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The Aggregation of Divalent Impurities and their Associated Cation Vacancies in Alkali Halides

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A detailed study of the aggregation of pairs consisting of cations and cation vacancies has been made in NaCl containing Ca^{++} and in NaCl containing Mn^{++} by measuring dielectric absorption. Each of the pairs forms a dipole and the decay with time of the dipole concentration at various temperatures, following heat treatment, has been measured. In NaCl:Mn^{++} the aggregation proceeds in a similar manner to that reported previously in KCl: Ba^{++} and KCl: Sr^{++}. In NaCl: Ca^{++} although the aggregation proceeds in two stages, the manner in which the complexes grow during the second stage is different.

1. Introduction

When a divalent cation is incorporated substitutionally in an alkali halide lattice $(e.g. \text{Sr}^{++} \text{ in KC1})$ a cation vacancy is created. The impurity ions and vacancies are of opposite charge and can associate to form dipoles. The number of the impurity ions present at any time as dipoles can be obtained from the intensity of the dielectric absorption. It is found, in general, that by heating a sample to 350-400°C and quenching



Fig. 1. Decay in dipole concentration in KCl containing 3.4×10^{-5} mole fraction of Ba⁺⁺ in free dipoles at the commencement of each experiment.

to room temperature all the impurity ions are present as dipoles. With annealing, the intensity of the dielectric absorption decreases. Decay curves typical of KC1:Sr⁺⁺ and KC1:Ba⁺⁺ are given in Fig. 1.

These curves consist of three parts; (i) an initial decay which is third order in dipole concentration *i.e.* $dx/dt = -kx^3$ where x=dipole concentration; (ii) a constant or nearly constant region; and (iii) a further decay

which is again third order in dipole concentration. It is concluded¹⁾ that the initial third order curve corresponds to the formation of trimers (or clusters of three dipoles), that the plateau represents an equilibrium between the dipoles and these trimers and that the third part of the curve representsthe growth of these trimers into large aggregates by the addition of further dipolesin groups of two.

Although the third order nature of the decay of dipole concentration was first observed²) in room temperature measurements on NaCl:Ca⁺⁺ this system was not studied thoroughly at the time. The manner in which divalent cations and cation vacancies are distributed in an alkali halide lattice is relevant to many optical and other physical properties of alkali halides. Because of the large number of investigations which has been made with NaCl containing Ca, either deliberately or accidentally present in the lattice, it was considered desirable to extend the dielectric measurements on NaCl:Ca⁺⁺.

The decay of dipole concentration in NaC1: Mn^{++} was measured in parallel with paramagnetic resonance studies on the same crystals.

2. Experimental

The method of growing the crystals, the chemical analysis for impurity concentration and a description of the electrical measurements have been described^{11,22}.

The heating of the samples of NaC1:Mn⁺⁺ at the commencement of each experiment and the annealing had to be performed in a vacuum, otherwise the samples developed a brown colour and the d.c. conductivity increased, obscuring the dielectric absorption.

3. Results and Discussion

As with KC1:Sr⁺⁺ and KC1:Ba⁺⁺ the decay curves, following an initial heating to 350-400°C and quenching, were in three stages. The detailed nature of the decay curves is different in the two systems and it is therefore more convenient to discuss them separately.

$NaCl: Ca^{++}$

Examples of the decay of dipole concentration with time at different annealing temperatures are given in Figs. 2 (a) and (b) for two different concentrations. It will be observed that the plateau in these curves is long and in many instances the measurements have to be continued for several months before there is any indication of the second stage of the aggregation. The decay curves following the plateau are not third order in dipole concentration but are of a higher order. Another difference to the KC1



Fig. 2. Decay in dipole concentration in NaCl: Ca⁺⁺. (a) crystal containing 2.2×10^{-4} mole fraction of Ca⁺⁺. (b) crystal containing $3.6 \times$ 10^{-4} mole fraction of Ca⁺⁺.

results and also to the NaC1: Mn^{++} observations is that the absorption curve does not remain a Debye curve during the aggregation. A second absorption region is apparent on the high frequency side even before the first stage equilibrium has been reached. The departure becomes more prominent during the second stage of the aggregation (Fig. 3). At a few points on these decay curves the area under the second absorption curve, expressed as a fraction of the area under the initial Debye curve, is given. If, as is unlikely to be the case, the



Fig. 3. Dielectric absorption in NaCl containing 3.6×10^{-4} mole fraction of Ca⁺⁺ (i) after quenching from 350°C (ii) after 20 hours at 60°C (first stage equilibrium) and (iii) after 280 hours at 60°C (during the second stage of the aggregation). Also shown are the curves (ii) and (iii) after scaling up so that the maxima correspond to the initial Debye curve.

dipole rotation responsible for this second absorption was one between different positions of equal energy these numbers would represent the fraction of dipoles contributing to this second absorption. Because, as is more likely, the alternative positions are unequal in energy, the fraction of the dipoles contributing to this absorption will be higher than the numbers shown in Fig. 2.

The values p_0 (dipole concentration)/(dipole concentration at t=0) at which the step in the decay curves occurs are listed in Table I, for samples taken from three crystals.

With the exception of 70°C, the quantity $\frac{c^2 p_0^3}{1-p_0}$ (where c=dipole concentration at the commencement of each experiment, expressed in mole fractions) is not a constant at

Temperature	Initial Concentration of Dipoles	p_0	
	9 ×10 ⁻⁵	0.55	
30°C	2.45×10^{-4}	0.38	
	3.4×10^{-4}	0.34	
40°C	9 ×10 ⁻⁵	0.62	
	$2.45 imes 10^{-4}$	0.58	
	3.2×10^{-4}	0.46	
50°C	9.5 ×10 ⁻⁵	0.74	
	2.6×10^{-4}	0.56	
	3.5×10^{-4}	0.53	
60°C	8.5 ×10 ⁻⁵	0.74	
	$2.5 imes 10^{-4}$	0.63	
	3.65×10^{-4}	0.54	
70°C	9 ×10 ⁻⁵	0.93	
	2.45×10^{-4}	0.75	
	2.95×10^{-4}	0.72	

Ta	h	P	T	
TC	101	C	т.	

each temperature as is the case for the simple equilibrium between dipoles and trimers found in KC1:Sr⁺⁺ and KC1:Ba⁺⁺.

The only conclusion that it seems possible to draw from these measurements is that at the plateau in the decay curves there are two types of clusters in equilibrium with the dipoles, one type of cluster being a trimer similar to those which occur in KC1 and the other being responsible for the second absorption. If the further aggregation occurs on the second type of cluster this could explain the differences between the rate of the second stage aggregation in NaC1:Ca⁺⁺ and the other systems investigated. There are insufficient data available to make any speculation on the nature of the second type of cluster profitable.

From the initial third order curves, k_1 in the expression $dc/dt = -k_1c^3$ can be obtained for each temperature. From an Airhenius plot an activation energy of 0.92 eV and a pre-exponential factor of $2 \times 10^{17} \text{ sec}^{-1}$ can be obtained for k_1 . As discussed in an earlier paper¹¹ this activation energy should be the energy barrier opposing the diffusion of a Ca^{++} -vacancy pair through the lattice. Although 0.24 eV higher than the activation energy for the rotation of this dipole $(0.68eV^{3})$, this value is in agreement with a recent determination of 0.96 eV obtained⁴¹



Fig. 4. Decay in dipole concentration in NaCl containing 5×10^{-5} mole fraction of Mn⁺⁺ in free dipoles at the commencement of each experiment.

from the measurement of the diffusion of radioactive Ca through NaC1.

$NaCl: Mn^{++}$

Two curves typical of the decay of dipole concentration in NaCl: Mn⁺⁺ are given in Fig. 4. In this system the two stages of aggregation overlap to such an extent that a definite plateau does not develop. The general features (i) that this first stage equilibrium occurs at an earlier part of the decay curve with an increase in the annealing temperature and (ii) that the delay between the first and second stages of the aggregation also increases with annealing temperature are, however, apparent.

The mathematical expression for the model¹⁾ proposed for the aggregation of dipoles in KC1: Sr^{++} and KC1: Ba^{++} is

$$\frac{dp}{dt} = -k_1 p^3 - k_2 p^2 \frac{(1-p)}{3} + k_3 (1-p) \qquad (1)$$

provided that $p > p_0$. In this expression the



Fig. 5. The experimental results for the decay in dipole concentration in NaCl: Mn^{++} at various annealing temperatures plotted in relation to a family of curves drawn as solutions to Eqs. (1), (2) and (3).

first term denotes the probability per unit time of three dipoles uniting to form a trimer, the second term denotes the probability of two dipoles adding on to an existing trimer to form a complex containing 5 dipoles and the third term the probability of a trimer dissociating into three free dipoles. If k_1 and k_3 are related by the following expression

$$\frac{k_3}{k_1} = \frac{p_0^3}{1 - p_0} \tag{2}$$

then at $p=p_0$ the first and last terms in Eq. (1) are equal; this corresponds to the plateau in the decay curve. When $p < p_0$ an equilibrium is maintained between the concentration of free dipoles and trimers and the further decrease in dipole concentration occurs by dipoles adding, in pairs, to complexes containing either 3, 5, 7, 9 etc. dipoles. If it be assumed that the total number of complexes present decreases in proportion to p/p_0 from the number $(1-p_0)/3$ present at $p=p_0$ then

$$\frac{dp}{dt} = -k_2 p^3 \frac{(1-p_0)}{(3p_0)} \tag{3}$$

when $p < p_0$.

The curves of p as a function of time

plotted in Fig. 5 are solutions, obtained graphically, of Eqs. (1), (2) and (3) for various values of p_0 , making the extra assumption that $k_1=k_2$. This latter assumption implies that in this particular case the crosssection^{*} presented by trimers and higher complexes as nuclei for the precipitation of dipoles in pairs is the same as that presented by free dipoles. In plotting the curves of Fig. 5, k_1 has been kept constant.

Reference to Fig. 5 shows that the decay of dipole concentration does conform to this family of curves, provided that the time scale is moved with temperature in such a way as to be equivalent to k_1 having an activation energy of 0.64 eV^{**}. The aggregation of divalent impurity vacancy pairs in NaC1: Mn⁺⁺ is therefore similar to that in KC1: Sr⁺⁺ and KC1 : Ba⁺⁺.

References

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DISCUSSION

Kanzaki, **H**.: Do you have any free vacancies present just after quenching? Dr. Ninomiya in our laboratory carried out experimental studies on annealing process of quenched KC1-Ca crystals (T. Ninomiya: J. Phys. Soc. Japan 15 (1960) 1601). Just after quenching, the crystals contained free vacancies and impurity-vacancy complexes. During annealing at lower temperature, it was concluded that impurities joined to form some larger aggregates based on the facts that numbers of both free vacancies and complexes decreased during annealing.

Dryden, J.S.: There will of course be some dissociation of the impurity ionvacancy pairs. Our measurements show that there is only a small fraction dissociated, what fraction is limited by the accuracy of our dielectric measurements and of the chemical analysis, probably 2–5% depending on the particular crystals. The experiments you mention are consistent with our results.

Sosin, A.: The third order kinetics which are reported here are of concern to me. Are your data inconsistent with a model in which dimers are formed but with low binding energy? In this case, the concentration of dimers would always be small but these dimers would serve as suitable nuclei for trimers.

Dryden, J.S.: The data are not inconsistent with there being a few dimers present. The binding energy would need to be low because it is difficult to conceive any dimer arrangement in which the two dipoles are still active. The agreement

^{*} This term is meant to include geometrical factors *i.e.* the number of ways of building on to an existing aggregate or on to a dipole and the effects of stress fields around the dipoles and aggregates. ** This value is lower than reported previously¹, when insufficient allowance was made for the overlapping of the two parts of the decay curves at the lower temperatures (*i.e.* lower values of p_0).

between the initial dipole concentration and the concentration of divalent ions indicated that there are very few inactive dipoles following the quenching from 400°C.

Iida, Y.: Is there any possibility that dipoles dissociate into single defects instead of clustering and that you are observing the effects? Secondly, this effect is essentially related to aging. Dislocations may play a very important role.

Dryden, J.S.: If the decay of dipole concentration was due to the dissociation of the dipoles, then the dc conductivity would increase because of an increase in vacancy concentration. This does not happen.

At one stage of the investigation we thought that the step in the decay curves may occur because dipoles were trapped near dislocations. An etch pit count revealed that the density of dislocations was too low by several orders of magnitude. Also the variation of dislocation density between different crystals was inconsistent with the idea that dislocations have any part in the aggregation.

Nowick, A.S.: Can you see any theoretical reason why dimers should be unstable?

Dryden, J. S.: No, other than the fact that if two dipoles are arranged so as to form a square there is a region of the crystal where some ions have a large fraction of their nearest neighbors as either defects or impurity ions.

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Study of the Lattice Defects in Normal and Neutron Irradiated Lithium Fluoride by Dielectric Relaxation Measurements

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Carefully annealed LiF crystals do not show any dielectric relaxation phenomena between 0° C and 100° C for frequencies between 10^{2} and 10^{5} c/s. After heating and quenching, divalent impurities associated with Li vacancies give a Debye domain of losses.

The effects on the dielectric properties of neutron irradiation at the reactor temperature is a complete inhibition of divalent impurities and creation of dipolar defects revealed by two domains of losses; the mobile part of the dipoles giving one of these domains are Li vacancies. The point defects created by low temperature irradiation are essentially different.

1. Non-Irradiated Samples

Carefully annealed LiF crystals do not show any dielectric relaxation phenomena between 0° C and 100° C for frequencies between 100 and 10° c/s. However the content of divalent impurities (mainly magnesium) is of the order of 10^{-4} as given by optical spectrometry. Were those impurities normally distributed in the lattice, in substitution, they would be accompanied by lithium ion vacancies for charge compensation and there would therefore be dipolar complexes Mg^{++} [Li⁺] which would give rise to a measurable dielectric relaxation effect such as has been observed by Dryden and Rao¹¹.

It must therefore be concluded that in those well annealed crystals the divalent impurities are inhibited and that no dipolar complexes of the type Mg^{++} $[Li^+]$ take place.

To remove this inhibition it is sufficient