AN INVESTIGATION OF THE IMPURITY DISTRIBUTION INFLUENCING THE MECHANICAL BEHAVIOUR OF NaCl CRYSTALS BY MEANS OF THE ELECTRON MICROSCOPICAL DECORATION METHOD AND MICROHARDNESS MEASUREMENTS

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The investigation of the impurity distribution of the real crystals at various temperatures is important from the view-point of producing extremely pure crystals as well as with regard to a better understanding of the structural properties depending upon the impurity distribution. The greater part of the experimental methods (chemical methods, optical or X-ray spectroscopy etc.) are only suitable to detect the total impurity content. The electron microscopical decoration method, on the other hand, enables the topographical investigation of the various formations of the contaminants, which became separated from each other. This method is based on the fact that the decorating particles are preferably condensed on the crystalline surface at point defects formed by impurity ions [1].

Beside the electron microscopical decorating method suitable to investigate directly the impurity distribution, also many other indirect methods are used (e.g. electrical conductivity measurements) [2, 3]. In this paper experiments are described which combined small load microhardness measurements as carried out previously by MORLIN [4] with the electron microscopic decoration method.

The point defect structure was introduced into the samples by quenching, assuming that the quenching fixes with good approximation the impurity distribution formed at the temperature the crystals were quenched down from. The quenching rate was approximately 200 °C/minute, and the crystals were quenched down to about 160 °C in an evaporating equipment. At this temperature first gold and then carbon was evaporated onto the samples. Other samples were treated similarly in a furnace of small heat capacity. With these latter crystals micro-hardness measurements were carried out with a load of 4 ponds.

Since among the contaminants which are usually present in the alkali halides, the mono-, and bivalent cation impurities play a basic role, partly extremely pure crystals, and partly crystals with dominant monovalent or bivalent cation impurities were chosen for the experiments.

The following types of samples were used:

a) single crystals grown from the melt, the starting material was pro analysi purity. According to our measurements these crystals contained mainly 10^{-2} mol/mol calcium,

b) crystals grown from the same basic material to which, however, 0.1 mol/mol silver was added,

c) rock-salt single crystals from the mines of Wieliczka with a calcium content as low as 10^{-4} mol/mol, and finally

d) NaCl single crystals with an overall impurity content as low as $2 \cdot 10^{-7}$ mol/mol.

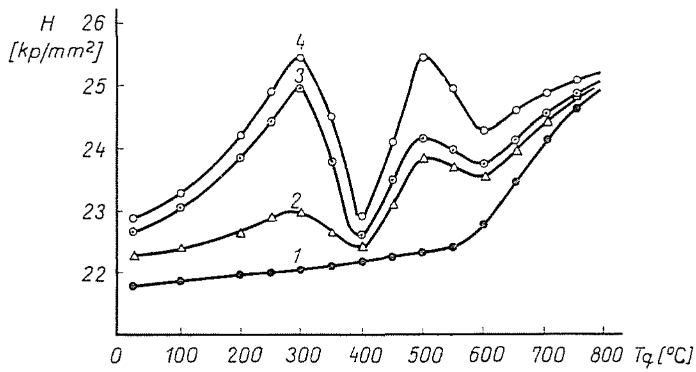


Fig. 1. Impurity induced changes in the microhardness values on quenching

During the quenching no plastic deformation took place, and according to the etch pit technique, the dislocation density remained practically constant; consequently the role of the plastic deformation in the change of the microhardness values could be practically neglected. The dimensions of the samples were $2 \times 5 \times 5$ mm^3.

The role played by the impurities in the change of the micro-hardness values due to the quenching of the crystals is presented in Fig. 1.

Curve 1 refers to high purity material, this curve has neither maxima nor minima. The contaminated crystals, however, show both maxima and minima.

With the crystals from Wieliczka (curve 2) the mono-, and bivalent impurities were present only in traces. Here two weak maxima and minima developed. With the so-called "pure" crystals grown from the melt the first maximum increases considerably (curve 3) whereas with the crystals contaminated deliberately with silver the second maximum becomes more pronounced.

From the fact that the maxima and minima develop below 600 °C, while above 600 °C the curves tend to converge it seems to follow that the change in micro-hardness due to quenching can be traced back to two different types of processes. The changes below 600 °C can be mainly put down to the impurity content of the crystals whereas the convergence of the curves observed above 600 °C seems to indicate the presence of precipitates formed from vacancies. They presumably develop during quenching by the association of large mobility thermal vacancies.

In order to test this hypothesis quenching experiments were carried out in an evaporating equipment at a pressure of 10^{-5} torr.

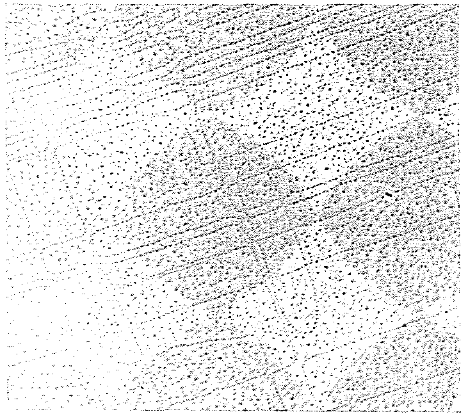
The crystals were annealed at various temperatures for several hours, and then quenched down to 160 °C at a rate of 200 °C/minute. At this temperature (160 °C) nearly the same amount of gold and carbon was evaporated onto the quenched surfaces. The gold nuclei tracing the structure of the crystal surface adhered to the carbon film which was detached from the crystal surface, placed on a microgrid and investigated electron microscopically [4].

Fig. 2 presents electron micrograms of NaCl crystals containing various amounts of impurities and quenched from 300 °C, 400 °C, 500 °C and 700 °C.

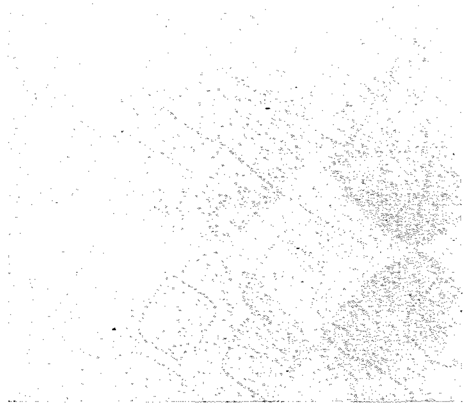
The two main characteristics of the pictures — disregarding certain repeatedly appearing lines which are not typical to the quenching temperature — is conspicuous. One feature seems to point to the fact that the precipitation of impurities takes place only with quenching temperatures of 600 °C and 700 °C except for the very pure materials, which do not show precipitation at all (see the first column of the pictures). Another interesting feature shows the crystal, and quenching temperature dependence of the precipitating impurity distribution and the shape of the individual precipitates (second, third and fourth column).

According to the micrograms one may say in connection with the micro-hardness changes that in the case of quenching from 300 °C, 400 °C and 500 °C the impurities are fully dissolved and no precipitates can be observed, consequently at these temperatures the increase of hardness at 300 °C and 500 °C, and its decrease at 400 °C are not so much related to large impurity complexes but may be rather due to small groups of impurity ions, vacancies or even individual ions. The coagulations in the contaminated crystals observed upon quenching from 600 °C may be regarded as a purifying process taking place in the samples. As a consequence the micro-hardness decreases which means that the mechanical state of the contaminated material approaches that of the pure crystals. At quenching from 700 °C this effect becomes more pronounced.

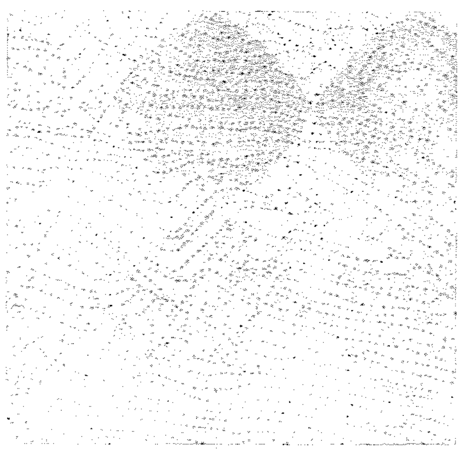
As a result one may conclude that the observed convergence of the curves can be explained by this purifying effect or else by the decrease of the role played by the contaminants, at the same time the increase of the curves above 600 °C indicates the formation of new complexes of thermal vacancies.



a) 300 °C

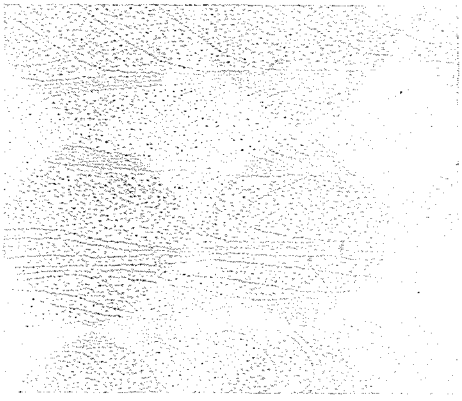


b) 600 °C

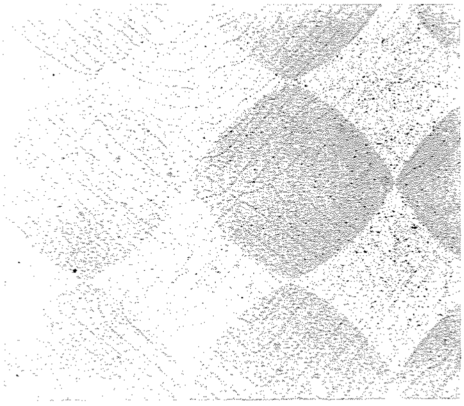


c) 700 °C

Fig. 2. Column 1. The development of the surface of a "pure" crystal on quenching. No formation of precipitates can be observed. $2 \cdot 10^{-7}$ mol/mol Ca contamination



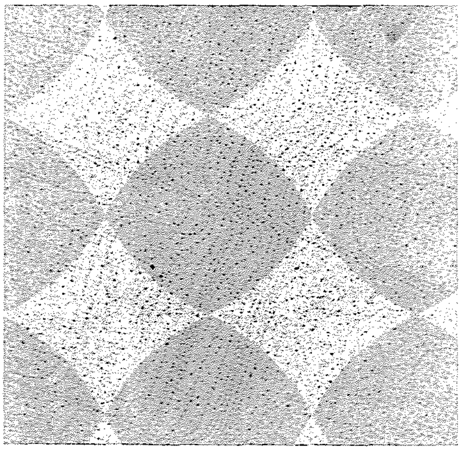
a) 300 °C



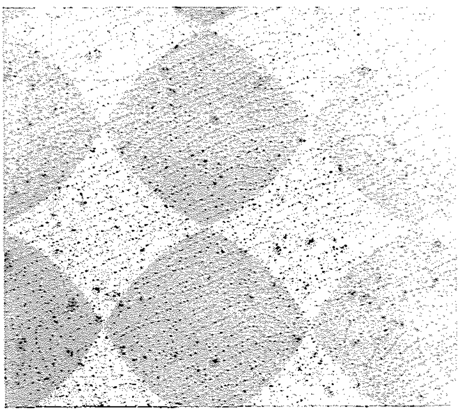
b) 600 °C

c) 700 °C

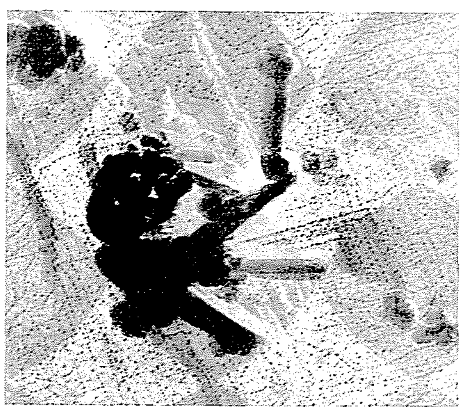
Column 2. The development of the surface of rock salt from the mines of Wieliczka on quenching. At higher temperatures, formation of precipitates can be observed (600 °C, 700 °C). 10^{-4} mol/mol Ca contamination



a) 300 °C

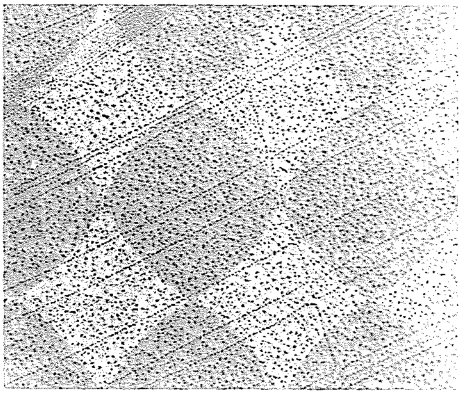


b) 600 °C

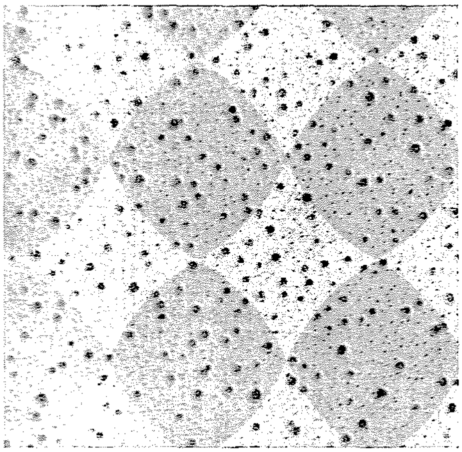


c) 700 °C

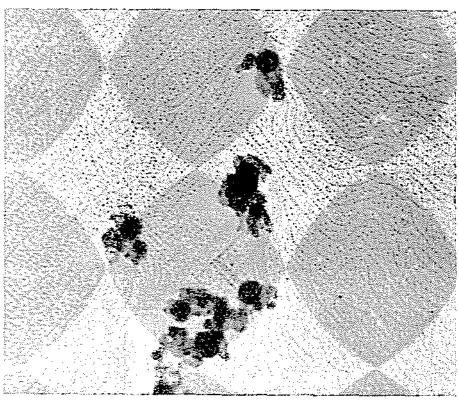
Column 3. The development of the surface of NaCl crystals grown from the melt on quenching. At 600 °C and 700 °C, formation of precipitates can be observed. 10^{-2} mol/mol Ca contamination



a) 300 °C



b) 600 °C



c) 700 °C

Column 4. The development of the surface of NaCl crystals grown from the melt on quenching. 0.1 mol/mol silver contamination. At 600 °C and 700 °C, formation of precipitates can be observed

A further analysis of the formations which can be observed in the pictures should be carried out by experiments with crystals of greater purity and containing a single type of contaminant.

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Summary

Simultaneous microhardness measurements and electron microscopical investigations were carried out with quenched NaCl crystals containing various concentrations of mono-, and bivalent cation impurities. The microhardness values are not monotonous functions of the quenching temperature, but show maxima and minima, not present, however, in extremely pure crystals. According to electron micrograms at quenching temperatures at and above 600 °C, precipitate complexes are formed.

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