PHYSICAL REVIEW B VOLUME 31, NUMBER 12 15 JUNE 1985

Aggregation kinetics of Eu^{2+}-cation vacancy dipoles in the alkali halides: Dimer versus trimer formation

A. Muñoz F., E. Cabrera B.,* H. Riveros R.,* Marco Patrón, and J. Rubio O.†
Departamento de Física, Universidad Autónoma Metropolitana, Unidad Iztapalapa, 09340 México, Distrito Federal, Mexico

(Received 17 April 1984; revised manuscript received 7 August 1984)

The aggregation of Eu^{2+}-cation vacancy dipoles in Eu-doped NaCl, KCl, KBr, and RbBr single crystals has been carefully studied by measuring the evolution of dipole concentration as a function of the annealing time at 333, 343, 348, 353, 363, and 373 K using the electron-paramagnetic-resonance technique. The experimentally determined data were analyzed in terms of both pure second- and third-order kinetics equations with back reaction. In order to make the former, the formalism developed by Unger and Perlman was followed. In the other case, the data were analyzed in terms of an analytical solution to the pure third-order kinetics equation with back reaction which is presented in this paper for the first time. It is clearly shown that the experimental data can be fitted with the same accuracy to both the dimerization and trimerization models. In order to get additional information which could help to make a decision between the dimerization and trimerization models, a calculation of the activation energies for both processes was also performed in each of the systems investigated. The values obtained for both processes are quite similar and in the range expected for impurity diffusion in the alkali halides. This result indicates that, even with this knowledge, it is not possible to take any decision about the nature of the complex formed during the initial stage of dipole aggregation. Taking into account all these results, we have also analyzed the only possibility left to determine the order of the reaction involved, i.e., the concentration dependence of the rate constant in the kinetics equation at the very initial stage of aggregation. To do that, a large number of dipole-decay data points were measured at short annealing times after the quenching treatment in order to get a good knowledge of the dipole-decay curve when only a small amount of dipoles had been clustered to form aggregates into the alkali halide matrix. The analysis of the data taken at the earlier stage of aggregation, without assuming any reaction order *a priori*, indicates unambiguously that this dependence is the one expected for a pure second-order kinetics equation. This result indicates conclusively that dimers are really the complexes which are formed during the very initial stage of the clustering process. With all the experimental evidence presented in this paper, it appears that the long-existing controversy of dimer versus trimer formation in the aggregation kinetics of doubly valent impurity ions in the alkali halides may be definitively solved. It is also inferred that considerable caution must be exercised in using previous works in which dimers have been claimed to be the complexes formed during the initial stage of the aggregation process just by fitting the experimentally determined data to only the pure second-order kinetics equation with back (dissociation) reaction.

MS code no. BR2382 1985 PACS numbers: 78.50.Ec, 76.30.Da

I. INTRODUCTION

It is well recognized that when an alkali halide crystal doped with a low concentration of M^{2+} impurities is heated near the melting point and then quenched at room temperature all the divalent ions present in the sample are paired with cation vacancies forming the so-called I-V dipoles. If after this process the crystal is then annealed at a constant temperature, the initial concentration of dipoles decreases with time. This phenomenon of dipole aggregation has been the subject of a large number of investigations during the last two decades. In particular, Dryden and co-workers[1,2] were the first to analyze the kinetics of dipole aggregation of several divalent impurities in NaCl and KCl using the dielectric absorption technique. These authors found that the dipole-decay curve consisted, generally, of three well-defined stages. During the first stage, dipole decay is fast up to a plateau (stage II) in which the decay is extremely slow in comparison with that observed during stage I. On the other hand, stage III is characterized by a further step decrease in the concentration of the isolated dipoles. The part of the decay curve at which the plateau occurs, as well as its length, was found to be dependent both on the initial concentration and the annealing temperature. From the analyses of the dipole-decay curves obtained at several temperatures, Dryden and co-workers deduced that the initial stage of the aggregation process was governed by a third-order kinetics law and the activation energy for the process was determined. This finding is equivalent to considering that the first aggregation product is a trimer formed directly from three I-V dipoles. This conclusion was very surprising since pure third-order reactions are rare, even in the gas phase, due to the low probability of three-body encounters; in fact, the simultaneous encountering of three complexes is surely less probable than that of only two. Since that time there have been some efforts made at trying to find an alternative mechanism which will lead to the experimentally determined third-order kinetics. Among them, Crawford[3] proposed that the third-order kinetics law which govern the aggregation process could be accounted for by a two-stage reaction: (a) the formation of a loosely bound dimer, which then (b) captures a third dipole to form a trimer. If the dimers are in equilibrium with the isolated I-V dipoles, then the observed reaction will be proportional to the third power of the dipole concentration.

During the last few years, however, Unger and Perlman[4,5] have criticized the analyses performed by Dryden and co-workers and have established, by analyzing the original data of these authors as well as their own, that the first stage of the aggregation process of M^{2+}-impurity vacancy dipoles in the alkali halides is consistent with a pure second-order reaction when the dissociation (back) term of dimers into dipoles is taken into consideration in the kinetics equation. Unger and Perlman have also emphasized that a common characteristic in all of the work of Dryden and co-workers is the neglect of the reverse process in the theory of trimer formation. However, according to Unger and Perlman the back term appears to be quite important and misleading results could be obtained if there is no strong physical basis which could justify neglect of it in the analysis of the experimentally determined data.

Recent work performed by several authors,[6–9] as well as some reexaminations of the published data in terms of the Unger-Perlman model, established that dimers are the initial products in the aggregation process. However, evidence has also been gathered to show that trimers are the predominant clusters formed, as can be inferred from the very recent work performed by McKeever and Lilley[10] dealing with the aggregation process of Mg^{2+}-cation vacancy dipoles in LiF. Despite this, it appears that the knowledge of the aggregation phenomena is still contradictory, chiefly with regard to the nature of the first aggregation product, as can also be seen from some published comments in this journal.[11,12] The reason for the latter is probably the lack of sufficient dipole-decay data over a wide temperature and impurity-concentration range. This conclusion is based on the work performed by Dienes,[13] who analyzed an aggregation kinetics scheme composed of bimolecular, trimolecular, and nucleation reactions with back reactions included, and arrived at the conclusion that the kinetics of dipole aggregation is quite dependent on the initial dipole supersaturation. In fact, this author found that, at high supersaturation, third-order kinetics dominate the initial dipole decay, while at low supersaturation a bimolecular approach gives a good fit to the rate of monomer decay. From these results, Dienes suggested that it is quite necessary to have enough dipole decay and equilibrium data at several temperatures and especially over a wide range of initial impurity concentrations in order to firmly establish the consistency of any proposed kinetics scheme. On the other hand, to our knowledge, an analysis of the dipole-decay data in terms of an analytical solution to the pure third-order equation in which the back reaction has been taken into consideration has not yet been performed. Therefore, a meaningful comparison between the fitting of the experimental data to pure second- and third-order kinetics laws, both including the dissociation term, is lacking. This comparison appears to be important if the nature of the initial aggregation product is to be definitively established.

The purpose of the present paper is mainly to gain better insight into the controversy of dimer versus trimer formation in the aggregation process of M^{2+} impurities in the alkali halides. To do this we have carefully measured the dipole-decay curves of Eu^{2+}-cation vacancy dipoles in four different alkali halides, i.e., NaCl, KCl, KBr, and RbBr, at different annealing temperatures and for several europium concentrations (i.e., from ~ 20 up to ~ 400 ppm).

The Eu^{2+} ion was selected to obtain this information in view of its paramagnetic nature, which allowed us to use the EPR technique. With use of this technique several advantages can be obtained with respect to those which have been traditionally employed to monitor the clustering processes of doubly valent impurity ions in alkali halides (ionic thermocurrents and dielectric absorption). In particular, one of the main advantages is that measurements can be performed in shorter times, and therefore, a much better knowledge of the dipole-decay curve, especially at the earlier stage, can be achieved. This last point is quite important if the nature of the complex which is formed at the very initial stage of the aggregation process is to be established. On the other hand, we are reporting for the first time an analytical solution of the pure third-order kinetics equation with back reaction, which allowed us to make a meaningful comparison between the fitting of the experimentally determined data to the pure second- and third-order kinetics laws.

The results obtained in this investigation indicate unambiguously that dimers are really the complexes which are formed during the very initial stage of the clustering process. It appears that with all the experimental evidence presented in this paper the controversy of dimer versus trimer formation in the aggregation kinetics of doubly valent impurity ions in the alkali halides could be definitively solved.

II. EXPERIMENT

Four alkali halide single crystals, i.e., NaCl, KCl, KBr, and RbBr, doped with Eu^{2+} ions have been used in the present investigation. They were grown by Guerrero at the Institute of Physics, Universidad Naciònal Autónoma de México Crystal Growth Laboratory, following the Czochralski method under a controlled atomosphere of dry argon. Eu doping was achieved by adding to the melt $EuCl_2$ which was obtained from $EuCl_3 \cdot 6H_2O$ using standard reduction techniques.[14] The impurity concentration in the crystals was determined from the optical-absorption spectrum of the freshly quenched samples following the same procedure as one described elsewhere.[15] To do this, a Perkin Elmer model 330 double-beam recording spectrophotometer was employed.

The as-grown crystals were always heated for ~ 1 h at 850 K and then fast-quenched in acetone. This thermal treatment has been reported by Taylor *et al.*[16] to be the more adequate one to prevent clustering during cooling. However, in order to corroborate this last point, ionic thermocurrent (ITC) measurements were performed immediately after the quenching treatment using a homemade cryostat evacuated to a pressure of at least 10^{-5} Torr and a Keithley model 616 electrometer. From the area under the observed ITC peak, assuming nearest-neighbor reorientation,[17] the concentration of Eu^{2+}-cation vacancy dipoles in the quenched samples was found to be the same, within experimental error ($\pm 10\%$), as the total concentration of Eu^{2+} ions as determined from the optical spectrum. This result indicated, therefore, that for the range of impurity concentration employed in this work (~ 20 up to ~ 440 ppm), all the Eu^{2+} ions were forming dipoles isolated in the matrix after the quenching treatment. This determination is quite important in measurements on clustering kinetics in order to ensure that all the impurity ions are in the form of *I-V* dipoles isolated in the matrix at the start of the aging process. Otherwise, the annealing experiments may not be quite as simple to interpret because at the beginning of an experiment some clusters will be present.

The rate of disappearance of dipoles as a function of the annealing time was monitored using the EPR technique. It is well known[13] that the EPR spectrum of Eu^{2+}-doped alkali halides is the superposition of two groups of seven fine-structure lines, each split into two sextets arising from the hyperfine interaction with the two europium isotopes. The spectrum has been ascribed to *I-V* complexes in which the Eu^{2+} ion is associated with a nearest-cation vacancy along the [110] direction. It should be emphasized that the EPR technique was employed since the signal intensity from isolated Eu^{2+}-cation vacancy dipoles can be reliably detected over a broad temperature range and changes in the concentration of the centers in question can be inferred from changes in the signal intensity. In order to perform the measurements a Varian *E*-4 spectrometer was employed, in view of the fact that its working conditions can be fixed in a quite fast and easy manner; these advantages over other spectrometers are quite useful in order to perform the measurements reported in this paper. After the quenching treatment the sample was quickly dropped into a quartz tube which was already located in the EPR cavity and held at the temperature at which the dipole redistribution kinetics were to be studied. Sample temperature was held constant within ± 0.2 K in the EPR cavity by employing a Hakee thermal bath which circulated either oil or diesel fuel through the cavity at the desired temperature. Only about 12 sec or less were spent to obtain sample orientation and the final working conditions of the spectrometer, after which measurements of the intensity of dipole spectra were made. To do the latter, two experimental procedures were followed. In the first, the lowest hyperfine line of the lowest-field electronic transition,[18] $|+\frac{5}{2}\rangle \rightarrow |\frac{7}{2}\rangle$, when $\mathbf{H} \| [001]$, was recorded as a function of the annealing time every 10 sec, the time employed to perform the recording being less 3 sec. In the other case, the pen of the recorder was fixed at the position of maximum intensity of the EPR line after it was recorded for the first time, and then its continuous decrease as a function of the annealing time was obtained in an *X-t* recorder. The results obtained following both procedures were quite similar and did not differ by more than $\sim 5\%$. With these experimental procedures, it was possible to take a large number of experimental dipole-decay data points, specifically at short annealing times after the quenching treatment, and, therefore, very good knowledge of the very initial stage of the dipole-decay curve was attained. This last point was quite important in order to determine the order of the kinetics equation involved during the earlier stage of the aggregation process unambiguously. In all systems investigated the dipole-decay curves at each temperature were obtained at least three times and the reproducibility of measurements was within $\pm 5\%$.

III. THEORY

A. Dimer formation

Taking into account that plateaus are really observed in the dipole-decay curves and that encountering two isolated dipoles is more probable than simultaneously encountering three, Unger and Perlman[4,5] proposed the following rate equation for the reaction between dipoles and dimers:

$$\frac{dn}{dt} = -C_1 n^2 + C_2 p \ , \qquad (1)$$

where C_1 and C_2 are the rate constants, and n and p are the concentration of dipoles and dimers, respectively. Equation (1) is only valid when (a) the formation and dissociation of trimers are neglected, (b) the concentration of trimers is negligible, and (c) the plateau region in the dipole-decay curve is obtained for $n/n_0 \gg \frac{1}{3}$. Under these circumstances, the solution to Eq. (1) is given by

$$\ln[(n-b)/(n-a)] = (a-b)C_1 t + \ln[(n_0-b)/(n_0-a)] \ , \qquad (2)$$

where

$$a = n_s \text{ and } b = -n_0 n_s/(n_0 - n_s) \ .$$

n_s and E are the equilibrium dipole concentration at the plateau and the activation energy for the dimerization process, respectively. It is observed from Eq. (2) that if the dimerization process is the only one which occurs during the aggregation process, then a plot of $\ln[(n-b)/(n-a)]$ versus the annealing time should be a straight line.

B. Trimer formation

The rate equation for the reaction between trimers and dipoles is given by

$$\frac{dn}{dt} = -C_5 n^3 + C_6 q \ , \qquad (3)$$

where C_5 and C_6 are the rate constants, and n and q are the concentration of dipoles and trimers, respectively. The first term in Eq. (3) corresponds to the formation of trimers from the simultaneous encounter of three dipoles and is the one considered by earlier workers.[1,2] The second term takes into account the back reaction when trimers dissociate.

In the pure third-order kinetics equation given by (3), it is assumed that the concentration of dimers is negligible. Taking into account that, in this case, $n+3q=n_0$, Eq. (3) can be rewritten in the following form:

$$\frac{dn}{dt}=-C_5n^3+C_6(n_0-n)/3 \ , \tag{4}$$

which can then be integrated by factorization of the cubic equation in n only if the following auxiliary conditions are taken into consideration:

$$n(t=0)=n_0 \ , \tag{5a}$$

and the equilibrium condition at the plateau,

$$C_5n_s^3=C_6(n_0-n_s)/3 \ , \tag{5b}$$

where n_s has the same meaning as before. Under these conditions, the solution to Eq. (4) is given by

$$\ln(n-a)=-n_s^2(3n_0-2a)C_5t/(n_0-a)+\ln(n_0-a) \ . \tag{6}$$

Reference to Eq. (6) shows that if the trimerization process is the only one occurring during the initial aggregation process, then a plot of $\ln(n-a)$ versus the annealing time should be a straight line.

By now having analytical solutions to both the pure second- and third-order kinetics equations with back reaction, a meaningful comparison between the dimerization and trimerization processes can be performed, and then a more firm decision between the nature of the initial aggregation complex can be advanced.

C. Concentration dependence of the rate constant at the very initial stage of aggregation

A clustering process in which n (M^{2+}-V^-) dipoles combine to form an n-mer may be expressed by a kinetic equation of the form

$$\frac{dX}{dt}=-K_1X^n+K_2X_n \ , \tag{7}$$

with the condition $X+nX_n=X_0$, where X is the concentration of dipoles still isolated in the matrix at each time, X_n the concentration of n-mers, and X_0 the initial concentration of dipoles. If Eq. (7) is rewritten in terms of the fraction of dipoles ($p=X/X_0$) remaining after some annealing time t, the following equation is obtained:

$$\frac{dp}{dt}=-K_1p^nX_0^{n-1}+\frac{K_2}{n}(1-p) \ . \tag{8}$$

Reference to Eq. (8) shows that the rate constant for aggregation is a function of the initial dipole concentration X_0. This functional dependence can be easily obtained under the condition in which the dissociation term $(K_2/n)(1-p)$ in Eq. (8) may represent only a very small contribution to the first term in the same equation, and, therefore, can be neglected. It could be thought that this can be done, in principle, if and only if $K_1p^nX_0^{n-1} \gg (K_2/n)(1-p)$. However, since the values for K_1 and K_2 are not known *a priori*, it is necessary to have another condition which may allow us to safely neglect the back reaction in Eq. (8). The relationship between the rate constants K_1 and K_2 can be obtained from the equilibrium condition in the plateau region of the dipole-decay curve. In this case it is straightforward to obtain

$$K_2=nK_1p_s^nX_0^{n-1}/(1-p_s) \ , \tag{9}$$

where p_s represents the equilibrium fraction of dipole concentration at the plateau region. Substituting the value given above for K_2 in Eq. (8),

$$\frac{dp}{dt}=-K_1p^nX_0^{n-1}+K_1p_s^nX_0^{n-1}\frac{1-p}{1-p_s} \ . \tag{10}$$

Now, it is clear that the dissociation term in Eq. (10) can be neglected if and only if the following condition is obeyed:

$$\frac{p^n}{1-p} \gg \frac{p_s^n}{1-p_s} \ . \tag{11}$$

Therefore, if the dipole-decay curve is carefully measured for some selected impurity concentration and annealing temperature in such a way that the plateau region is reached at a value of p_s in the range 0.4—0.6, and the analysis of the data is carried out for p values in the range 0.95—0.98, then the dissociation term in Eq. (10) represents a contribution of, at most, 5% of the first term (using either $n=2$ or 3), and can be safely neglected in the analysis of the experimentally determined data. In fact, the experimental data cannot be obtained with a better precision than this small contribution. Under these conditions, the time,

$$\tau=\frac{-p^{1-n}}{(1-n)K_1X_0^{n-1}} \ , \tag{12}$$

taken to reach a fractional dipole concentration in the range of p values mentioned above will give information about the order of the kinetics equation involved in the very initial state of the clustering process. In particular, if the reaction is of a pure second order, then τ (0.95—0.98) should be proportional to X_0^{-1}, whereas for a pure third-order reaction it should be proportional to X_0^{-2}.

IV. RESULTS AND DISCUSSIONS

Figure 1 shows, as an example, some of the dipole-decay curves that were obtained in the systems investigated at some specific annealing temperatures. It is clear from this figure that stages I and II are clearly observed in the dipole-decay curves. It should be pointed out that in our experiments the annealing time was not extended up to stage III in the dipole-decay curve in view of the fact that for the main purpose of this paper knowledge of this region is unimportant.

On the other hand, it should be noted that as an important difference with all similar previous works dealing with the aggregation processes of M^{2+} impurities in the

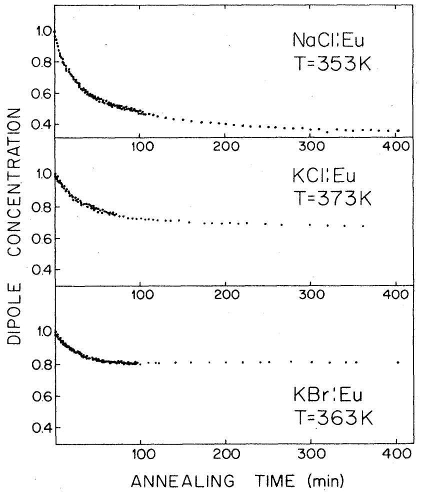

FIG. 1. Dipole-decay curves for Eu^{2+}-cation vacancy dipoles in NaCl (80 ppm), KCl (260 ppm), and KBr (180 ppm) at selected temperatures.

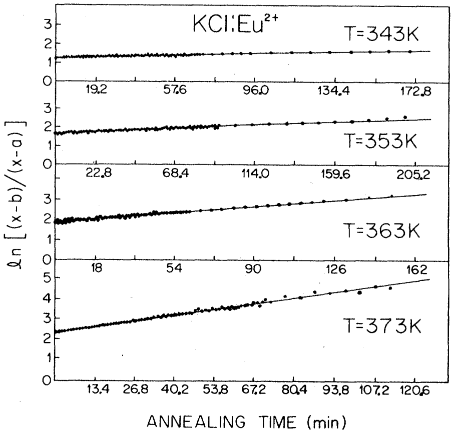

FIG. 3. Fitting of pure second-order kinetics to the decay of Eu^{2+}-cation vacancy dipoles in KCl (260 ppm) at 343, 353, 363, and 373 K, according to Eq. (2).

alkali halides, in this investigation a large number of experimental data points were obtained during stage I of the dipole-decay curves, specifically at very short times, in order to gain better knowledge of the dipole-decay process involved during this stage. This fact allowed us to make a meaningful comparison between the fit of the data to pure second- and third-order kinetics laws, both including the back reaction.

Figures 2–5 show a plot of $\ln[(n-b)/(n-a)]$ as a function of annealing time at four different temperatures in NaCl, KCl, KBr, and RbBr, respectively. It should be mentioned that in europium-doped RbBr the dipole-decay data at 343 K were not analyzed, and, therefore, are not presented here, since the plateau region occurred at a value of $n/n_0<\frac{1}{3}$ where Eq. (2) is not valid. Reference to these figures shows that in all the systems investigated the straight-line fits are all quite good up to the plateau region, in agreement with Eq. (2). The correlation coefficient calculated from a least-squares fit of the straight lines shown in the figures is 0.990 or better in all cases. With only these results, it may be inferred that the aggregation process of Eu^{2+}-cation vacancy dipoles in NaCl, KCl, KBr, and RbBr follows initial pure second-order kinetics by considering dimer dissociation as well as formation in the dipole-decay theory.

On the other hand, the fit of the experimental data to the pure third-order kinetics equation with back reaction, according to our Eq. (6), is portrayed in Figs. 6–9 for NaCl, KCl, KBr, and RbBr, respectively. The straight-line fits in these figures are all quite as good as in those cases in which the dimerization theory was considered according to Eq. (2). Also, the values for the correlation coefficients obtained from a least-squares method in each

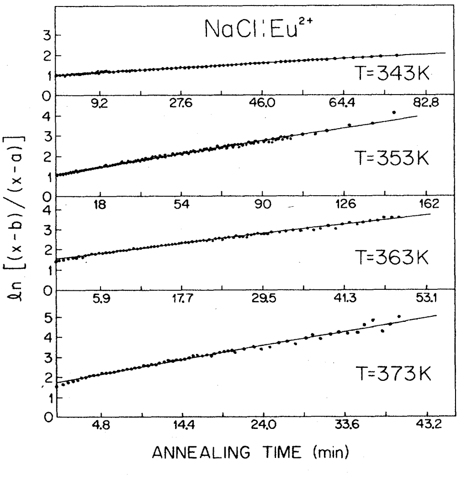

FIG. 2. Fitting of pure second-order kinetics to the decay of Eu^{2+}-cation vacancy dipoles in NaCl (80 ppm) at 343, 353, 363, and 373 K, according to Eq. (2).

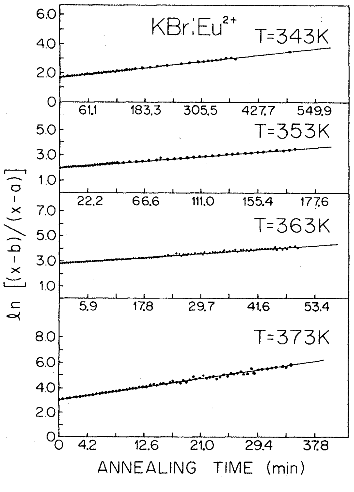

FIG. 4. Fitting of pure second-order kinetics to the decay of Eu^{2+}-cation vacancy dipoles in KBr (180 ppm) at 343, 353, 363, and 373 K, according to Eq. (2).

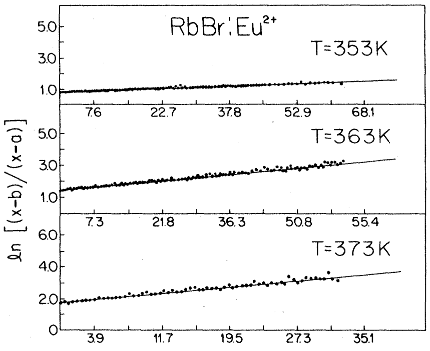

FIG. 5. Fitting of pure second-order kinetics to the decay of Eu^{2+}-cation vacancy dipoles in RbBr (170 ppm) at 353, 363, and 373 K, according to Eq. (2).

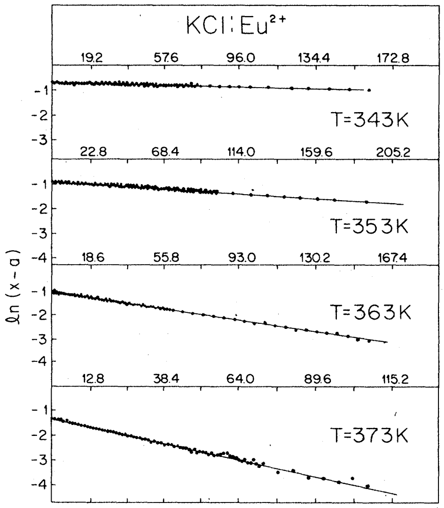

FIG. 7. Fitting of pure third-order kinetics to the decay of Eu^{2+}-cation vacancy dipoles in KCl (260 ppm) at 343, 353, 363, and 373 K, according to Eq. (6).

case were similar to those found for the straight lines given in Figs. 2—5.

These results indicate that in all the systems investigated the experimentally determined data can be fitted with the same accuracy to both the pure second- and third-order kinetics laws including the back reaction. This is the first time in which this fact has been evidenced. Therefore, the fit alone has, consequently, hardly any physical meaning, and cannot be used to firmly deduce the nature of the complex formed (dimer or trimer) during the initial stage of the dipole aggregation process.

In order to gain additional information which could help in making a decision between the dimerization and trimerization models, a calculation of the activation energy (E) for both processes was also performed in each of the systems investigated. To do that, from the slopes of the straight lines, portrayed in Figs. 2—5, and 6—9, values for the constants C_1 and C_5 in Eqs. (2) and (6), respectively, were obtained at the different annealing temperatures for each host crystal. Then an Arrhenius plot of $\ln C_1$ ($\ln C_5$) versus $1/T$ was performed and the results are given in Figs. 10 and 11 for the dimerization and trimerization processes, respectively. The values calculated for E, from the slopes of the straight lines adjusted by the least-squares method in these figures, and reported in Table I for both processes, are nearly identical and are in the range expected for impurity diffusion in the alkali halides. Moreover, in both cases the activation energies are, in general, larger than those previously reported[17] for

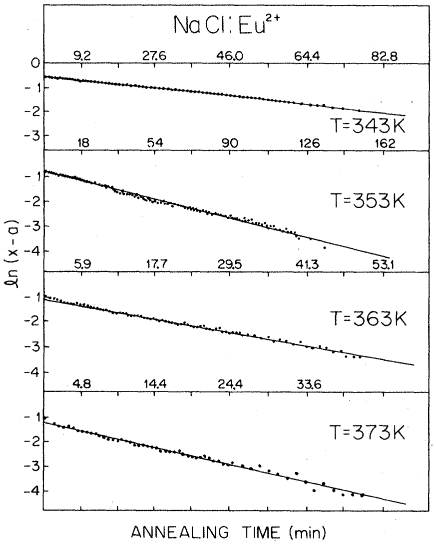

FIG. 6. Fitting of pure third-order kinetics to the decay of Eu^{2+}-cation vacancy dipoles in NaCl (80 ppm) at 343, 353, 363, and 373 K, according to Eq. (6).

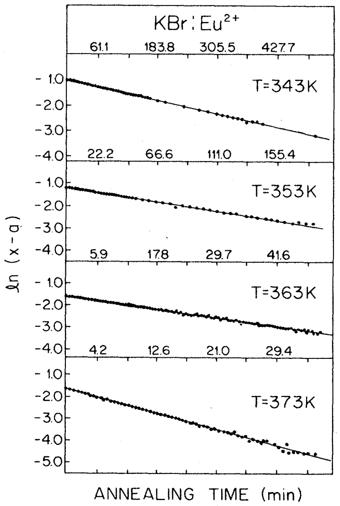

FIG. 8. Fitting of pure third-order kinetics to the decay of Eu^{2+}-cation vacancy dipoles in KBr (180 ppm) at 343, 353, 363, and 373 K, according to Eq. (6).

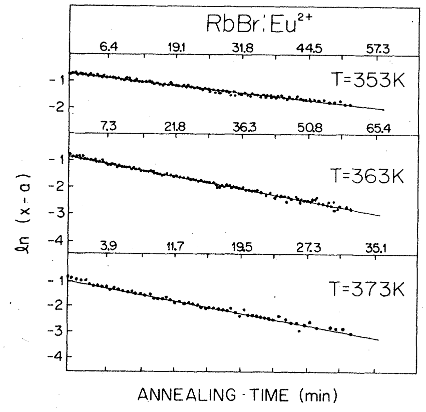

FIG. 9. Fitting of pure third-order kinetics to the decay of Eu^{2+}-cation vacancy dipoles in RbBr (170 ppm) at 353, 363, and 373 K, according to Eq. (6).

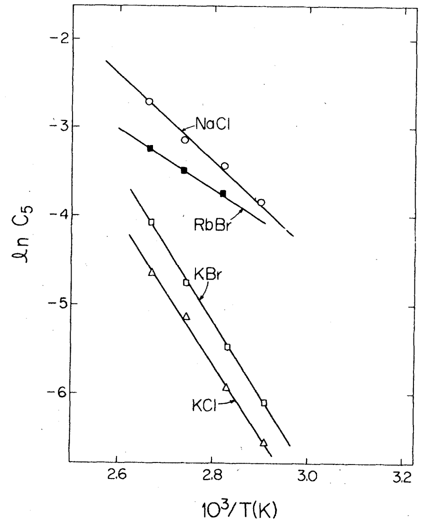

FIG. 11. Arrhenius plot to determine the activation energy for trimer formation in europium-doped NaCl, KCl, KBr, and RbBr single crystals.

Eu^{2+}-cation vacancy dipole rotation. This result is expected in view of the fact that the dipole diffusion process necessary for producing the aggregation phenomenon also requires impurity-vacancy interchange, which is a higher-energy mechanism.

The results above indicate that even with the knowledge of the activation energies for both the dimerization and trimerization processes, it is not possible to take any decision about the nature of the complex formed during the initial stage of the dipole aggregation process. Therefore, it appears that the only possibility left of finding the order of the reaction is to determine the concentration dependence of the rate constant in the kinetics equation at the very initial stage of the aggregation process. It could be possible that, with this information at hand, a clear distinction between the dimerization and trimerization models can arise, and, therefore, the nature of the initial aggregation product could be firmly established.

Considering the importance of this determination in order to solve the controversy of dimer versus trimer formation, the concentration dependence of the rate constant for Eu^{2+}-cation vacancy dipole aggregation in NaCl and KBr at the earlier stage of the clustering process also has been carefully analyzed in the present investigation in the temperature range 333–363 K and for a wide range of europium concentrations (i.e., from ~20 up to ~400 ppm). The two crystals above were selected in view of the fact that the europium precipitation processes occurring in these two lattices are quite different. Therefore, it could be suggested that the complex which is initially formed

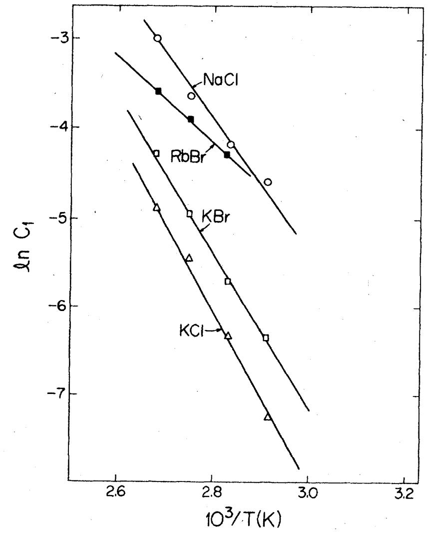

FIG. 10. Arrhenius plot to determine the activation energy for dimer formation in europium-doped NaCl, KCl, KBr, and RbBr single crystals.

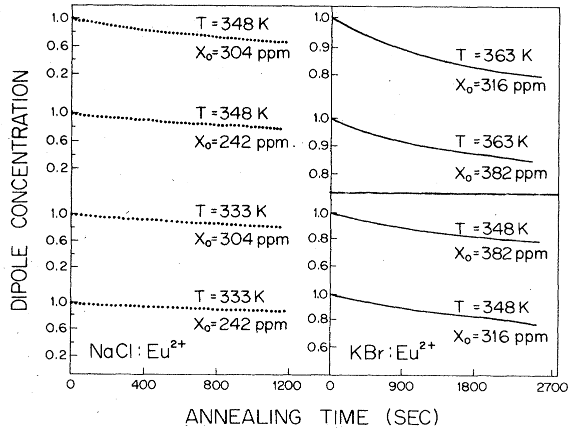

FIG. 12. Decay of Eu^{2+}-cation vacancy dipoles in NaCl and KBr as a function of impurity concentration and annealing temperature. The data shown were taken following the two experimental procedures mentioned in the text.

TABLE I. Values of the activation energies for the dimerization (E_d) and trimerization (E_t) processes of Eu^{2+}-cation vacancy dipoles in some alkali halide single crystals. Values for the reorientational energy (E_r) of the Eu^{2+}-cation vacancy dipole in a nearest-neighbor position are also included for the sake of comparison. The numbers in parentheses are the errors in the last significant figure.

	NaCl	KCl	KBr	RbBr	Ref.
E_d (eV)	0.64(5)	0.86(2)	0.78(2)	0.44(4)	This work
E_t (eV)	0.53(5)	0.72(2)	0.78(2)	0.40(4)	This work
E_r (eV)	0.58(1)	0.66(2)	0.54(1)	0.39(2)	Ref. 17

during the Eu-aggregation processes in NaCl may be of a different nature than that in KBr.

Figure 12 shows some the experimentally determined dipole-decay data for europium-doped NaCl and KBr as a function of impurity concentration and sample temperature. It should be pointed out that the dipole decay portrayed in this figure mainly corresponds to short annealing times and for some of the highest concentrations employed. However, for both host crystals, annealing temperatures, and Eu concentrations selected, the measurements were carried out up to the plateau region in the dipole-decay curve to be sure that the value of p_s was in the range 0.4—0.6, and that, therefore, the criteria mentioned above that neglected the dissociation term in the kinetics equation (10) will be operative. The obtained dipole-decay curves up to the plateau region in these cases are quite similar to those given in Fig. 1, and they are again not shown here for the sake of brevity.

From the dipole-decay data obtained, the time τ taken to reach a fractional dipole concentration of either 0.98 or 0.95 was determined as a function of Eu concentration at a fixed annealing temperature for both host crystals. Then, a plot of log τ versus $\log X_0$ was carried out in each case; the results are portrayed in Figs. 13 and 14 for NaCl and Figs. 15 and 16 for KBr. Maximum estimated uncertainties are shown by the horizontal and vertical lines through each point. In all cases, a least-squares fitting of the experimentally determined data gave a slope of -1.0 ± 0.1 and a correlation coefficient of 0.995 or better. In fact, the line drawn in Figs. 13—16 has a slope of -1. From these results it can be established unambiguously that the kinetics equation involved during the earlier stage of the clustering process of Eu^{2+}-cation vacancy dipoles in these two systems is pure second order over a wide range of impurity concentrations. Therefore, we may conclude that dimers are the complexes which are definitively formed during the very initial stage of aggregation. It should be strongly emphasized that this conclusion holds for both NaCl and KBr, even though the Eu-precipitation processes occurring in these two lattices are quite different.[19,20] In fact, in KBr the annealing of quenched samples in the temperatures range 300—373 K produces the nucleation of a second-phase precipitate which appears to be related to the Suzuki phase of the Eu^{2+} ions in this lattice with the structure $6KBr{:}EuX_2$. The aging at higher temperature ($\sim$473 K), however, produces the formation of at least one metastable precipitate, from which grows the stable dihalide phase $EuBr_2$, the structure of the metastable precipitate being quite similar to that of the stable dihalide phase. At variance with these results, evidence supporting the nucleation of the Suzuki phase in NaCl has not been found up to date even after a wide variety of heat treatments. Rather, the annealing of quenched samples in the temperature range 300—573 K produces only the formation of several metastable precipitates in addition to the stable dihalide-phase $EuCl_2$. This difference in precipitation behavior could suggest that the nature of the complex initially formed during the Eu-aggregation process may be different in

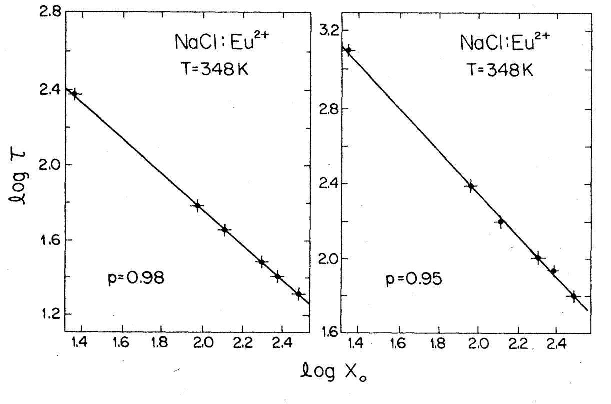

FIG. 13. Plot of logarithm of the time (in sec) taken to reach a fractional dipole concentration of either 0.98 or 0.95 vs the logarithm of europium concentration (in ppm) in NaCl for a sample temperature of 348 K.

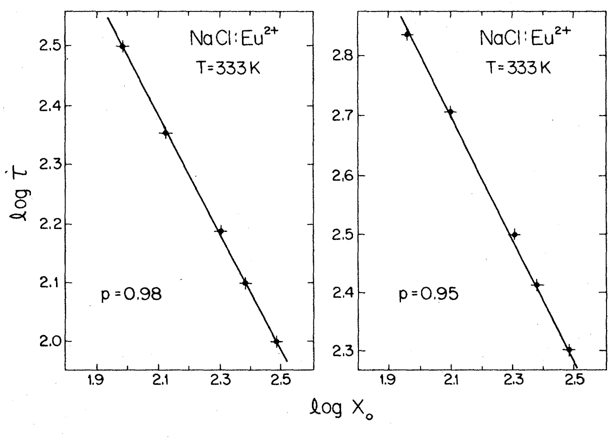

FIG. 14. Same as in Fig. 2, but for a sample temperature of 333 K.

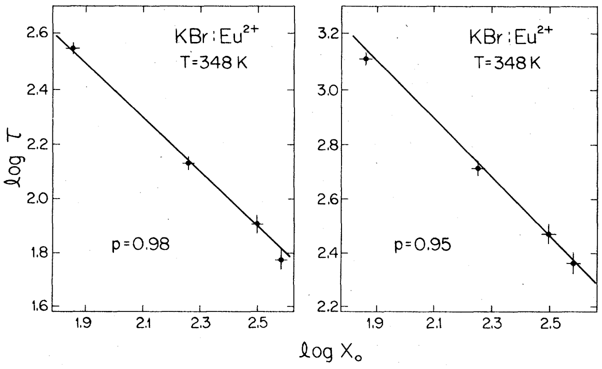

FIG. 15. Plot of logarithm of the time (in sec) taken to reach a fractional dipole concentration of either 0.98 or 0.95 vs the logarithm of europium concentration (in ppm) in KBr for a sample temperature of 348 K.

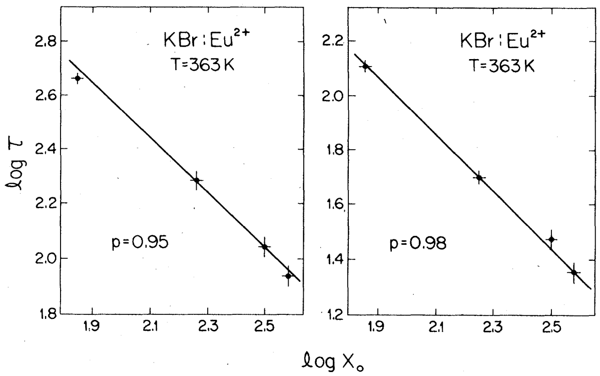

FIG. 16. Same as in Fig. 4, but for a sample temperature of 363 K.

these two crystals. However, the results presented in this paper clearly indicate that this is not the case, and that in both cases dimers are the complexes formed during the very initial stage of the clustering process. We expect that this conclusion may be valid for other doubly valent impurity ions and host crystals. Unfortunately, the type of measurements reported in this paper can only be performed in crystals doped with paramagnetic impurities, for which the EPR technique can be employed to monitor dipole decay at the earlier stage of aggregation. This is not the case for impurities such as Ca^{2+}, Sr^{2+}, Cd^{2+}, Ba^{2+}, etc., which have been traditionally employed to study the aggregation kinetics of M^{2+}-V^- dipoles in the alkali halides and for which other techniques such as ITC are needed for this particular purpose. With the use of these other techniques, however, it is extremely difficult to obtain reasonably good knowledge of the very initial stage of the aggregation process after the quenching treatment, in view of the time taken to perform each measurement.

Finally, we may conclude, in view of all the results presented in this paper, that the establishment of the nature of the complex formed during the initial stage of the aggregation process of I-V dipoles in the alkali halides just by fitting the experimentally determined data to only one of Eqs. (2) or (6) may be quite doubtful. Therefore, considerable reserve must be applied toward all previous works in which the dimerization process has been claimed by following this procedure. On the other hand, it will be interesting to reanalyze the reported data for the rate of disappearance of dipoles in those cases in which dimers have been established to be the initial aggregation complexes just by fitting the data to Eq. (2) in order to determine if the same data can be also fitted to our Eq. (6). This has the disadvantage, however, of involving large errors in view of the difficulty of reading data from published papers. On the other hand, it is important to emphasize that this is the first time in which the aggregation kinetics of doubly valent impurity ions in the alkali halides has been analyzed at the very initial stage of the clustering process. With the appropriate analysis of the data obtained, the order of the kinetics equation involved during this stage was unambiguously determined without assuming any reaction order *a priori*. Moreover, taking into account all the experimental evidence presented in this paper showing conclusively that dimers are the complexes which are really formed during the earlier stage of aggregation, it appears that the long-existing controversy of dimer versus trimer formation may be definitively solved. This finding is in agreement with the physical expectation that a two-body simultaneous encounter is quite more probable than that of a three-body one.

ACKNOWLEDGMENTS

The authors would like to thank A. Gamietea and I. Camarillo for the technical assistance.

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[*] Permanent address: Instituto de Física, Universidad Naciōnal Autónoma de México, Apartado Postal 20-364, 01000 México, Distrito Federal, México.

[†] On Sabbatical leave from Instituto de Física, Universidad Naciōnal Autónoma de México.

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