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THE AGGREGATION PROCESSES OF IMPURITIES IN KCl:Mn^{2+} AND KCl:Mn^{2+}, Pb^{2+}

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The aggregation kinetics of impurities in KCl:Mn^{2+} and KCl:Mn^{2+}, Pb^{2+} crystals has been studied. For decay measurements of Mn^{2+} – cation vacancy dipoles the EPR method was applied. The results were evaluated assuming kinetics of the I,II and III order, taking into account and neglecting the reverse reaction. Calculations show that aggregation kinetics can be described using the first order with some contribution from of higher orders. This lead to a conclusion that the aggregation processes occurs in few ways.

Key words: alkali–halide crystals, dipoles aggregation, decay of dipoles, reaction order.

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I. INTRODUCTION

In halogen alkaline crystals with impurities of divalent cations, after heating to temperatures close to melting point and after fast cooling, dipoles of the impurity ion–cation vacancy (I – V) appear. These dipoles aggregate, i.e. it is possible to form dimers, trimers, as well as precipitates of foreign phases, while their form is still a matter of controversy. Cook and Dryden [1, 2] showed the presence of an initial third–order process for the aggregation of several different impurities in KCl and NaCl crystals. This implied trimer formation, an encounter of tree dipoles. Furthermore, the initial decay was followed by a plateau region, after which decay of the number of I–V dipoles continued which indicated that initial trimer formation was followed by a period of dipole–trimer equilibrium and then by further aggregation into higher–order complexes. The initial third–order decay was confirmed for many impurities in several papers [3–5]. Moreover, Capelletti and De Benedetti [6] have reported an initial second–order fit to data for NaCl:Sr^{2+} at room temperature. Unger and Perlman [7] found that dimers are formed as the primary from of aggregation. Concerning of the initial stage of aggregation of Mn^{2+} and Eu^{2+} halogen alkaline crystals Munoz et al. [8, 9] prove that the second order reaction prevails. More probable was the suggestion of Crawford theory [10] that the aggregation process progresses in two steps: first a weakly bound dimer is formed which is trapping the third dipole and forming the final trimer.

The aggregation of I–V dipoles can be monitored by the decay of the polarization with time. This has usually been done using electron paramagnetic resonance (EPR).

In this paper, based on the analysis of the EPR spectrum versus time, we present process of dipole decay in KCl:Mn and KCl:Mn, Pb crystals at various concentrations of the impurities. The results were also used oneself for evaluate the order of aggregation kinetics, taking into account and neglecting the reverse reaction.

II. THEORY

The reaction order of the process for the aggregation of divalent cation impurities in halogen alkaline crystals has been assumed by previous papers [7, 8, 9, 11].

The first order reaction (monomolecular) rely on the decay of the substrate molecule A into reaction products P or on the change of the molecule structure (isomerisation): $A \rightarrow P$. The reaction rate is given by the equation

$$v = -\frac{dc}{dt} = k_1 c_1, \tag{1}$$

where c is the concentration of the dipoles, k_1 is the rate constant. For $t = 0, c = c_0$, thus $c = c_0 e^{k_1 t}$. Assuming that $c_0 = 1$ equation (1) may by written as

$$\ln c = -k_1 t. \tag{2}$$

The second order reactions proceed according to the scheme $A + A = D$, where A is a dipole and D is a dimer. The reaction rate is given by

$$v = -\frac{dc}{dt} = k_2 c_2, \tag{3}$$

and the solution has the form

$$\frac{1}{c^2} = 2k_2 t + \frac{1}{c_0^2}. \tag{4}$$

The third order reaction: $A + A + A = T$, T being a trimer, is described by the relation

$$v = \frac{dc}{dt} = k_3 c^3. \tag{5}$$

Thus the solution of eq. (5) becomes

$$\frac{1}{c^2} = 2k_3t + \frac{1}{c_0^2}. \tag{6}$$

In all the above mentioned cases, the back reaction has been neglected. These reactions were taken into account by Unger and Perlman [7] and by Munoz et al. [8]. In this case the second order reaction is described by the equation

$$\frac{dc}{dt} = -k_4c^2 + k_5p, \tag{7}$$

where k_4 is the rate constant, k_5 is the rate constant for the back reaction, p is the dimer concentration. In this case

$$c + 2p = c_0. \tag{8}$$

The solution of eq. (7) yielding

$$\ln\frac{c-b}{c-a} = k_4't + k_5', \tag{9}$$

where

$$\begin{aligned} a &= n_s, \\ b &= -\frac{c_0n_s}{c_0-n_s}, \\ k_4' &= (a-b)k_4, \\ k_5' &= \ln[(c_0-b)(c_0-a)]. \end{aligned} \tag{10}$$

The third order reaction is described by

$$\frac{dc}{dt} = -k_6c^3 + k_7q, \tag{11}$$

where k_6 and k_7 are the rate constants, q is the trimer concentration. The solution of eq. (11) may be written as

$$\ln(c-n_s) = -n_s\frac{(3c_0-2n_s)k_6t}{(c_0-n_s)} + \ln(c_0-n_s). \tag{12}$$

A well suited method for determining the reaction order is to study of the time $\tau_{\frac{1}{2}}$, in which the $\frac{1}{2}$ of the initial number of dipoles aggregate, as a function of the initial concentration of the dipoles c_0.

The clusterisation process can be obtained from [8]

$$\frac{dc}{dt} = -K_1c^n + k_2c_n, \tag{13}$$

where n is the reaction order, c is the dipole concentration, c_n is the concentration of n–meres. In this case

$$c + nc_n = c_0. \tag{14}$$

If the relative dipole concentrations adequate to the time $\tau_{\frac{1}{2}}$ ($p_{\frac{1}{2}}$) and to equilibrium conditions abide by the relation

$$\frac{p_{\frac{1}{2}}}{1-p_{\frac{1}{2}}} \gg \frac{p_s^n}{1-p_s}, \tag{15}$$

then

$$\tau_{\frac{1}{2}} = \frac{-p_{\frac{1}{2}}^{1-n}}{(1-n)K_1c_0^{n-1}}. \tag{16}$$

The results shown on a graph with coordinates $\ln\tau_{\frac{1}{2}}$ and $\ln c_0$ lead to a straight line with a slope

$$a = -(n-1), \tag{17}$$

and consequently allow to determine the reaction order from the relation

$$n = -a + 1. \tag{18}$$

III. EXPERIMENTAL PROCEDURE

Samples used are the single crystals of KCl with various concentration of impurities (single and dual) $MnCl_2$ and $PbCl_2$ received by the Bridgeman method. Prior to measurements the samples were first annealed at 723 K to bring about the dissolution of pre–existing aggregates and then quenched to room temperature an a metal block. The concentration of the paramagnetic impurity was determined by the EPR method applying $CuSO_4{\cdot}5H_2O$ and MgO:Mn standards, depending on the spectrum in the sample. Lead content in the samples was determined by atomic absorption spectrophotometry. The EPR measurements were performed using the spectrometer SE–X/28 working in the band X (9.4 GHz). The measurement of isotherm decay of Mn^{2+}–cation vacancy dipoles in KCl crystals was performed at room temperature (295 K). From the EPR spectrum of Mn^{2+} ions well isolated lines from the low–field part were selected. The intensities of these lines which determine the dipole concentrations were measured as a function of time.

IV. RESULTS AND DISCUSSION

The concentration of impurity–vacancy (I–V) dipoles (c) versus time (t) for singly and doubly doped KCl crystals at various concentration of the impurity are shown in figs. 1a–b, respectively. As can be seen the decay of the dipole with time in single doped crystals increases with increasing concentration of the Mn^{2+} ions. However in doubly doped crystal KCl:Mn, Pb this process depends not only on the increase of the concentration of the Mn^{2+} ions but also on the increase of the concentration of paramagnetic Pb^{2+} ions.

The fit of the data to first–, second– and third–order kinetics without and with back reaction according to eqs. (2), (4) and (9) in KCl + 61 ppm Mn and KCl + 51 ppm Mn, 25 ppm Pb are shown in fig. 2. It is evident that for as many fits is good only for the first order reaction; after which the straight line is obtained. Similar results were obtained for singly (KCl:Mn) and doubly (KCl:Mn, Pb) doped crystals with admixture concentration of 4.5 ppm to about 500 ppm as well. It is worth noticing that at low concentration the EPR signal is very weak but at high concentrations the decay is very fast and so the results are changed with a significantly larger error.

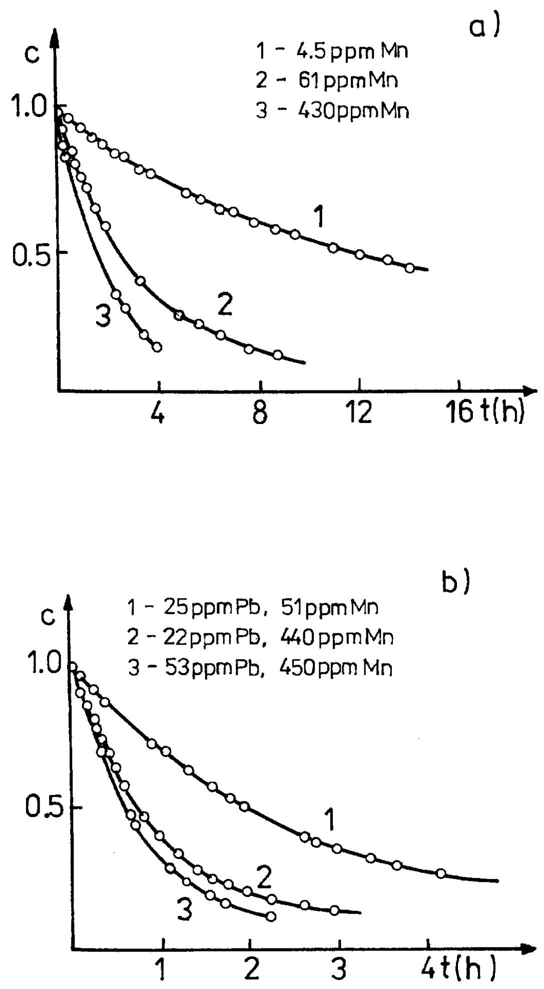

Fig. 1. Concentration of impurity–vacancy dipoles (c) versus time (t) in KCl:Mn^{2+} (a) and KCl:Mn^{2+}, Pb^{2+} (b) crystals at various concentration of the impurities at 295 K.

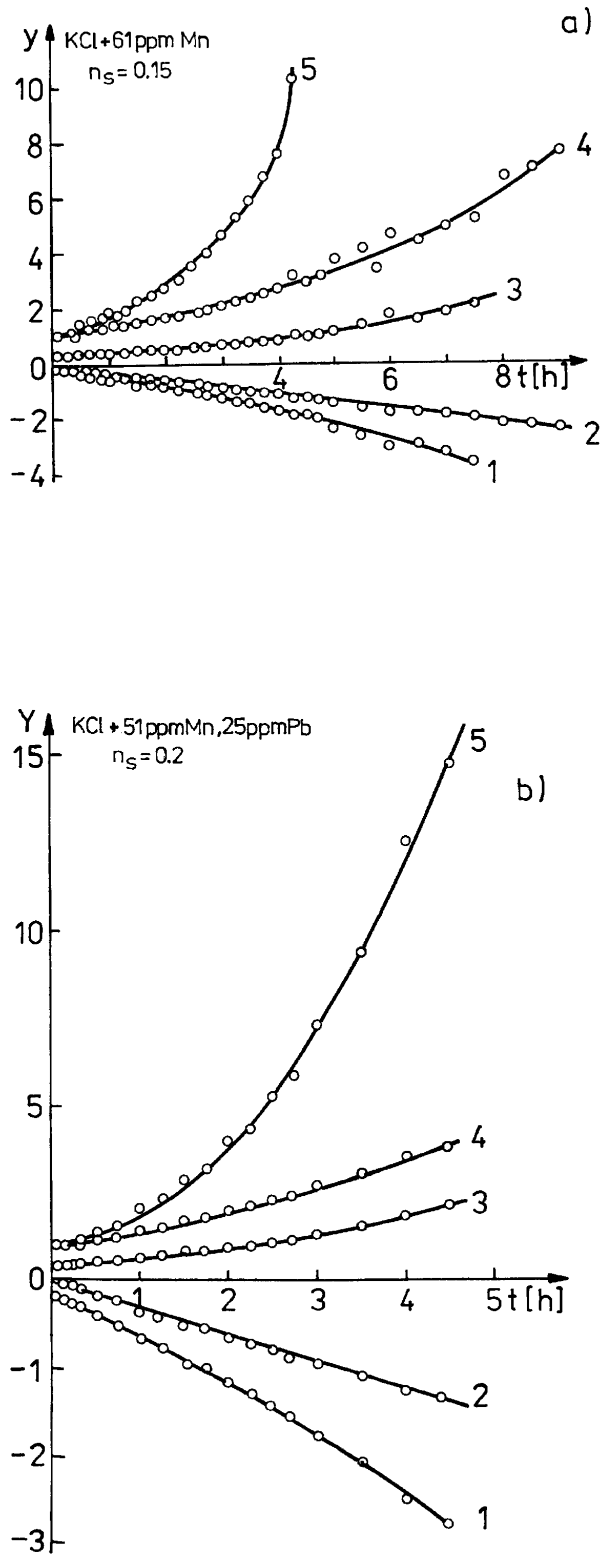

Fig. 2. Decay of dipoles in KCl + 61 ppm Mn (a) and KCl + 51 ppm Mn, 25 ppm Pb (b) crystals at 295 K. The curves 1 and 3 were obtained applying Unger's theory including the back reaction; the curves 2, 4 and 5 without back reaction. The curves 1 and 5 to the third order reaction, while curve 2 for the reaction of the first order. For curve : 1— $y = \ln(c-a)$, 2— $y = \ln c$, 3— $y = \ln[(c-b)/(c-a)]$, 4— $y = \frac{1}{c}$, 5— $y = \frac{1}{c^2}$.

The dependencies $\ln \tau_{\frac{1}{2}}$ versus $\ln c_0$ for the examined samples are shown in fig. 3. The declination of the straight line for all concentrations is close to -0.5 leads, according to eq. (18), to the reaction order of n=1.5.

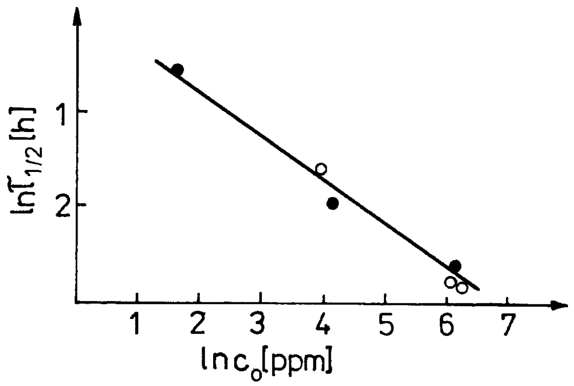

Fig. 3. Logarithm of time ($\tau_{\frac{1}{2}}$) in which the $\frac{1}{2}$ of the initial concentration of the impurity–vacancy dipoles aggregates versus the logarithm of the initial concentration of the dipoles (c_0) in KCl crystal at various concentration of Mn (•) and Mn, Pb (o) at 295 K.

Analysing the obtained results one has to keep in mind that the reaction order is a calculated quantity (resultant). Thus the aggregation of impurity in singly and doubly doped KCl crystals can be described using the reaction of the first order with some contributions from reactions of higher orders. This leads to a conclusion that the aggregation processes occur in a few ways. The first order n=1 suggest a direct attachment of the dipole to the existing precipitate with its simultaneous decay. The EPR measurements support this suggestion. In the spectrum taken immediately after hardening, the lines appear which are present in the spectrum for well annealed samples and arising from isolated Mn^{2+} ions in the neighbourhood of high symmetry (see fig. 4). In as – grown crystals, the spectrum is more distinct (fig. 4), more nonparamagnetic impurities are contained in the crystal (they are often accidentally contained in the crystal). The solubility of the double valence impurity in KCl crystal is very small and therefore even a long annealing at high temperature does cause the total solubilization of the precipitates and aggregations in the crystal lattice. The centers cause the strong attraction of the dipoles ion Mn^{2+}–cation vacancy which leads to the reaction of the first order. Our observation of the EPR spectrum changes as a function of time after hardening the sample supports this conclusion. The spectrum originating from Mn^{2+}–cation vacancy dipoles evolves directly into the characteristic spectrum for aggregated Mn^{2+} ions.

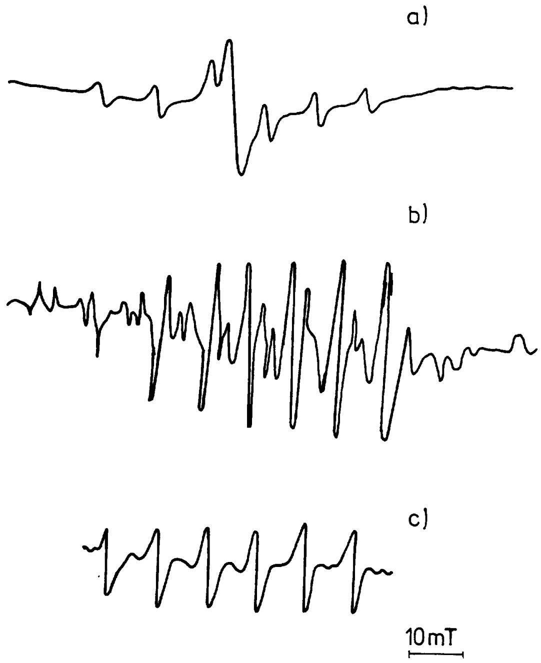

Fig. 4. The EPR spectra of the KCl + 51 ppm Mn, 25 ppm Pb crystal: a — as grown, b — quenched from 723 K and 15 min stored at 295 K, c — quenched from 723 K and 3 months stored at 295 K.

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ПРОЦЕСИ НАГРОМАДЖЕННЯ ДОМІШОК У $KCl{:}Mn^{2+}$ ТА $KCl{:}Mn^{2+}$, Pb^{2+}

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Вивчена кінематика нагромадження домішок у $KCl{:}Mn^{2+}$ та $KCl{:}Mn^{2+}$, Pb^{2+} кристалах. Для вимірювання розпаду Mn^{2+} вакансних диполів був застосований метод ЕПР. Результати опрацювали, виходячи з кінетики I, II та III порядку, при цьому враховуючи та нехтуючи зворотну реакцію. Обчислення показують, що кінетику нагромадження можна описати, використовуючи перший порядок з деяким внеском від вищих порядків. Це приводить до висновку, що процеси нагромадження відбуваються кількома шляхами.