

DISTRIBUTION OF POINT DEFECTS IN X-IRRADIATED NaCl CRYSTALS AGED AFTER QUENCHING

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The differences in the concentration of lattice defects in X-irradiated NaCl single crystals aged after quenching, and without thermal treatment, and in as cleaved crystals have been examined. Optical absorption in the 380 to 810 nm range, dielectric losses at 1 kHz in the 50 to 450°C range, and density measurements have been performed. It is presumed, that the peculiar behaviour of the near-surface layer of a quenched crystal revealed by these measurements may be attributed to OH⁻ ions and vacancy aggregation, which appear in this layer in higher concentration.

1. Introduction

Quenching is one of the processes which provides a means of introducing a well-defined concentration of point defects into a crystal. It differs from other processes, such as irradiation with a high dose of X or γ rays or nuclear particles, and plastic deformation. Namely, under proper conditions essentially only vacancies are generated in this way, without any other lattice defects being produced [1]. Quenching a crystal from a temperature T_q to, say room temperature, yields a concentration of vacancies which is characteristic of the thermal equilibrium at temperature T_q [2]. This procedure is used very often for preparing alkali halide crystals [3, 4, 5].

Ageing of crystals consists in maintaining them at a definite temperature for a period of time long enough for thermal equilibrium under these conditions to be achieved. The distribution of point defects in a quenched crystal during this process changes, and the form in which they were in the crystal prior to quenching changes, too. Crystal properties (e.g. mechanical) obtained as a result of quenching may become restored after ageing to those before quenching. Such a phenomenon was observed in KCl crystals when investigating the dependence of microhardness on the concentration of Sr²⁺ impurity ions [6].

This effect, however, does not have to appear in all cases of ageing. The near-surface layer of quenched crystals was observed to behave peculiarly [7, 8], and the explanation of this behaviour given in [7] is far removed from the hypothesis of a non-uniform distribution of point defects stipulated in [8].

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The peculiar behaviour of the near-surface layer of coloured crystals was also mentioned in [9]. The authors of this paper observed a near-surface bleached layer in electrically coloured KBr crystals which were heat treated under approximate conditions. The main considerations of this work concerned the effect of annealing on crystal structure defects, however, and this layer was not dealt with in any detail.

In the present work we try to find what the distribution of point defects is like in *X*-irradiated synthetic NaCl single crystals aged after quenching. An attempt is also made to obtain the quantitative differences in the concentration of the various types of point defects. The conclusions and estimations are arrived on the basis of measurements of optical absorption, dielectric losses, and density.

2. Experimental procedure

Synthetic NaCl single crystals were used. The measurements were done for three types of crystals: quenched, irradiated, and as cleaved from crystalline boules. Samples of all three types were cleaved in the form like that described in [8] from the same boules. The quenched crystals were the same as those described earlier [8]. The irradiated crystals were submitted to *X*-ray exposure under the same conditions as the quenched ones without thermal treatment. All the crystals were stored in darkness for a period of several months.

Slabs about 1 mm thick were cleaved from the crystals prepared in the manner just outlined perpendicularly to their length. The samples obtained from the coloured crystals were bleached in daylight. Next, they were *X*-irradiated for 5 hours (anode voltage 65 kV and anode current 10 mA) at a distance of about 10 cm from the anode of the *X*-ray tube. Typical absorption curves in the wavelength range from 380 to 810 nm were obtained with the use of a VSU 2G Zeiss spectrophotometer. The measurements of absorption in the F-band were made with a Zeiss Spekol spectrophotometer.

Measurements of dielectric losses were carried out in the range of temperatures from 50 to 450°C at a frequency of about 1080 Hz. The temperature was measured with an Fe-Konst thermocouple. The dielectric losses were measured by the well-known ac bridge technique (*cf.* [10]). The input signal from a ZOPAN RC generator was led to a Tesla BM 401 capacitance bridge. The output signal was detected with a typical valve amplifier. The dielectric losses in the range of $\tan \delta$ up to 0.5 may be measured with this apparatus.

The density measurements were performed by the suspension method [11]. A specially matched liquid was used in the experiment. The density of the liquid was higher than that of the crystal at room temperature. The two densities equalized at a temperature somewhat above 30 °C. Bromoformium constituted the basic substance of this admixture. This liquid was put into a cylindrical glass tube about 20 cm long. The temperature of the liquid at the bottom and top of the tube was kept constant through its contact with the brass stoppers. The temperature of the brass stoppers was stabilized in turn by a continuous flow of water from ultrathermostats. Many temperature intervals between the upper and lower stoppers were used in the measurements. The best reproducibility of results was obtained when the temperature of the upper stopper was 35 °C and that of the lower one 25 °C. Subsequent measurements were performed under these conditions.

3. Results

A typical absorption spectrum for the crystals used in the experiments is shown in Fig. 1. Two maxima appear in the relevant region of absorption. These maxima are referred to the electron colour centres, namely *F*- and *M*-centres. The optical absorption is given in arbitrary units because of the representative character of the given absorption curve. In every case we observe distinct correlation between absorption at the *F*-band maximum

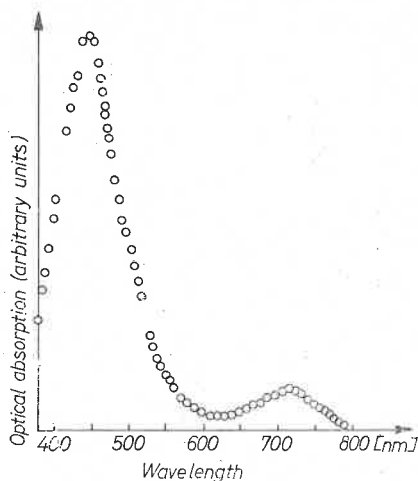


Fig. 1. Typical wavelength dependence of optical absorption of *X*-irradiated specimens. The optical absorption is given in arbitrary units.

α_F and the *M*-band maximum α_M , according to the quadratic relation between α_M and α_F [13].

The concentrations of *F*-centres in the investigated samples, calculated on the basis of Smakula's formula with an oscillator strength $f = 0.81$ [14], are given in Table I. The numbers of the samples used in this table and in the following considerations refer respective-

TABLE I

Concentration of <i>F</i> -centres $n_F \times 10^{17}$ per cm^{-3}	
Sample number	$n_F \times 10^{17}$
1	0.80
2	1.33
3	1.35
4	1.40

ly to the near-surface specimen of the quenched crystal (1), the specimen cleaved from the inner part of the quenched crystal (2), the sample obtained from the *X*-irradiated crystal without thermal treatment (3), and the as cleaved from crystalline boule specimen (4). It is seen from this table that the concentration of *F*-centres in specimen 1 is somewhat

higher than the half of the concentration of F -centres in other specimens. On the other hand, the concentration of F -centres in the remaining samples is almost the same.

The measured dielectric losses are presented in Fig. 2. The maximum of these losses, located for the given frequency of external electric field at about 270 °C, is associated with the conduction losses effected by anionic and cationic impurities [15]. The numbers of

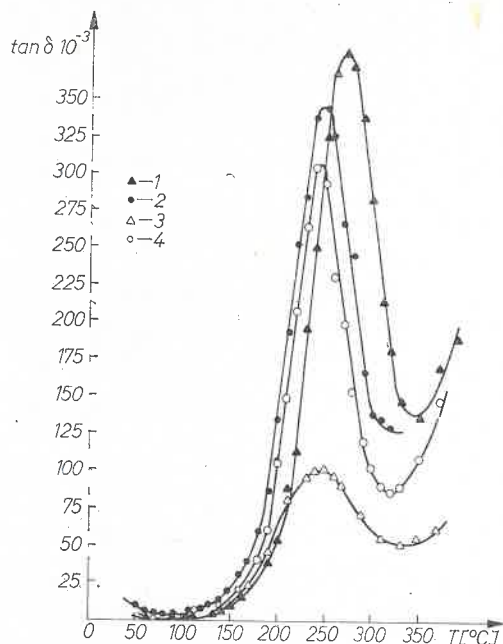


Fig. 2. The temperature dependence of $\tan \delta$. 1 — near-surface slab of quenched crystal, 2 — slab cut from inner part of quenched crystal, 3 — sample of irradiated crystal without thermal treatment, 4 — as cleaved specimen

the curves have the same meaning as before. It may be noticed from this figure that the maximum of dielectric losses for the near-surface specimen is shifted by about 30 °C towards the higher temperatures.

The densities of the investigated samples found on the basis of suspension experiment are given as averages of three independent measurements in Table II. The numbers in the table refer to the same samples as in Table I. The value of density was obtained from measurements with a 10 °C gradient of temperature (the temperature at the top of the

TABLE II

Density of samples in g/cm ³	
Sample number	Density
1	2.19046
2	2.19067
3	2.19075
4	2.19080

tube was 35 °C and that at the bottom was 25 °C). From Table II one may conclude that only density of the near-surface specimen is distinctly different than that of the sample cleaved from the inner part of the quenched crystal.

There remains the question of the experimental accuracy of the result of density measurements. We shall estimate only the error made when determining the relative density, because we are interested in the differences between the densities of the various samples. To do this, we must take account of the accuracy with which the location of the samples immersed in the liquid is determined, together with the variations of liquids density with temperature. For the latter, the temperature gradient in the region of the tube used in the experiment had to be known. On consequence, this estimation shows that the differences of crystal densities were obtained with an accuracy not worse than 0.00007 g/cm³.

Recapitulating, we may conclude that the differences in the densities of samples 2, 3 and 4 which are seen in Table II are due to experimental error. Considering the errors in determinations of the liquid density, temperature and the location of the samples yields the accuracy with which the absolute densities of the samples are established.

4. Discussion

The results of the optical absorption measurements given in Fig. 1 suggest that the possibility of optical bleaching of the near-surface layer may be excluded. The optical absorption curve of Fig. 1 has the same run for the quenched samples immediately after ageing at room temperature bleached and *X*-irradiated again, as well as the curves for *X*-irradiated and as cleaved specimens. The absorption differs from sample to sample by the magnitude of optical absorption only, but in every case we observe only two bands due to the *F*- and *M*-centres. The absorption curve of the near-surface specimen immediately after ageing in darkness at room temperature is the sole exception from this regularity. In this case the curve is smooth; the optical absorption coefficient is $k = 0.05 \text{ cm}^{-1}$ with a slight increase at the shorter wavelengths. If the near-surface layer has been bleached in daylight, maxima associated with more complicated electron centres should appear (e.g., [16]). The peculiar behaviour of the near-surface layer of the quenched crystal remains. The results given in Table I were obtained after bleaching the crystals in daylight under *X*-irradiation conditions, which yield saturation colouration of the crystals. As the *F*-centre concentration at this saturation is a function of initial concentration of single-anion vacancies [17], we may conclude that the near-surface slab contains such vacancies in concentrations lower than that of the other specimens. In an earlier paper [8] it was suggested that slow ionic processes cause the destruction of the colour centres, and the electrons released from these centres become trapped. The anion vacancies from these centres might annihilate or form a new type of defects. Which of these processes actually takes place is still unknown.

Now, we shall try to explain what happens in the uncoloured near-surface layer. This bleached layer arises in quenched crystals only and this was stated to be so because of the increased concentration of OH⁻ ions in the near-surface layer [8]. This assumption is confirmed by dielectric losses measurements, because the temperature of the maximum

of $\tan \delta$ in the near-surface layer is shifted towards the higher temperatures. It was shown in [15] that the location of the $\tan \delta$ maximum shifts towards the higher temperatures with increasing concentration of anionic impurity.

The magnitude of the $\tan \delta$ maximum described above only depends on the thickness of the specimen. It seems that conduction losses and the space charge accumulated at the electrodes due to the concentration of the anion or cation impurity are responsible for these maxima [18]. These losses are not associated with impurity-vacancy dipoles or their complexes, as is observed at lower temperatures. Hence, information regarding the concentration of these defects and, indirectly, about the concentration and form of the anion vacancies released from the F -centres after electron are trapped, is unavailable.

It is possible, however, to estimate the concentration of vacancies in the near-surface layer relative to that in other crystals on the basis of known densities of these specimens. The density of the near-surface slab was 0.00021 g/cm^3 lower than that of the specimen taken from the bulk of the same quenched crystal. If we assume that divacancies are responsible for this difference in density, we may estimate the difference in their concentration [19]. As an outcome of their measurements Esterman *et al.* [19] obtained that the concentration of the divacancies is about twice the concentration of F -centres. We obtain from our calculation that the concentration of divacancies in sample No 1 is higher by $2 \cdot 10^{18} \text{ cm}^{-3}$ than in the remaining samples.

This value, obtained as an estimation from the density measurements is seen to be too large, when compared with the data given in the Table I. Indeed, the difference goes in the wrong direction (the concentration of anion vacancies found from Table I is smaller by about $0.6 \cdot 10^{17}$ in the near-surface layer, *i.e.* the concentration of the divacancies is smaller by about 10^{17}). However, if we take into account that the rate of colouration of the near-surface specimen is lower than that of the other samples, we may conclude that the concentration of vacancies is higher in this layer than in the bulk. Furthermore, we may conclude that these vacancies stay in this layer as aggregates around lattice defects (*e.g.*, dislocations) [20].

The latter assumption is in accord with previous investigations. Matei and Serban [21] observed that in KCl crystals stored in darkness at room temperature there is a transformation of F -centres to α -centres. It was suggested that aggregation of the F -centres was especially efficient at the charged lattice defects (*e.g.*, dislocations, impurities *etc.*). The processes leading to the formation of an uncoloured layer in quenched crystals have a rather slow diffusion character and they cause aggregation in near-surface layer. The character of the processes of aggregation may be analogous, as had been observed in the near-surface layer of KI crystals freshly cleaved in vacuum [22]. The centres of such aggregation may be attributed to charged OH^- ions.

5. Conclusions

In NaCl crystals grown *in situ*, X -irradiated after quenching, the uniform distribution of colour centres and vacancies changes once they are aged at room temperature. It has been suggested that an outcome of quenching is a higher concentration of OH^- ions in the

near-surface layer than in the bulk of the crystal. It seems that this anionic impurity may constitute a trap for electrons released in the ionic processes of colour centre destruction and may form a centre of vacancy aggregation. The aggregates of the vacancies, which appear in the near-surface layer, cause a change in the properties of the crystals at the surface, such as colouration, density, and presumably many others.

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