Dimerization of impurity-vacancy dipoles in alkali halides*

S. Unger and M. M. Perlman

*Groupe de Recherches sur les Semiconducteurs et Diélectriques, Department of Physics,
Collège Militaire Royal de Saint-Jean, Saint-Jean, Quebec, Canada*

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The aggregation of impurity-vacancy dipoles in KCl and NaCl doped with various divalent impurities is shown to follow initial second-order kinetics. This is accomplished by including dissociation as well as formation of dimers in the theory of dipole decay. An apparent initial third-order process, reported by many workers over the past dozen years, arose because dissociation was neglected in the analyses previously made.

I. INTRODUCTION

The aggregation of divalent cation impurities in alkali-halide crystals has been the subject of intensive investigation in recent years.[1-6] These impurity ions are compensated by cation vacancies, and give rise to impurity-vacancy $(I - V)$ dipoles and higher-order complexes below 300 °C.[7] The precipitation process can be monitored by the decay of the polarization with time. This has usually been done using dielectric-loss measurements, and more recently, by the ionic-thermocurrent technique.[8] In the case of paramagnetic impurities,[2] or $I - V$ dipoles which possess optical transitions peculiar to the nonaggregated state,[4] electron paramagnetic resonance (EPR), and optical absorption and emission spectra have been used, respectively, to follow the aggregation.

Measurements by Cook and Dryden[1] showed the presence of an initial third-order process for the aggregation of several different impurities in KCl and NaCl. This implied trimer formation, an encounter of three dipoles. Furthermore, the initial decay was followed by a plateau region, after which decay of the number of $I - V$ dipoles continued. The interpretation given was 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 by several other observers,[2,3,6] although they did not report the appearance of plateaus.

In spite of this evidence favoring initial trimer formation, skepticism persisted due to the fact that a random encounter of three dipoles is far less probable than the encounter of two dipoles to form a dimer.[9] In addition,[10] the planar quadrupole (dimer) is of comparable stability to the hexagonal trimer configuration proposed by Cook and Dryden.[1] This prompted Crawford[10] to suggest that stable dimer formation is being inhibited by dipolar pairs being in a loosely bound state in quasiequilibrium with free dipoles. If the loosely bound state retains a residual dipole moment due to electrostatic constraints inhibiting the formation of the planar quadrupole, and if it is quickly established, then dipole decay would still appear to follow a third-order process. This theory suggests that a second-order decay might be visible in crystals with a low impurity content, where the loosely bound state would not be reached as quickly. Capelletti and De Benedetti[3] have reported an initial second-order fit to data for NaCl: Sr^{++} at room temperature, but recent measurements[5] on low concentration KCl: Pb^{++} have yielded a decay which is neither second nor third order. Using a different approach, Wintle[11] has shown that the data of Capelletti and De Benedetti[3] for NaCl: Cd^{++} can be made to fit diffusion-controlled second-order kinetics.

A common characteristic in all of the above work was neglect of the reverse process in the theory of the formation of trimers or dimers. Dissociation of these complexes was left out of the analyses leading to a determination of the order of the kinetics. Since the existence of equilibrium stages has been proven,[1] this is an important omission.

The purpose of this paper is to show that a second-order process is indeed measured, if one analyzes the decay including dissociation. A reason for previous observations of apparent third-order processes is suggested by this analysis.

II. THEORY

The precipitation of $I - V$ dipoles has been assumed by previous workers to follow the chemical rate equation

$$dn/dt = -\nu_0 n^\alpha e^{-E/kT}, \tag{1}$$

where n is the concentration of dipoles at time t, α is the order of the kinetics, T is the absolute temperature, E is the activation energy for the

aggregation process, and ν_0 is the frequency factor. For the initial condition $n = n_0$ at $t = 0$, this equation integrates to

$$(n_0/n)^{\alpha-1} = (\alpha - 1)n_0^{\alpha-1}\nu_0 t e^{-E/kT} + 1. \qquad (2)$$

The term $(n_0/n)^{\alpha-1}$ is then usually plotted versus t for different α, and the value of α for the best straight-line fit is taken as the order of the kinetics. A series of such straight-line plots for different temperatures is used to determine E and ν_0. These are found from an Arrhenius plot either at a fixed time t, or for a fixed fractional decay, at different temperatures.

Equation (2) implies that $(n/n_0) \to 0$ as t becomes large, which is usually *not* the case.[1, 12] In fact, if n_s is the equilibrium concentration, Eq. (2) becomes grossly inaccurate as n approaches n_s, unless n_s is negligible.

In general, one should write the following equation for dipole decay:

$$dn/dt = -C_1 n^2 + C_2 p - C_3 np - C_4 n^3 + C_5 q, \qquad (3)$$

plus terms involving higher-order complexes. Here n, p, and q are dipole, dimer, and trimer concentrations, respectively, and the C's are constants. The first two terms represent formation and dissociation of dimers; the third term represents trimer formation involving one dimer and one dipole; the fourth term trimer formation from three dipoles; and the fifth term, the dissociation of trimers. Since it is customary to express the C's as inverse relaxation times, n, p, and q must be dimensionless quantities, such as molar fractions. Neglect of this fact has in the past led to the incorrect postulate[11] that trimer formation dominates over dimer formation if n_0 is large enough ($n^3 > n^2$). Expressed correctly, $n \leqslant 1$, and the latter condition is impossible.

To simplify Eq. (3), we assume that trimer formation due to the simultaneous encounter of three dipoles is negligible, and that, at least initially, the formation of trimers from dimer plus dipole may also be neglected. Thus Eq. (3) reduces to

$$dn/dt = -C_1 n^2 + C_2 p. \qquad (4)$$

Neglecting the third term in Eq. (3) is reasonable as long as the number of dimers formed is still small, i.e., $p \ll n$. In this case,

$$n + 2p = n_0, \qquad (5)$$

and $p \ll n$ implies $\frac{1}{2}(n_0 - n) \ll n$, or $n/n_0 \gg \frac{1}{3}$. In other words, if Eq. (4) is to be valid until equilibrium is reached, a plateau must occur in the decay curve at a relatively high value of n/n_0.

Equation (4) may be written as

$$dn/dt = -C_1 n^2 + C_2 p \geqslant -C_1 n^2, \qquad (6)$$

because quantities C_1, C_2, n and p are positive. Therefore, since $n \leqslant 1$, the approximation $dn/dt \simeq -C_1 n^3$ is more likely to fit the data than $dn/dt \simeq -C_1 n^2$, as n/n_0 moves away from 1. In other words, when the decay data are plotted using Eq. (2), third-order kinetics can be made inadvertently to look better than second order, in this oversimplified case.

Equation (4) is solved by substitution for p using Eq. (5), yielding

$$dn/dt = -C_1 n^2 + \tfrac{1}{2}C_2(n_0 - n), \qquad (7)$$

Therefore, we have

$$\int dn \Big/ \Big(n^2 + \frac{C_2 n}{2C_1} - \frac{C_2 n_0}{2C_1}\Big) = -C_1 t + A, \qquad (8)$$

where A is an integration constant. Using the equilibrium condition $dn/dt = 0$, and Eq. (5),

$$C_2/C_1 = n_s^2/p_s = 2n_s^2/(n_0 - n_s). \qquad (9)$$

The integral in Eq. (8) is solved by the method of partial fractions, with the result

$$\ln[(n - b)/(n - a)] = C_1' t + C_3', \qquad (10)$$

where a and b are roots of the quadratic appearing in the integral $\{a = n_s, \; b = -n_0 n_s/(n_0 - n_s), \; C_1' = (a - b)C_1$, and $C_3' = \ln[(n_0 - b)/(n_0 - a)]\}$. In terms of measurable quantities, Eq. (10) may be written

$$\ln\{[n/n_0 + 1/(n_0/n_s - 1)]/(n/n_0 - n_s/n_0)\}$$
$$= C_1' t + C_3' = (a - b)\nu_0 t e^{-E/kT} + C_3'. \qquad (11)$$

III. EXPERIMENTAL PROCEDURE

The ionic-thermocurrent technique was used to monitor the decay of the $I - V$ dipole density with time. Details of crystal preparation and experi-
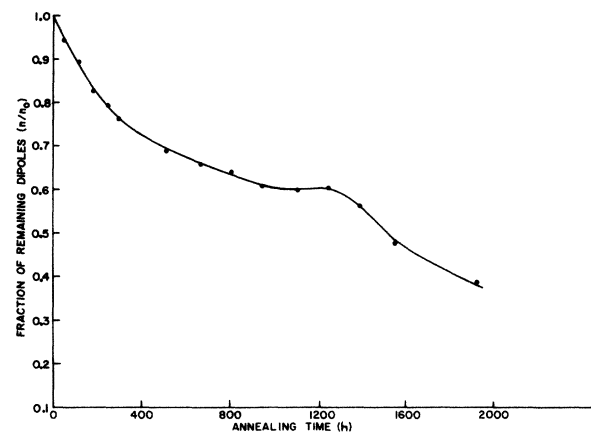

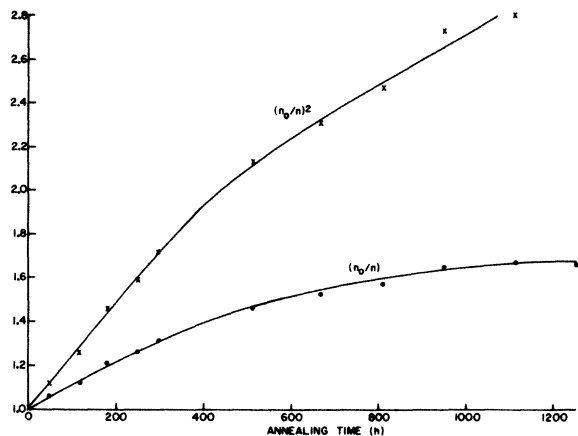FIG. 1. Precipitation of I-V dipoles in KCl:Eu^{++} (30 ppm) at 50 °C.

FIG. 2. Fitting of second- and third-order kinetics to the decay of I-V dipoles in KCl:Eu^{++} (30 ppm) at 50 °C, according to Eq. (2).

mental procedure have been given in a previous paper.[6]

IV. RESULTS

The aggregation of I- V dipoles was monitored in KCl doped with a low concentration (~ 30 ppm) of Eu^{++} ions. The decay at 50 °C is shown in Fig. 1.
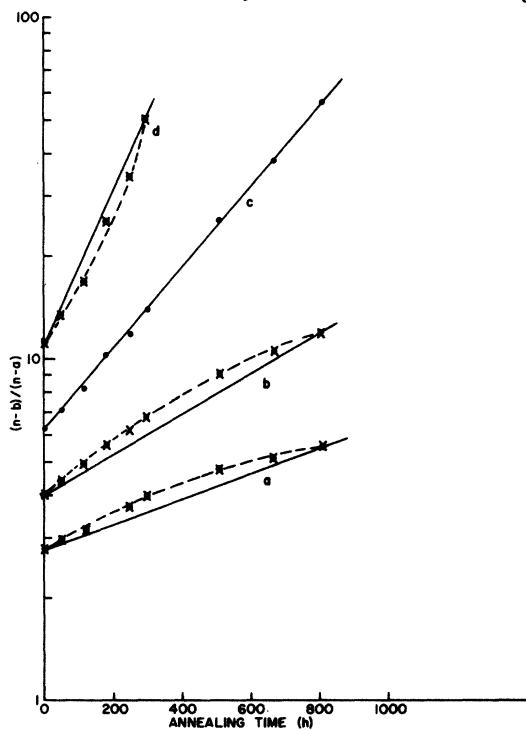

FIG. 3. Fitting of second-order kinetics to the decay of I-V dipoles in KCl:Eu^{++} (30 ppm) at 50 °C, according to Eq. (11) (curve C, using the experimental $n_s/n_0 = 0.6$). Attempted fits for other, arbitrarily chosen values of n_s/n_0 are also shown: $n_s/n_0 =$ (a) 0.4, (b) 0.5, (c) 0.6, (d) 0.7.
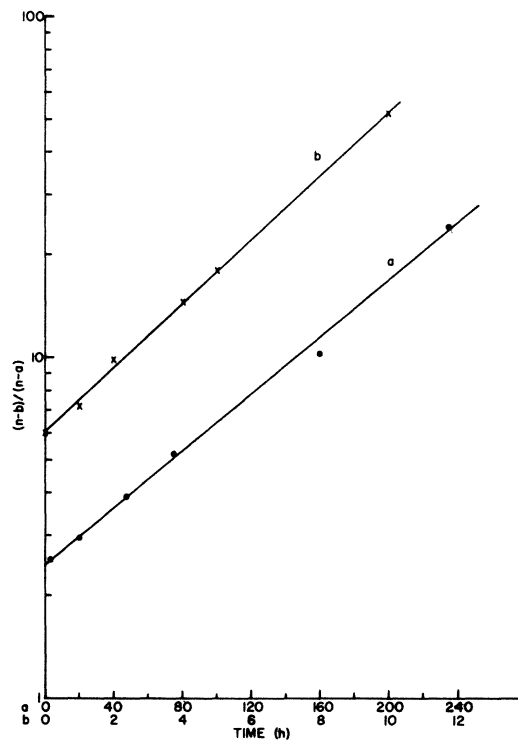

FIG. 4. Fitting of second-order kinetics to the decay of I-V dipoles in (a) KCl:Sr^{++} (140 ppm) and (b) KCl:Ba^{++} (34 ppm) at 50 °C. The data are taken from Ref. 1, Fig. 1, and Ref. 13, Fig. 1.
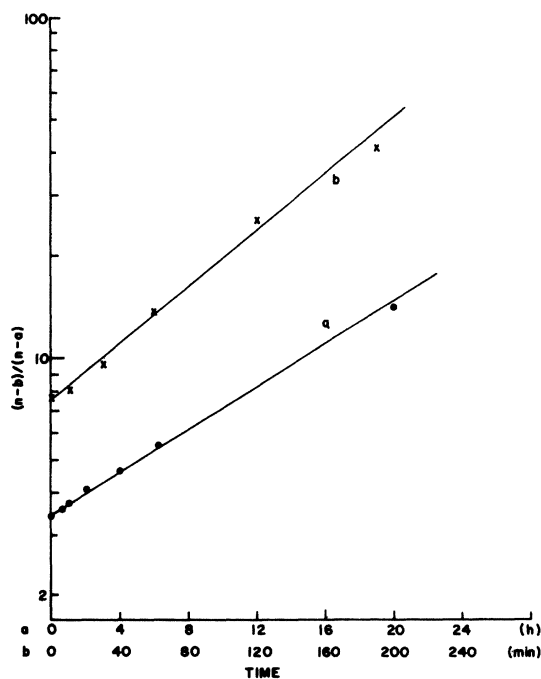

FIG. 5. Fitting of second-order kinetics to the decay of I-V dipoles in NaCl:Ca^{++} (220 ppm) at (a) 40 °C and (b) 60 °C. Data taken from Ref. 13, Fig. 2(a).

A plateau region is clearly visible at $n/n_0 = 0.6$, after which the decay continues.

The fit of the data in Fig. 1 to second- and third-order kinetics, according to Eq. (2), used by previous workers, is shown in Fig. 2. It is evident that either fit is good for the first 300 h or so, after which both curves deviate from straight lines. Thus, it is impossible to decide on the order of the kinetics using Eq. (2).

Because of the high plateau in Fig. 1, one expects Eq. (4) to be valid right up to the plateau region. The fit of the data to second-order kinetics, according to our Eq. (11), is shown in Fig. 3, curve C. The fit is excellent for all data points up to the plateau (~800 h of decay). The sensitivity of the plot to the true value of n_s/n_0 is shown on the same figure, by using arbitrarily chosen values of n_s/n_0, rather than the experimental value (0.6). Note that a good straight line is obtained only for $n_s/n_0 = 0.6$, and that the concavity changes for values of n_s/n_0 above and below the true experimental value.

Since a series of high-plateau curves (such as Fig. 1), at various temperatures, was not available and difficult to obtain, the activation energy and frequency factor associated with dimer formation was not obtained from an Arrhenius plot using Eq. (11).

The aggregation data of Cook and Dryden,[1] and Dryden[13] show the plateaus indicative of a situation where Eq. (11) should apply. Accordingly, their data was replotted using Eq. (11).

Figure 4 shows the results for KCl: Sr^{++} [(a), 140 ppm] and KCl: Ba^{++}[(b), 34 ppm]. Clearly defined plateaus were visible in the decay curves at $n_s/n_0 = 0.36$ and 0.59, respectively. Figure 5 shows the results for NaCl: Ca^{++} (220 ppm). Plateaus were visible at $n_s/n_0 = 0.46$ and 0.64 in the decay curves for 40 and 60 °C, respectively. The fits are all quite good, considering the errors involved in reading points off published graphs.

V. DISCUSSION

The results obtained by fitting aggregation data to Eq. (11) for several different impurities show that dimer formation is the initial aggregation process. This is particularly evident in cases where a high plateau is visible in the dipole decay curve, i.e., where Eq. (4) is expected to best

describe the situation. Dimer formation and dissociation occur until equilibrium is reached, and the formation of trimers and higher aggregates only becomes important beyond the plateau. In cases where dimer-dipole equilibrium cannot be established before the dimer density becomes comparable to the dipole density, trimer formation from dipole plus dimer combination becomes important, and Eq. (4) is no longer valid. This will occur if the dimers formed are too stable, and do not dissociate quickly. In such cases, there may be no indication on the decay curve of the inflexion point associated with the appearance of the plateau region. Note that when Eq. (4) becomes invalid, a poor fit to Eq. (11) should be obtained over the whole range of t, not just for large t. This is because the constants a and b in Eq. (10) depend on the establishment of an equilibrium between dimers and dipoles alone.

It should be noted that in the work of Cook and Dryden, [1, 13] where well-defined plateaus are clearly visible, the value of n_s/n_0 increases with annealing temperature. This is consistent with the model presented here. In general, one expects the equilibrium value of the dipole density to increase with temperature.[12]

When dimer dissociation is neglected, as has been the case in the past, and Eq. (1) is used, the rate of decay of n/n_0 is overestimated as t increases. n/n_0 is then underestimated, so that when the data are plotted according to Eq. (2), n_0/n is overestimated, and a better fit is obtained for $\alpha = 3$ than for $\alpha = 2$. Thus trimer formation has inadvertently been made to look like the initial aggregation process.

Since aggregation energies have previously been determined on the assumption of trimer formation, [3, 10] this analysis places them all in doubt. It is recommended that in future work, careful measurements be made to obtain a series of high-plateau curves at various temperatures. The aggregation energies may then be calculated using Eq. (11).

We do not find it necessary to invoke the idea of barriers inhibiting the formation of stable dimers, to get agreement with experiment, as does Crawford.[10] However, our theory does not necessarily negate Crawford's successive-reaction model. Rather we feel that it presents a simpler alternative model.

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