]. Raising the temperature further (curves 3, 4 and 5, taken for crystals respectively heated to 85, 130 and 195 °C), the efficiency of colour-centre production decreases markedly, since the rate of thermal bleaching of the colour centres exceeds the rate of their production. The colour of the crystals changed from dark ambre to light yellow and yellow-blue, for crystal number 5. One can also observe on curves 4 and 5 a peak, increasing in height, at the

FIG. 1. — Absorption spectra of NaCl crystals, irradiated 15 min. with 44 keV electrons at different temperatures : 1. ambient, 2. 45 °C, 3. 85 °C, 4. 130 °C, 5. 195 °C, 6. 260 °C, 7. 310 °C, 8. 340 °C.

wavelength corresponding to R-centres for NaCl, but we have to take into account that these centres are the most unstable to thermal bleaching and do not exist above 50 °C [18]. This 557 nm glow peak appears very markedly for the crystal irradiated at 260 °C, curve 6, the other peaks being very slightly visible. This absorption band, observed also after thermal annealing of heavily irradiated crystals [19], could belong to the colloidal centres [17, 20], formed by thermally activated diffusion of F-centres via a vacancy mechanism and agglomeration to give rise to colloids [21]. Further heating of the crystals during their irradiation, curves 7 and 8 at 310 and 340 °C respectively, results in the annealing of these centres also. The colour of these crystals was now from dark blue-violet to light blue. Irradiation at 400 °C leaves the crystal transparent.

After illumination with white light for 10 days, some of the optical absorption curves are given in figure 2. Judging from the shape of the curves, one can divide the crystals into two groups :

a) those labeled from 1 to 4, showing very slightly visible, optically bleached F and M bands,

b) those labeled from 5 to 8, showing the remaining colloidal peak.

FIG. 2. — Absorption curves of the crystals from figure 1 after 10 days' illumination.

The crystals from the first group have turned into gray, as usual, while the blue crystals have merely lightened.

3.2 POLYGONIZATION. — All the irradiated crystals were studied several times in the period of 10 days' illumination. The illuminated crystals, bombarded at room temperature, show the surface defects characteristic of the electron irradiation, with clusters of defects and strong Lichtenberg figures of electrical discharges along the surface [8, 22], figure 3a. Randomly arranged polygonization lines have appeared, but a pattern like in figure 3b was observed only after 1 day's illumination, on the edge of the bombarded spot.

As the temperature of the crystals during their irradiation is raised, a smaller number of microdefects is formed on the surface by the electron bombardment. Figures 4 and 5 show the polygonization patterns of the crystals heated during their irradiation to 45 and 85 °C respectively. The lines are much finer and the process is far less developed than that for crystals irradiated at room temperature. On the other crystals no polygonization effect was observed, even after

FIG. 3b. — Polygonization of the NaCl crystal surfaces irradiated at room temperature after 1 day's illumination.

FIG. 4. — Polygonization of the NaCl crystal surface irradiated at 45 °C after 10 days' illumination.

FIG. 3a. — Lichtenberg figures on NaCl crystal surfaces irradiated at room temperature.

FIG. 5. — Polygonization of the NaCl crystal surface irradiated at 85 °C after 10 days' illumination.

10 days' illumination. From these results we can conclude :

a) The F-centre concentration plays a major role in the appearance and development of the polygonization phenomenon. As this concentration is lowered, as is shown by the absorption curves, the process of surface polygonization becomes less effective, until it did not anymore appears.

b) The colloids formed in the blue crystals could be deposited at dislocations [22] and pin them. Such a process can hinder the development of the polygonization phenomenon.

From these conclusions, and taking into account that the electric field around the dislocations is reduced as the temperature of the crystals is raised, one can explain why no polygonization process appears when the F-centres were thermally annealed rather than optically bleached.

4. Conclusions. — 1) The heating of NaCl crystals during their medium-energy electron bombardment produces changes in the radiation damage and defect migration on the surface. So by raising the tempe-

rature during the irradiation, one can enhance the conductivity of the crystals, so that those irradiated above 200 °C show surfaces very similar to the freshly cleaved ones.

2) The polygonization effect appears after the sample illumination, and only on crystals which have an enhanced concentration of F-centres, from the first group. Crystals irradiated above 100 °C do not undergo this phenomenon.

3) Irradiation at temperatures between 200 and 300 °C could produce colloidal centres, which might act as pinning points for dislocations and hinder the development of the polygonization process. Also, the polygonization phenomenon was not observed on electron-bombarded crystals which were subsequently thermally annealed in darkness between 200 and 400 °C.

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