

NEAR SURFACE PROPERTIES OF QUENCHED X-IRRADIATED NaCl SINGLE CRYSTALS

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The distribution of crystal lattice defects has been investigated in quenched and X-irradiated synthetic NaCl single crystals. Optical absorption in the 380–810 nm range, X-irradiation time dependence of optical absorption at 465 nm and dislocation density were measured for the samples, which were stored for several months in darkness. The results of these measurements indicate that the concentration of anion vacancies near the surface of the crystals is smaller than that in the bulk of the crystal. It is suggested that this effect is due to the higher concentration of OH⁻ impurity in the near-surface layers of the crystals than that in the bulk of the crystal.

1. Introduction

The type and concentration of point defects found in crystals and interactions between these defects are reflected in some of the physical properties of the crystals. The occurrence of defects is connected mainly with the history of the crystal and in particular with its previous treatment. For example, a peculiar manner of thermal treatment may give a definite kind of point defects [1].

The crystal lattice defects arise in real crystals in temperatures not equal to absolute zero. However, the concentration of these defects is very small in thermal equilibrium in room temperature. It is necessary to obtain these defects in higher, not equilibrium concentrations, in order to investigate their behaviour and their influence on crystal properties.

Vacancies are one of the fundamental types of point defects. They influence such properties as electric conduction, strength of the crystals, optical absorption, thermal conduction *etc.* There are three main methods of obtaining vacancies in higher concentration. These are: quenching, irradiation with nuclear particles (*e.g.* neutrons, α -particles) as well as γ - and X-rays, and plastic deformation. The irradiation and plastic deformation generally give not only vacancies in crystals, but they cause the generation of many other

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defects (in the first case mainly interstitial atoms and dislocations in the second). Vacancies are principally generated as the result of quenching.

Quenching consists in heating the crystals at a high temperature, the so-called quenching temperature T_q , in which the crystal reach the thermal equilibrium condition and later cooling the crystals as rapidly as necessary, to freeze defects in quantity characteristic for temperature T_q . The concentration of point defects in this temperature is given by the equation [2]

$$n = N \cdot \exp(-E/kT_q),$$

where N is the number of lattice points, E the energy of defect generation, and k Boltzmann constant. The equilibrium in temperature T_q is obtained by continuous generation and annihilation of vacancies on the inner and outer surfaces of the crystals. This is connected with high mobility of vacancies in high temperature. As the crystal is strongly cooled to a lower temperature it may not reach the intermediate equilibrium states, because vacancies mobility exponentially decreases with decreasing temperature. The concentration of vacancies characteristic for high temperature T_q may be obtained in this manner.

The quenching is especially applied in cubic centered metals. It gives the possibility of investigation of the influence of vacancies on different properties of individual samples (e.g. [3, 4]). Investigations of vacancies, obtained by this method, may be enriched in alkali halide crystals due to colour centres connected with their existence (the influence of quenching on the colour centres was discussed in [5]) and due to the effective electric charge possessed by these vacancies. Schottky's defects are the predominant disorder in both sublattices in NaCl-type crystals [6]. Because of charge neutrality of the crystal and correlation between electron and hole centres connected with vacancies of respective sublattices [7], investigations of defects of one of them may give information about the vacancies of both sublattices.

The investigation of the influence of quenching on the behaviour of point defects in NaCl single crystals were performed by measurements of optical absorption and dislocation density. The results of the investigations of electron colour centres distribution, in particular F centres [7], allowed for conclusions to be drawn about the behaviour of these type of defects in quenched NaCl single crystals.

2. Experimental procedure

NaCl single crystals obtained by the Kyropoulos technique (*in situ*) were used for investigations. The crystals of about $7 \times 7 \times 20$ mm³ size were cleaved from the large boules obtained and heated *in situ* at 610°C for 6 hours. Next, they were quickly cooled at room temperature. The crystals were placed on thermally insulating material in order to avoid stresses on the surfaces of the crystal during this fast cooling. Crystals prepared in this manner were then enwrapped in Al foil and X -irradiated at anode voltage $U = 200$ kV and anode current $I = 6$ mA at a distance of about 15 cm from the anode of the radiation valve. These condition of irradiation allow for a homogeneous colouring of all the crystal to be achieved. The crystals were then stored in darkness for several months.

From prepared in this manner crystals slabs were cleaved perpendicularly to their length of thickness of about 1.0 to 1.5 mm, and measurements of optical absorption at 380–810 nm light wave-lengths were performed using a VSU 2G spectrophotometer. Next measurements of dislocation density were performed using the etch pits technique described in [8].

After absorption measurements and bleaching the crystals with daylight, the samples were *X*-irradiated again at the voltage $U = 65$ kV and $I = 10$ mA for 5 hours. After performing optical absorption measurements in the *F*-band, the samples were heated at 650°C for 24 hours and next cooled at a rate of about $0.5^\circ\text{C}/\text{min}$. They were *X*-irradiated in the conditions given previously and the optical absorption in the *F*-band was measured again.

Afterwards the optical absorption coefficient was measured as the function of irradiation time for a near surface slab and a second one obtained from the bulk of the large crystal also at irradiation conditions $U = 65$ kV and $I = 10$ mA.

3. Results

The results of optical absorption measurements as a function of the position of the cleaved slabs in relation to the external crystal surface are shown in Fig. 1. The numbers at the absorption curves refer to the position sequence of slabs with respect to the external

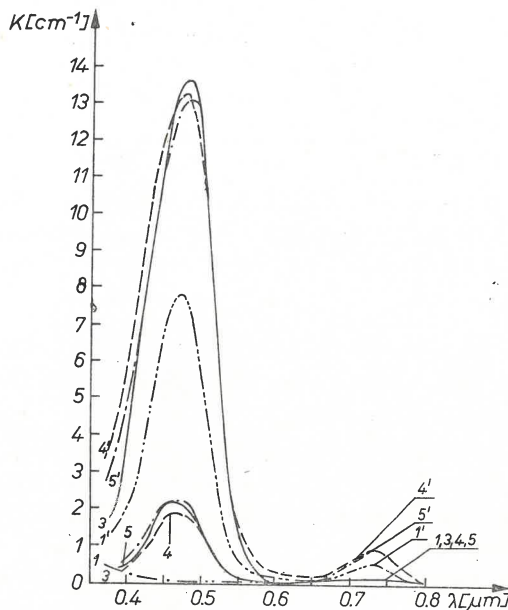


Fig. 1. Wave length dependence of optical absorption coefficient k for specimens obtained from quenched crystal. The curves are numbered according to the location of slabs in relation to the outer crystal surface. Curves designated with prime numbers correspond to optical absorption measured immediately after several months of storage in darkness, unprimed curves — after daylight bleaching and *X*-irradiation

crystal surface, which is perpendicular to its length. The curves designated by unprimed numbers refer to absorption measured on crystals immediately after several months of storage in darkness, primed numbers refer to absorption curves obtained after bleaching and another irradiation of samples. It may be noticed that optical absorption with maximum at 465 nm, which corresponds to the *F*-centre [7], of the near-surface specimen represents half of optical absorption of the remaining samples (for specimens which were bleached and *X*-irradiated again) and is approximately equal to zero for the near-surface specimen (nr 1). This optical absorption difference may be seen with eyes alone, and a distinct separation appeared between areas having colour centres and those with uncoloured ones. The *M*-band [7] appears for the 1', 3', 4', and 5' samples at 730 nm. In the discussed region of optical absorption the absorption spectrum of investigated samples shows a lack of other more complicated electron centres.

In order to compare the properties of the investigated crystals with initial material which did not undergo the thermal treatment described in Section 2, measurements of colourability under the influence of *X*-irradiation were performed for different samples. Optical absorption coefficient in the *F*-band of the samples obtained from the same boule *versus* irradiation time is shown in Fig. 2. Curves 1 and 2 refer to the samples cleaved

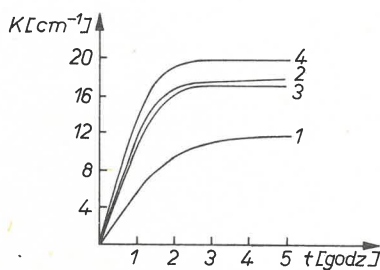


Fig. 2. *X*-irradiation time dependence of optical absorption coefficient at 465 nm. 1—near-surface slab of quenched crystal, 2—inner slab of quenched crystal, 3—as cleaved from crystalline boule slab, 4—*X*-irradiated slab after daylight bleaching obtained from the same crystalline boule.

from the near-surface and from the inner part of quenched crystals, respectively. Curve 3 corresponds to the sample as cleaved from the crystalline boule, curve 4 to the sample *X*-irradiated and bleached with daylight.

The absorption of samples obtained from the quenched crystal after daylight bleaching and *X*-irradiation is shown in Fig. 3a. The absorption of the same samples after heating them at 650 °C, as described in Section 2, is shown in Fig. 3b. Indices correspond to those of Fig. 1.

The results of dislocation density measurements are given in Table I. The samples were numbered according to their position in relation to the external crystal surface. The dislocation density was evaluated as the average calculated from measurements for five different areas of individual samples. The results given in the Table allow one to conclude that the dislocation density of different samples is approximately the same.

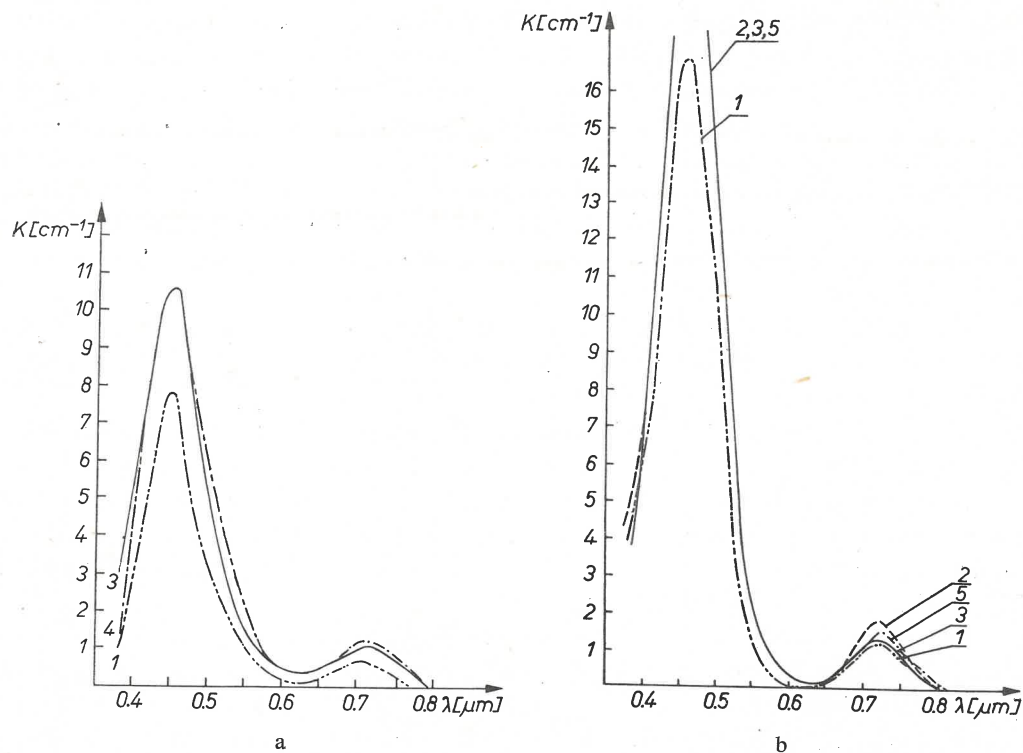


Fig. 3. Optical absorption of samples obtained from quenched crystals numbered as in Fig. 1. a — absorption of irradiated samples previously daylight bleached, b — absorption of the same samples X-irradiated after heating them at 650°C

Average dislocations density in 1 cm² of {100} surfaces

TABLE I

Sample number	$A \cdot 10^{-5}$
1	1.4
2	1.6
3	1.1
4	1.1

4. Discussion

The decreased optical absorption in the *F*-band which is characteristic for the near-surface specimens of quenched crystal (Fig. 1), may be explained by the ionization of *F*-centres by leaving electrons and anion vacancies in the near-surface layer, ionization colour centres connected with the diffusion of components to the surfaces, or *F*-centres diffusion to surfaces and their ionization at this stage. The appearance of an uncoloured

layer only in quenched crystals (the samples obtained from slowly cooled crystals were uniformly coloured throughout the crystals) suggests that in the near-surface layer traps are present either for the F -centre, or for its components. From our discussion the influence of dislocation, which may be the site of F -centre agglomeration or traps for its components, may be excepted. In the first case the increased resistance of the colour centres for bleaching will appear in the near surface layer [9], which is in contradiction with experimental data. The second case may be realized, if the dislocation density in the near-surface layer is very different from that in the bulk of the crystal, which is inconsistent with results given in Table I.

Ennow [10] in his investigations of thermally stimulated electron emission in quenched LiF crystals find surface and near-surface electron traps. The comparison of the thermally stimulated electron emission maximum due to surface traps with the maximum due to the F -centre indicates their different localization, but nevertheless the author suggests that both maxima are connected with anion vacancies. The difference in the maxima localization according to [10], is due to the fact that newly created F -centre is located in the outer atomic layer of the crystal. It was found in the cited paper that electrons trapped on the surface may be retrapped by traps lying at larger distances from the crystal surface. This problem was not sufficiently explained.

Our results show that electron traps which appear in the near-surface layer, give no absorption in the 380–810 nm range. It is known (*e.g.* [11]), that daylight bleaching of previously coloured samples does not cause the removal of defects connected with existing colour centres. It is known too [12], that the rate of colourability saturation is a function of initial concentration of point defects. In particular, in the F -band colouration, saturation is a function of the concentration of anion vacancies. The results given in Fig. 2 show that the concentration of anion vacancies in the near-surface layer is distinctly smaller than that in the bulk of the crystal. As may be seen from Fig. 3, the colour centre concentration does not reach the same value in all slabs of the crystal even after heating. Because of the originally homogeneous crystal colour, the explanation seems to be the following: according to [10] electron traps are present in the near-surface layer, but other than anion vacancies. The electrons follow to the traps leaving free vacancies. These may be due to ionic processes the destruction of colour centres, which occur in stored in darkness alkali halide crystals [13]. The free vacancies may diffuse to crystal surfaces or other sinks of vacancies, where annihilation or transformation to other kinds of defects (*e.g.* vacancies aggregation, jog on dislocation line, dipole impurity-vacancy *etc.*) occur.

Now we have to explain, which kind of defect may be responsible for electron trapping in the near-surface layer of the quenched crystal. It seems that this role may be ascribed to the OH^- groups which may build up to NaCl crystals from air environment both during growing and heating [14]. In [15] it was found that in photochemically coloured crystals the concentration of F -centres decreased when OH^- concentration increased. It is quite possible that this could take place in crystals coloured with X -rays. So, OH^- groups seem to be responsible for trapping of electrons released from colour centres as a result of ionic processes of their destruction. According to [16], OH^- groups may appear in higher concentration in near-surface layers with regard to the bulk in quenched crystals.

5. Conclusions

The uncoloured near-surface layer appears in crystals coloured with X -rays after quenching and storing them in darkness for several months. The concentration of vacancies is smaller in this layer than in the bulk of the crystal. It seems that this is connected with slow ionic processes of destruction of colour centres occurring in crystals at room temperature and with the appearance of OH^- ions in higher concentration in near-surface than in the bulk. This specific behaviour of the near-surface layer must be taken into account when discussing experimental data obtained for alkali halide crystals previously quenched and stored in room temperature.

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