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Activation energies for impurity-vacancy dipole dimer formation in alkali halides*

S. Unger† and M. M. Perlman

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

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We recently showed that the aggregation of impurity-vacancy dipoles in KCl and NaCl doped with divalent impurities followed initial second-order kinetics, by considering dimer dissociation as well as formation in the dipole-decay theory. Here, we present further proof that dimers form initially. We determine the activation energies for dimer formation in KCl:Ba^{++}, KCl:Sr^{++}, and NaCl:Ca^{++}, and they differ from those previously determined by others, who used incorrect theories.

I. INTRODUCTION AND THEORY

In Ref. 1, we examined the kinetics used by many workers (over the past dozen years) to treat the aggregation of impurity-vacancy ($I-V$) dipoles in alkali halides. The reverse process to aggregation, i.e., dissociation, was generally neglected in the theories describing dimer or trimer formation. The chemical rate equation used in the past to describe the decay was

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

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 initial aggregation process, and ν_0 the frequency factor. Trimer formation ($\alpha = 3$) was often found when the decay data were analyzed with this equation.

Knowing that plateaus in the dipole-decay curves had been observed in several materials,[2,3] and that dimer formation was more probable than trimer, we proposed the following simple rate equation for creation and dissociation of dimers:

$$\frac{dn}{dt} = -c_1 n^2 + c_2 p, \tag{2}$$

where p is the dimer concentration, and c_1 and c_2 are constants.

When the rate of formation of dimers is equal to the rate of dissociation, $dn/dt = 0$, and a "plateau" exists in the decay curves. Equation (1), used by previous workers, in which the back reaction is neglected ($c_2 \ll c_1$) predicts vanishing n as t gets large, i.e., no plateau.

Equation (2) is valid only if we neglect formation and dissociation of trimers, i.e., if the number of dimers is less than the number of dipoles ($p \ll n$). Taken together with $n + 2p = n_0$, these two conditions yield $n/n_0 > \frac{1}{3}$, i.e., Eq. (2) is valid for high plateaus only. The solution to Eq. (2) is

$$\ln[(n-b)/(n-a)] = c_1' t + c_3', \tag{3}$$

where

$$a = n_s, \quad b = -n_0 n_s/(n_0 - n_s),$$
$$c_1' = (a-b)\nu_0 e^{-E/kT},$$
$$c_3' = \ln[(n_0 - b)/(n_0 - a)],$$

and n_s is the equilibrium dipole concentration at the plateau.

Rearranging terms in Eq. (3) (and taking logarithms again), one has

$$\ln\left(\frac{1}{a-b} \ln \frac{(n-b)(n_0-a)}{(n-a)(n_0-b)}\right) = \ln(\nu_0 t) - \frac{E}{k}\left(\frac{1}{T}\right). \tag{4}$$

A series of dipole-decay curves at different temperatures then permits a determination of the activation energy E, using a semilog plot.

In Ref. 1, we fitted isothermal decay data to Eq. (3) using our measurements in KCl:Eu^{++}, and data of Cook and Dryden[2,3] in KCl:Sr^{++} and NaCl:Ca^{++}.

In this paper, we present further evidence of the dimerization process for another $I-V$ dipolar system, KCl:Ba^{++}, and determine the activation energy for aggregation. The aggregation energies in KCl:Sr^{++} and NaCl:Ca^{++} are also found approximately, using the decay curves of Cook and Dryden.[2,3]

II. EXPERIMENTS

The ionic thermocurrent technique is used to monitor the decay of $I-V$ dipoles in KCL:Ba^{++} (67 ppm). Details of crystal preparation and experimental procedure have been given in a previous paper.[4]

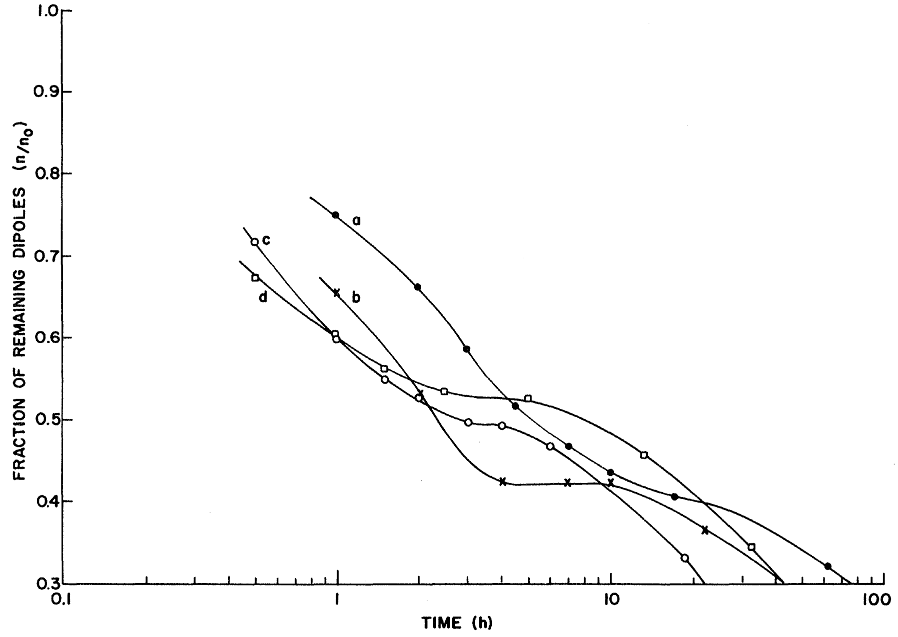

FIG. 1. Precipitation of $I-V$ dipoles in KCl:Ba^{++} (67 ppm) at (a) 44 °C; (b) 51 °C; (c) 55 °C; (d) 59 °C.

III. RESULTS AND DISCUSSION

Figure 1 shows the I - V dipole decay in KCl:Ba^{++} at various temperatures. A semilog plot is used to show the inflexion, occurring in the region of dimer-dipole equilibrium, more clearly. Definite plateaus occur at values of n_s/n_0 between 0.40 and 0.52, where Eq. (2) is valid (for $n_s/n_0 > 0.3$). The height of the plateau increases with increasing temperature, as expected for an equilibrium process.

The fit of the data in Fig. 1 to the dimerization theory given by Eq. (3) is shown in Fig. 2. The straight-line fits are all quite good, and lend themselves to a determination of the activation energy E. This is obtained from an Arrhenius plot using Eq. (4) and is shown in Fig. 3. The slope of the line gives $E = 0.92$ eV. Similarly, using the data of Cook and Dryden,[2,3] we obtain approximately $E = 0.89$ eV in KCl:Sr^{++} and 0.74 eV in NaCl:Ca^{++}.

The energies obtained for the dimerization process are all larger than those found for I - V dipole rotation,[5] which are about 0.7 eV. This is consistent with the view that, whereas dipole rotation is effected by vacancy jumps around the impurity ion, the dipole diffusion process necessary for aggregation also requires impurity-vacancy interchange, a higher-energy mechanism.

There is no obvious reason why the energy determined for NaCl:Ca^{++} should be considerably less than that for KCl:Ba^{++} or KCl:Sr^{++}. The energies obtained from diffusion coefficients of divalent impurities[6] in NaCl are typically between

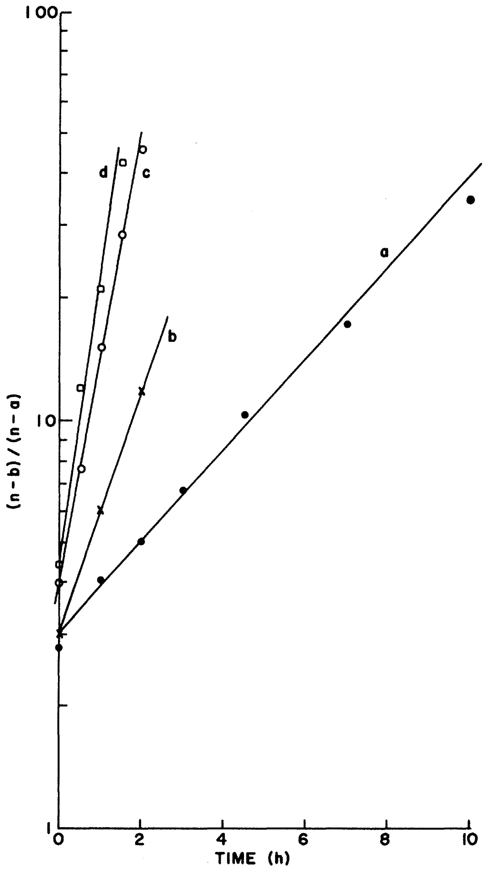

FIG. 2. Fitting of second-order kinetics to the decay of I-V dipoles in KCl:Ba^{++} (67ppm) at (a) 44 °C; (b) 51 °C; (c) 55 °C; (d) 59 °C.

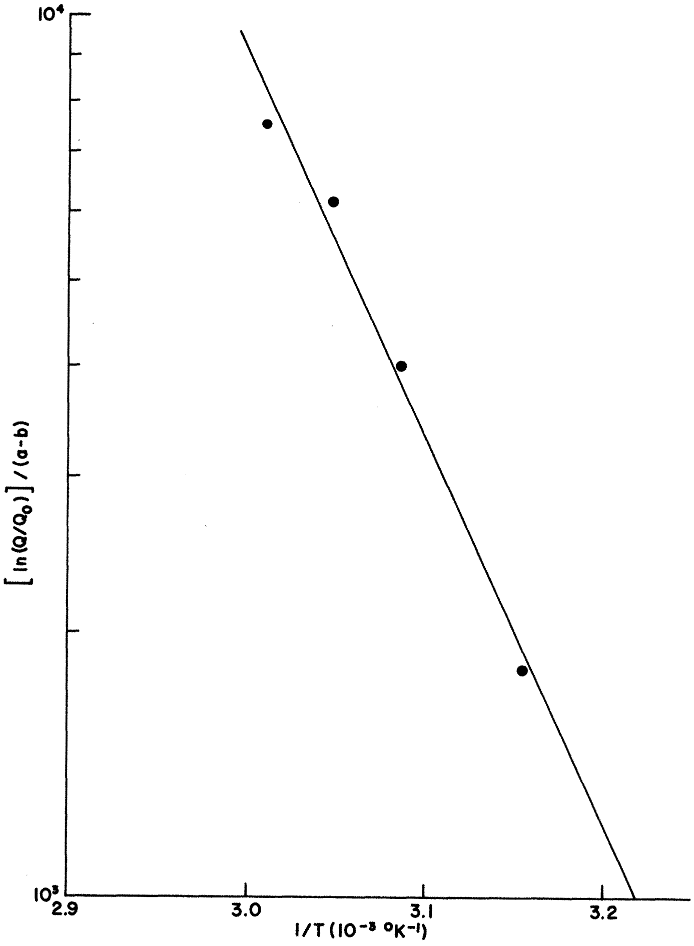

FIG. 3. Arrhenius plot to determine the activation energy for dimer formation in KCl:Ba^{++} [$Q = (n - b)/(n - a)$].

0.9 and 1.0 eV, and in KCl:Pb^{++}, 1.2 eV. It should be noted that the Arrhenius plots from which these energies were determined contained only three points in the cases of NaCl:Ca^{++} and KCl:Sr^{++} (all that were available from Cook and Dryden's[2,3] data), and four points in the case of KCl:Ba^{++}. The principal difficulty, (as discussed in Ref. 1) is in obtaining several decay curves over a considerable temperature range, all of which show high plateaus. (It took 4 months to obtain the data of Fig. 1.) This situation is required to satisfy Eq. (2), which is valid only where $n_s/n_0 > 0.3$. At relatively low temperatures, insufficient decay time is available for the dimer formation-dissociation equilibrium to be established, and plateaus are not observed. On the other hand, at relatively high temperatures, equilibrium is established so quickly that an insufficient number of data points is available before the plateau. Thus, one is left with a small temperature range in which to work, making energy determination difficult. The decay curves of Cook and Dryden[2] for KCl:Sr^{++}, and our Fig. 3, demonstrate this point well at both ends of the temperature scale.

The energies quoted here are different from those previously found for I-V dipole aggregation in these systems. We believe that our values are the correct ones, because they are determined from a theory of dipole decay which includes dimer dissociation, neglected in all previous theories.

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

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[6] See Table I in J. H. Crawford Jr., J. Phys. Chem. Solids 31, 399 (1970).