

Trimer formation due to dimer-dipole aggregation in alkali halides*

S. Unger[†] and M. M. Perlman

Groupe de Recherches sur les Semiconducteurs et les Diélectriques, Département de Physique, Collège Militaire Royal de Saint-Jean, Saint-Jean, Quebec, Canada

(Received 13 September 1976)

We previously showed that impurity-vacancy dipole density in KCl and NaCl, doped with various divalent impurities, decreases with time, due to dimer formation and dissociation, initially. This decay period is followed by a plateau where the rates of formation and dissociation of dimers are equal. Here, we show that further decay beyond the plateau region is due to a simple dimer-dipole association to form trimers.

We previously showed¹⁻³ that the aggregation of impurity-vacancy dipoles in KCl and NaCl doped with various divalent impurities followed initial second-order kinetics, if one included dissociation as well as formation in the dipole-decay theory. Thus, during annealing at any temperature, dipoles disappear by combining in pairs to form dimers, and there is a back reaction assumed, whereby dimers break up into dipoles. Accordingly, the dipole density decreases with time until an equilibrium is reached between dipoles and dimers, and a plateau is observed in the decay curves. This theory proved to be in excellent agreement with experiment. The results are in disagreement with the mechanism proposed by many other workers, who assumed an initial third-order process (see footnotes in Refs. 1-3). Recent EPR work on aggregation in AgCl:Mn²⁺ by Dutta and Slifkin⁴ is in complete agreement with our initial second-order theory.

This note is concerned with the decay in the post-plateau region, where the dimers and dipoles combine to form higher aggregates.

A general description of the dipole decay is given by

$$\frac{dn}{dt} = -c_1 n^2 + c_2 p - c_3 n p - c_4 n^3 + c_5 q, \quad (1)$$

where n , p , and q are the dipole, dimer, and trimer densities, respectively, and the c 's are constants.

In our preplateau theory,¹ the formation of trimers from dimer plus dipole or from three dipoles, and their dissociation was neglected. Thus, combining Eq. (1) minus the last three terms and

$$n + 2p = n_0, \quad (2)$$

where n_0 is the original dipole density, a solution was obtained for the dipole density n as a function of time. At the plateau, $dn/dt = 0$, and hence,

$$c_1 n_s^2 = c_2 p_s, \quad (3)$$

where n_s and p_s are the equilibrium dipole and dimer densities, respectively.

In the post-plateau region, we propose that trimers are formed and dissociate, and general equation (1) holds. We neglect the next to last term on the right-hand side because the formation of trimers from a three-body encounter is much less probable than two-body dipole-dimer association (middle term). The difficulty with the solution of the remaining equation is that the rate constants c are unknown. A number of different assumptions were then made, one of which was eminently successful in its agreement with experiment.

In our first attempt, we neglected trimer dissociation [the last term in Eq. (1)] and assumed that the number of trimers was small, for times not much larger than the equilibrium time. One then has

$$\frac{dn}{dt} = -c_1 n^2 + c_2 p - c_3 n p, \quad (4)$$

and Eq. (2) is approximately correct. c_1 and c_2 are related by Eq. (3), but an additional assumption is needed for c_3 . We tried $c_3 = c_1$, i.e., that the cross section for aggregation of dipole plus dimer was equal to that for the aggregation of two dipoles. A similar assumption has been made by Symmons and Kemp.⁵ Then, eliminating p in Eqs. (4) and (2), we solved for the dipole density n as a function of time, and compared the theory with experiment. Agreement was poor.

Next, we included trimer dissociation, but made the somewhat artificial assumption that the dimer-dipole equilibrium was maintained (i.e., $c_1 n^2 = c_2 p$) for times not much larger than the equilibrium time. Equation (1) then became

$$\frac{dn}{dt} = -c_3 n p + c_5 q \quad (5)$$

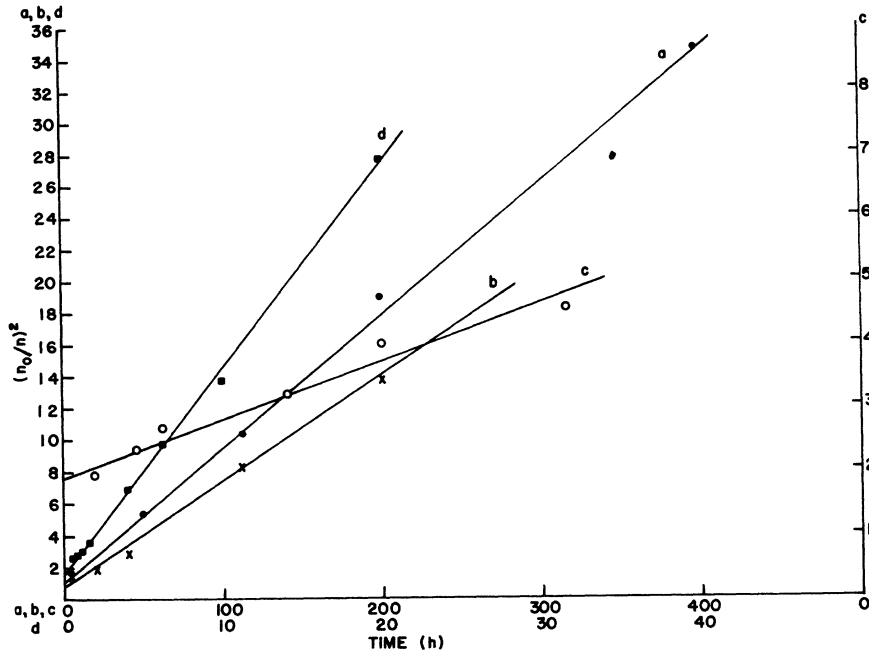


FIG. 1. Fitting of third-order kinetics to the decay impurity-vacancy dipoles in the post-plateau region. (a) NaCl:Mn²⁺ at 97.5 °C, (b) KCl:Sr²⁺ at 108 °C, (c) NaCl:Ca²⁺ at 70 °C, (d) NaCl:Mn²⁺ at 70 °C.

and

$$n + 2p + 3q = n_0 \quad (6)$$

In order to solve Eqs. (5) and (6), an additional assumption was needed for the c 's. We tried $c_3/c_3 = c_2/c_1$, i.e., that the ratios of the rate constants for trimer and dimer dissociation and association were equal. Again, agreement with experiment was poor.

All other attempts to solve Eqs. (1) (save one) led either to insoluble equations or physically unreasonable solutions. It became evident that attempts that included assumptions about the relations between rate constants were doomed *a priori*.

We then decided to neglect trimer dissociation, but to keep the dimer-dipole equilibrium assumption ($c_1 n^2 = c_2 p$), i.e., we solved

$$\frac{dn}{dt} = -c_3 np = -c_3 \left(\frac{c_1}{c_2}\right) n^3 \quad (7)$$

a simple third-order decay. The solution is

$$\left(\frac{n_0}{n}\right)^2 = \left(\frac{2c_1 c_3 n_0^2}{c_2}\right) t + \left[\left(\frac{n_0}{n_s}\right)^2 - \left(\frac{2c_1 c_3 n_0^2}{c_2}\right) t_s\right] \quad (8)$$

Thus a plot of $(n_0/n)^2$ vs t after the plateau in the dipole decay should be a straight line independent of any assumptions as to the rate constants.

Figures 1(a) and 1(b) use Cook and Dryden's results⁶ for the systems NaCl:Mn²⁺ (140 ppm) at 97.5 °C, and KCl:Sr²⁺ (140 ppm) at 108 °C, respectively. Figures 1(c) and 1(d) use Dryden's results⁷ for the systems NaCl:Ca²⁺ (360 ppm) at 70 °C and NaCl:Mn²⁺ (50 ppm) at 70 °C, respectively. Fairly good straight lines were obtained in all four cases.

Both Cook and Dryden⁶ and Symmons and Kemp⁵ have fitted third-order curves to the second stage of dipole decay. Their assumed mechanism is that dipoles add in pairs to the trimers they believe to be formed in the first stage of decay. We believe that decay in the post-plateau stage, for times not too much larger than the equilibrium time, is due to the simple addition of a dipole to dimers formed in the first stage.

*Work supported by the Defence Research Board of Canada.

† Present address: Dept. of Physics, Vanier College, St. Laurent, Québec, Canada.

¹S. Unger and M. M. Perlman, Phys. Rev. B **10**, 3692 (1974).

²S. Unger and M. M. Perlman, Phys. Rev. B **12**, 809 (1975).

³S. Unger and M. M. Perlman, Phys. Rev. B **12**, 5997

(1975).

⁴J. M. Dutta and L. M. Slifkin, Bull. Am. Phys. Soc. **21**, 323 (1976).

⁵H. F. Symmons and R. C. Kemp, Brit. J. Appl. Phys. **17**, 607 (1965).

⁶J. S. Cook and J. S. Dryden, Aust. J. Phys. **13**, 260 (1960); Proc. Phys. Soc. Lond. **80**, 479 (1962).

⁷J. S. Dryden, J. Phys. Soc. Jpn. Suppl. **18**, 129 (1963).