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## RELAXATION MAXIMA OF CALCIUM AND CADMIUM DOPED NaCl CRYSTALS WITH MAXIMA TEMPERATURES DEPENDING ON ADMIXTURE CONCENTRATION

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### INTRODUCTION

In a recently published paper [1] somewhat "peculiar" relaxation maxima of "pure" undoped and  $\text{CaCl}_2$  doped NaCl crystals have been described. These maxima occurred at a frequency of 1 kc/s, in addition to the well known relaxation maxima of calcium complexes at  $\sim 67^\circ\text{C}$ , at temperatures between  $140$ – $300^\circ\text{C}$ . The same kind of maxima were apparently observed also by Trnka, Kaderka and Bohun [2] at  $170^\circ\text{C}$  and  $180^\circ\text{C}$  for  $\text{CaCl}_2$  doped crystals grown from an aqueous solution and from the melt. The temperature of the maxima  $T_{\text{max}}$  proved to depend considerably [1] on the calcium concentration in the crystals. It decreases with an increase of the concentration, whereas the value of the relaxational loss angle maximum  $\tan \delta_{\text{rel max}}$  seems practically independent of the concentration. We could make sure by unpublished yet extensive investigations that maxima of that kind occur also in crystals doped with several chlorides, oxides and some sulphides.

The purpose of this paper is to give a more detailed and accurate account of the concentration dependence of  $T_{\text{max}}$  for calcium-doped crystals in the largest possible concentration range and to compare it with the concentration dependence of the same kind of maxima as exhibited by cadmium-doped crystals. Cadmium was chosen because its ionic radius is near in value to that of calcium, whereas the activation energy of the association of complexes with vacancies is reported to have for both substances a different value.

The measurements were meant to provide not only a more profound knowledge about the dependence of  $T_{\text{max}}$  on the admixture concentration to allow an explanation of the observed phenomenon. An attempt was made to fix this relation as precisely as possible also for practical reasons. The shift of the

maximum can be used as a comfortable means to follow the building in of divalent admixtures into the lattice, the solubility of admixtures, etc.

## RESULTS OF MEASUREMENTS AND THEIR EVALUATION

The loss angle measurements were carried out as described in paper [1] and the temperature dependence established at a frequency of 1 kc/s for all samples in question. The samples were taken from undoped crystals of different degrees of purity: from crystals grown by Kyropoulos' method in an inert atmosphere from chemically repurified raw materials with an admixture content less than 0,001 mol%, and from raw materials repurified by special chemical processes achieving slightly less than 0,0001 mol% of admixture content, and finally from a natural crystal, tempered and not tempered. The latter was found by spectral analysis to contain nearly 0,001 mol% of divalent admixtures but, as shown in paper [3], only a very small fraction of these admixtures is built into the lattice. On the other hand samples from crystals were used, all of which were grown in an inert atmosphere and doped up to their maximum of solubility with different quantities of calcium or cadmium.

The admixture content was established by spectral analysis. The results of this analysis revealed that calcium forms in "pure" crystals the main part of the impurity background. For this reason down to a content of some  $5 \cdot 10^{-4}$  mol% of original admixtures, the crystals were considered as if "pure", with calcium or calcium and cadmium doped. Because in the natural crystal only a very small fraction of the calcium content is built into the lattice, the built in calcium content of these samples could be estimated only on the basis of conductivity data. In doing so, the amounts of calcium forming calcium-vacancy complexes were considered negligible though.

In Fig. 1 the dependence of  $T_{\max}$  on the logarithm of the calcium concentration,  $T_{\max} = f(\log c)$  is plotted first for concentration values estimated by spectral analysis (the more pronounced dispersion at lower concentrations indicates the fact that these values represent the limit of reliability of spectral analysis). Further there is a set of values based on concentration values computed from conductivity data of the samples using a formula given by Lidiard [4] for the mobility of vacancies:

$$\mu = \frac{21\,200}{T} \exp\left(-\frac{9\,750}{T}\right) \text{ cm}^2/\text{Volt sek.}$$

As can be seen, the calculated values are in the whole concentration range from 0,1 to 0,0002 mol% in fairly good agreement with the values estimated

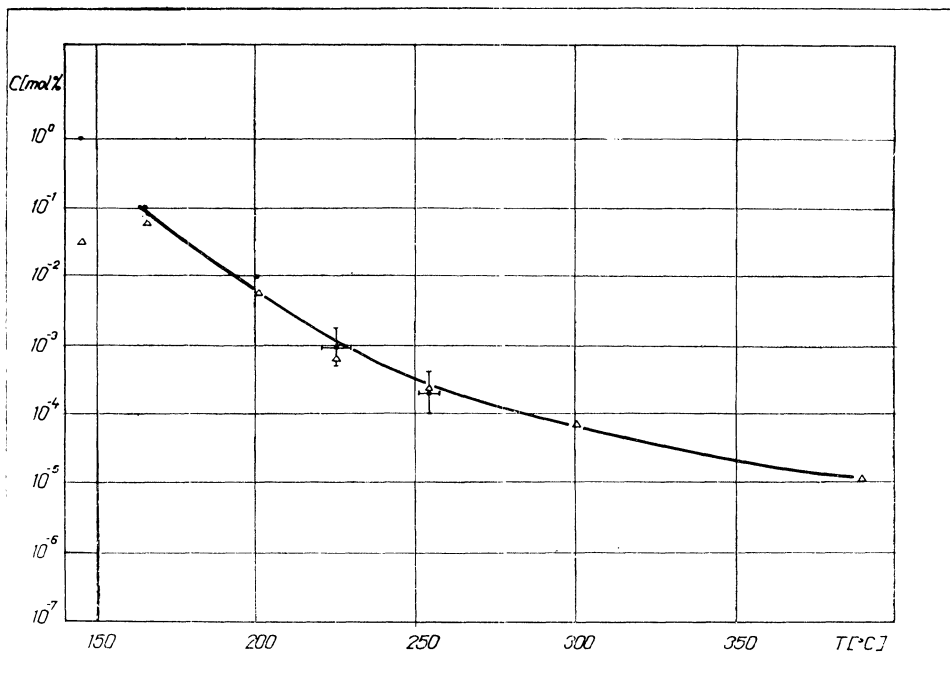


Fig. 1. The dependence of  $T_{\max}$  on calcium concentration:  
 ● concentration estimated by spectral analysis,  
 △ concentration computed from conductivity data.

by spectral analysis.<sup>(1)</sup> We, therefore, felt authorized to give an account of  $T_{\max} = f(\log c)$  down to calcium concentrations of  $10^{-5}$  mol %. With regard to the fact that calcium constitutes more than 9 in 10 parts of the admixtures, it could be taken for granted that practically only calcium is built into the lattice. To the value of 1 mol %, estimated by spectral analysis, not too much weight was ascribed, because the maximum solubility of calcium is some few tenth of a percent only. This fact is indicated by the respective value based on conductivity data.

In Fig. 2 the relation  $T_{\max} = f(\log c)$  is plotted for calcium, as well as for cadmium. All the concentration values are estimated by spectral analysis. For cadmium the dispersion of these values proved to be fairly high. The "origin" of the crystals was therefore carefully scrutinized. It turned out

(1) One should expect that at higher concentrations at least, not the whole quantity of calcium as estimated by spectral analysis is built in the lattice. The values calculated from conductivity data should therefore be smaller than the latter. That in fact occurs in Fig. 1. The value of this finding is limited though, because we have no direct method how to establish the quantity of calcium not built in.

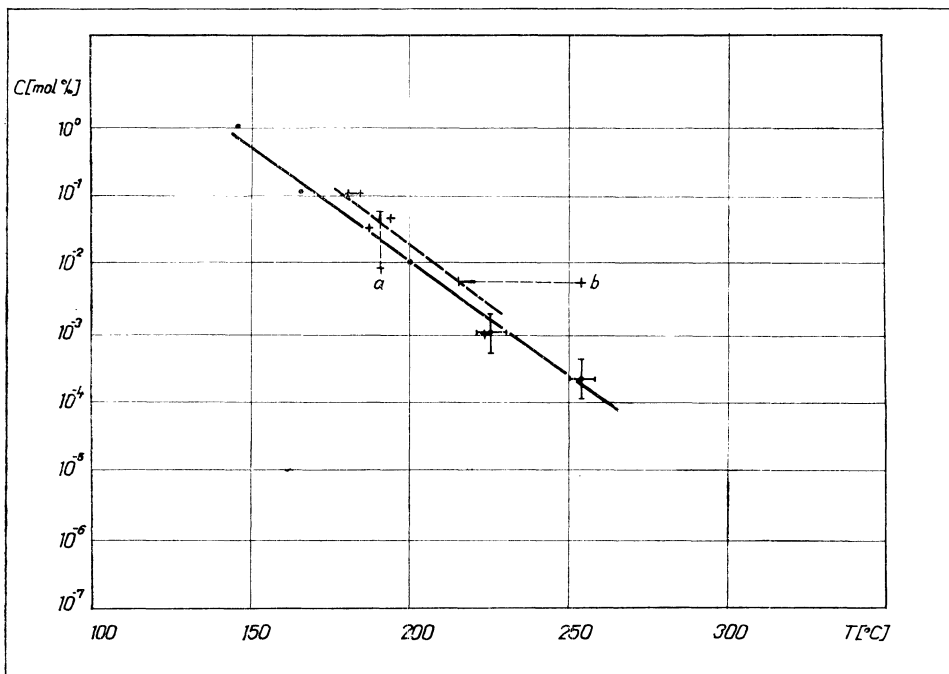


Fig. 2. The dependence of  $T_{\max}$  on the admixture concentration: dots (.) and full line for calcium, cross (+) and broken line for cadmium.

that sample "a", e.g. contains a considerable quantity of calcium (background). Taking into account this fact and setting for  $c$  in  $\log c$  the sum of the calcium and cadmium concentrations, the point will fit well into the sequence of experimental points. Sample "b" cleaved out of a crystal grown as an exception by Stockbarger's method in air, was found considerably alkaline. Considering the shift of  $T_{\max}$  with the increasing alkalinity of the crystals, as described e.g. by Kaderka [5] (this takes place in the opposite direction as in the case of an increasing calcium content) and supposing that the effect of cadmium is compensating the effect of alkalinity (as if there were less cadmium), and vice versa, even this point will fit the succession of the other experimental points.

#### SUMMARY

The plot of  $T_{\max} = f(\log c)$  proved to be a straight line, as found originally in [1] only down to concentrations of some  $5 \cdot 10^{-4}$ . At lower concentrations a surprisingly high increase for  $T_{\max}$  was obtained, as if the admixtures enhanced the observed effect in an increasing measure. For cadmium  $T_{\max} =$

$= f(\log c)$  gives a similar straight line in a smaller concentration range, naturally, from 0,1 to 0,001 mol % only. This line however proved to be somewhat paralelly displaced in the direction towards higher temperatures.

Another interesting result becomes apparent; it looks as if the admixture effects were summed up additatively: The effect of two cation-admixtures adds up; cation and anion admixtures give an effect equal to the difference of their quantities.

#### APPENDIX

Attention should be paid to two more facts resulting from our measurements. Firstly, the shift of  $T_{\max}$  constitutes a comfortable means (as shown e.g. in paper [3]) for studying the building in of divalent admixtures, for regognizing the disturbing influence of an admixture background, etc. Secondly, the results given in Fig. 1 show that the formula given by Lidiard [4, pg. 310] for the mobility of vacancies is in fairly good agreement with the results of the spectral analysis.

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#### МАКСИМУМЫ РЕЛАКСАЦИОННЫХ ПОТЕРЬ NaCl КРИСТАЛЛОВ С ПРИМЕСЯМИ КАЛЬЦИЯ И КАДМИЯ С ТЕМПЕРАТУРАМИ ПРИ КОТОРЫХ МАКСИМУМЫ ЯВЛЯЮТСЯ ЗАВИСИМЫМИ ОТ КОНЦЕНТРАЦИИ ПРИМЕСЕЙ

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#### Резюме

Была определена зависимость температуры при которой наблюдается максимум релаксационных потерь в кристаллах NaCl с содержанием примесей кальция или кадмия. Эти потери наблюдаются при 1 Ггерц и температурах 140 °C—300 °C [1].