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# ON THE ELECTRIC CONDUCTIVITY AND DIELECTRIC LOSS OF "PURE" ARTIFICIALLY GROWN AND NATURAL NaCl CRYSTALS

## AN ATTEMPT AT A BETTER DEFINITION OF "PURE" NaCl CRYSTALS

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In this paper the d.c. conductivity and dielectric loss of a "pure" artificially grown and a natural NaCl crystal, with practically the same impurity content, are compared. Among the impurities calcium prevails. But only a very small part of it, obviously because of its very low solubility at room temperature, is built into the lattice of the natural crystal, whereas in the artificially grown crystal the whole quantity of calcium is "frozen" into the lattice (i.e. is not in an equilibrium state).

### *Introduction*

One of the problems we often have to face in experimental solid-state physics is the inadequate definition of "pure" materials available for research purposes. When studying the electric conductivity and dielectric loss mechanism of ionic crystals this difficulty is usually avoided by doping the crystals with a known amount of wanted admixtures. Thus the influence of the natural admixture background in the "pure" material is excluded. This procedure cannot, however, be used in all cases.

In a recently published paper [1] the authors have described some relaxation loss maxima of NaCl crystals, where the temperature of the maxima varies greatly with the admixture content. In order to be able to study this effect in greater detail, it appeared to be of great importance to determine the temperature of the maxima for extremely "pure" crystals. The authors tried, therefore, as a first step, to get an idea of the degree of purity and the "state" of the different "pure" crystals available. To this purpose they carefully analyzed their impurity content and measured their electric conductivity and dielectric loss. They thus found considerable differences in quality even with crystals of artificial and natural origin which proved to have practically the same impurity content. As the differences in quality of these crystals allow certain very interesting conclusions concerning the way the impurities are built-in we want to discuss them here.

### *Method of Measurement*

The dielectric loss was measured in the same way as described in [1]. The d.c. conductivity was measured on the same material and also in a furnace with a protective nitrogen or argon atmosphere. The samples and electrodes were heated indirectly by a surrounding cylindrical heating element. To measure the conductivity, the samples were provided on the contact surfaces with electrodes of colloidal graphite.

Samples of artificially grown crystals (1) were annealed for one hour at 550 °C and then quickly cooled. Some of the samples of the natural crystal were measured after being thermally treated as mentioned above (2) and some after being annealed for three hours at 750 °C and then quickly cooled (3). The heat treatment was carried out in the same protective atmosphere as the measurements.

The natural crystal was found to contain the following impurity background:  $\text{CaCl}_2 \sim 0,001 \text{ mol } \%$  and  $\text{Mg} \sim 1 \cdot 10^{-4} \text{ mol } \%$ . The artificial crystal grown by Kyropoulos' method exhibited the same calcium concentration as the natural crystal, i.e.  $\sim 0,001 \text{ mol } \%$   $\text{CaCl}_2$ , and some  $1 \div 3 \cdot 10^{-4} \text{ mol } \%$  Al and Cu and  $1 \cdot 10^{-4} \text{ mol } \%$  Mg, Fe and Si. Both crystals were found to be, both before and after heat treatment, less alkaline than  $1 \cdot 10^{-4} \text{ mol } \%$ . This fact was also confirmed by absorption measurements. No noticeable absorption lines of  $\text{OH}^-$  or  $\text{CO}_3^{2-}$  complexes were detected.

### *Results*

The dependence of the d. c. conductivity on temperature  $T$  is plotted as  $\log \sigma$  vs.  $1/T$  in Fig. 1. The conductivity of the artificially grown crystal (1) exhibited two characteristic knees, i. e. three different regions: the intrinsic conductivity region, the region where admixture conductivity prevails, and the region where obviously precipitation of admixtures already sets in [2]. The slope of all three regions was found to be identical with the slope in the corresponding regions both for a crystal with a calcium content of only 0,0001 mol % (grown from raw-material purified by a special process at the Institute of Solid State Physics, Prague, by Léb1), and for a crystal doped with  $\text{CaCl}_2$  to contain 0,01 mol %  $\text{CaCl}_2$ . We can, therefore, be sure that the conductivity depends on the same admixture, i. e. on calcium only. Samples of the natural crystals annealed at lower temperatures (2) also exhibited a conductivity with two knees, although the slope behind the first knee differed greatly from the slope in the corresponding region for the artificially grown crystal. It approached the slope in the "precipitation" region for the artificial crystals. Provided the second knee is taken as a real one, the slope behind the second knee is decreasing, which makes sample (2) differ even more at that point from (1). A further important difference was born out by the fact that the first knee for samples (2) occurred at a value more than two orders lower than the value for sample (1). From this fact it might be concluded that the number of divalent impurity ions built into the lattice

and responsible for the admixture conductivity is considerable lower than in sample (1).

The natural crystal sample, annealed at 750 °C (3), exhibited, in principle, the same conductivity features as the artificial crystal. Only the position of the first knee

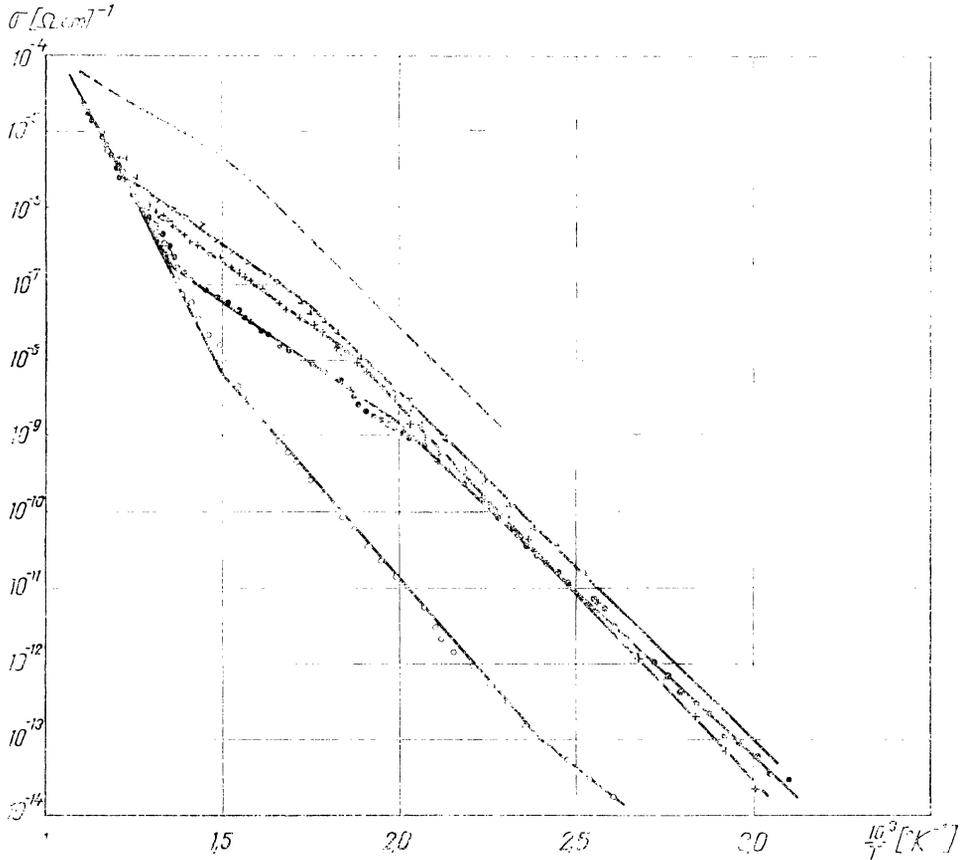


Fig. 1. Temperature dependence of conductivity:

artificial crystal with 0,01 mol %  $\text{CaCl}_2$  — — —, (1) with 0,001 mol %  $\text{CaCl}_2$  · · · · ·, with 0,0001 mol %  $\text{CaCl}_2$  — — —, natural crystal annealed 1 hour at 550 °C (2) with 0,001 mol %  $\text{CaCl}_2$  content ○ · · · · ·, natural crystal annealed 3 hours at 750 °C (3) with 0,001 mol %  $\text{CaCl}_2$  content · · · · ·, natural crystal annealed 1 hour at 550 °C with 0,01 mol %  $\text{CaCl}_2$  content × · · · · ·

suggested a higher content of divalent built-in admixtures (responsible for the conductivity) than in sample (2). The calcium content estimated from the conductivity data was, however, lower than 0,0001 mol %.

The temperature dependence of the dielectric loss of the samples at 1 kHz is plotted in Fig. 2. Sample (1) exhibited the same loss maximum at 225 °C, as already

reported in a previous paper [1]. Sample (2) exhibited also a loss maximum, but at 390 °C, whilst sample (3) (annealed at 750 °C) showed a maximum at 300 °C.

Furthermore, there was observed in sample (1) a loss maximum due to calcium-vacancy complexes at ~67 °C. This kind of maximum was, however, not observed in samples (2) and (3). This indicates that samples (2) and (3) contain far less complexes built into the lattice than (1). When considering the influence of the quantity of

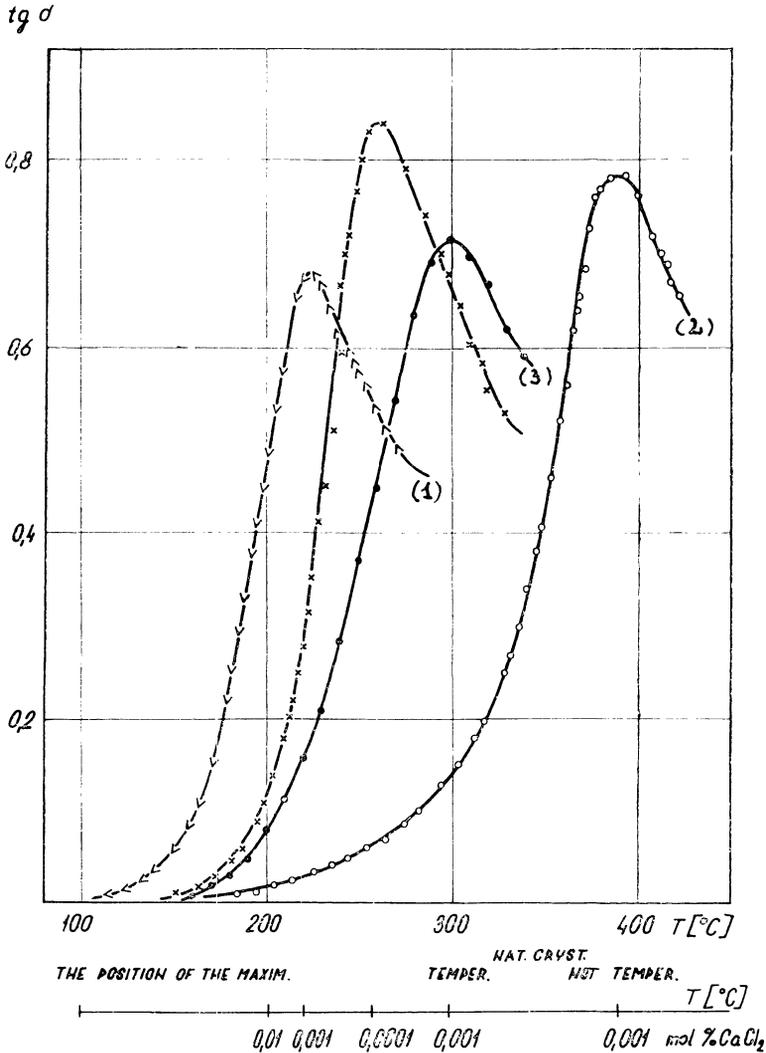


Fig. 2. Temperature dependence (and position) of dielectric loss maxima:

$\bullet\bullet\bullet$  artificial crystal (1) with 0,001 mol %  $CaCl_2$ ,  $\times\times\times$  artificial crystal with 0,0001 mol %  $CaCl_2$ ,  $\dots$  natural crystal (3) annealed 3 hours at 750 °C,  $\circ\circ\circ$  crystal (2) annealed 1 hour at 550 °C.

substitutional built-in calcium on the position of the maxima, as described for loss maxima at higher temperatures in paper [1], another fact is confirmed. The position of the maxima at higher temperatures implies that in both samples (2) and (3) there is much less calcium built into the lattice than in (1), and moreover it indicates that, as a consequence of annealing, the quantity of built-in calcium has increased in sample (3) considerably.

### *Discussion of Results*

The measurements show that in the natural crystal only a minor part of the calcium content is built into the lattice. The rest most probably forms microcrystals of its own kind; whereas undoubtedly in the artificially grown crystals the main part, if not the whole of the calcium content, is built into the lattice. With artificial crystals we find the quantity of calcium estimated from both spectroscopical and electrical measurements to agree within the limits of accuracy of the measurements. With the natural crystal, the calcium does not manifest itself proportionally to its content as estimated by spectral analysis; neither is the conductivity in accordance with the respective quantity of dissociated complexes, nor is the relaxational loss maximum at 67 °C with the respective quantity of associated complexes, as one would expect. The substitutional built-in quantity of calcium seems to be so low that the slope of the “admixture” conductivity region could be understood as being fixed by all divalent admixtures together. In agreement with this the second knee would be a result of “admixture” conductivity due to several kinds of participating divalent admixtures (i. e.  $\sigma = A_1 \cdot e^{-\frac{U_1}{kT}} + A_2 \cdot e^{-\frac{U_2}{kT}} + \dots$ ).

The change in the loss maximum temperature and conductivity after heating sample (3) at 750 °C, i.e. just under the melting point, is caused, no doubt, by building substitutionally into the lattice a certain amount of the calcium content which was originally not built into the lattice. By annealing for a shorter period of time, or at lower temperatures, the loss maximum temperature and conductivity of the natural crystal did not change in principle. The differences between both kinds of crystals shown by our measurements will find a plausible explanation by the assumption that a spontaneous and very low-rate precipitation process takes place at temperatures below the melting point.

In artificially grown crystals practically the whole content of admixtures dissolved at melting point temperatures remains built-in. But with natural crystals there has been time enough during the geologic periods of their existence for the admixtures to precipitate, so that in the lattice there remained only the quantity corresponding to the solubility at room temperature. This may, in accordance with theory, be really very low, as it is proportional to Boltzmann's factor of the respective free energy of dissolution. This explanation seems to contradict the interpretation of the second conductivity knee as the beginning of the precipitation process (see e.g. [2] or according to A. B. Lidiard, *Encyclopedia of Phys.* XX/2, Zückler K., Dissertation,

University of Göttingen 1949). The slope behind the knee, of course, does not show any dependence on the speed of the temperature change, but it has to be borne in mind that the knee is usually observed above the value of  $10^3/T = 1.7$ .

If the temperature of the natural crystal is raised, the dispersed microcrystals of the divalent impurities dissolve only very slowly, as could be observed. Only after annealing the sample for 3 hours at 750 °C an observable quantity, a fraction of 0,0001 mol % only (from the whole calcium content of 0,001 mol %), was built into the lattice.

Apart from all this another very interesting fact was established i.e. that calcium forms the main part of the admixtures and that its abundance is the same both for natural and artificially grown crystals. The explanation in artificially grown crystals is that the distribution coefficient equals 1. After zonal melting of the "pure" material 30-times, the calcium content was found practically unchanged (0,001 mol %). A recently published paper by Gründig and Wassermann [3] points out this fact as a serious obstacle to obtaining purer NaCl crystals.

### *Conclusion*

By comparing some electrical properties of "pure" artificially grown NaCl-crystals with natural ones it was found that, even if the impurity content of divalent admixtures is the same, the crystals differ greatly. This difference seems to be due to a large surplus of admixture ions, mainly calcium, frozen into the lattice of artificially grown crystals above the concentration corresponding to the equilibrium solubility at room temperature. In natural crystals this surplus is no doubt precipitated. This fact should be borne in mind when experimenting with material of low admixture concentrations. Besides that, the observed facts also show the necessity for a more profound study of the precipitation process.

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### REFERENCES

- [1] Kessler A., Mariani E., Czech. J. Phys., sect. B 14 (1964), 757.
- [2] Cook J. S., Dryden J. S., Proc. Phys. Soc. 80 (1962), 479.
- [3] Gründig H., Wassermann E., Z. f. Phys. 176 (1963), 293.

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# ИЗУЧЕНИЕ ЭЛЕКТРОПРОВОДНОСТИ И ДИЭЛЕКТРИЧЕСКИХ ПОТЕР „ЧИСТЫХ“ ИСКУССТВЕННО ВЫРАЩЕННЫХ И ЕСТЕСТВЕННЫХ КРИСТАЛЛОВ

Попытка нахождения более удобного определения „чистых“ кристаллов

Арношт Кесслер, Эмил Марьяни

## Резюме

В настоящей работе сравниваются проводимость одного направления и диэлектрические потери „чистого“ искусственно выращенного и естественного кристаллов NaCl с одинаковым содержанием загрязнений. Оказывается, что основную долю загрязнений образует кальций. В естественном кристалле только небольшая часть кальция, обусловленная, по-видимому, и малой растворимостью при комнатной температуре, вставлена в решетку, в то время как в искусственно выращенном кальций весь „заморожен“ в решетку (следовательно, не находится в равновесном состоянии).