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PHYSICAL REVIEW B VOLUME 4, NUMBER 10 15 NOVEMBER 1971

Aggregation of Pb^{2+} Impurities in NaCl and KCl[†]

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The aggregation of Pb^{2+} impurity-vacancy complexes has been studied by measurement of dielectric loss and ionic thermocurrents (ITC) in KCl and NaCl and by the decay of luminescence in NaCl. A third-order reaction has been observed to govern the loss of complexes in crystals with high Pb content (above 100 ppm), while for dilute crystals (under 20 ppm) the reaction order is neither second nor third. The decay of luminescence in dilute NaCl was also neither second nor third order but was faster than the ITC decay.

Precipitation of impurities from solid solution in ionic crystals is a topic of considerable interest and the aggregation of divalent cation impurities in alkali halides has been the subject of extensive investigations in recent years.[1-4] Because of charge compensation by cation vacancies and Coulombic interactions between the compensating defect and the doubly charged impurity ion, nearly all of the dissolved impurity is in the form of dipolar impurity-vacancy complexes at temperatures below ~ 150 °C. This configuration provides a ready means of impurity transport[5] since both vacancy-impurity interchange and reorientation occur with appreciable rates above room temperature. The rate of the transport process and hence the rate of impurity precipitation from supersaturated solution will be limited by the slowest of these two steps. Since the complexes possess a permanent dipole moment, their rate of loss from solution during the aggregation process can be monitored conveniently via measurements of (a) dielectric loss,[5] (b) transient depolarization current,[6] or (c) ionic thermocurrent (ITC).[7] Moreover, in the case of paramagnetic impurities the progress of the aggregation reaction can be observed by means of electron paramagnetic resonance[8] (EPR) or, in the rare event that the impurity in the complex has an optical transition which is distinct from that in the aggregated form, the exciting or emitted photon can be used as an index of the concentration of impurity-vacancy complexes. It has been established[9,10] that the 315-nm emission band of NaCl : Pb is of this type; the 315-nm emission decreases in intensity as aggregation occurs.

Cook and Dryden[1] first measured the aggregation of divalent impurity-vacancy dipoles in NaCl : Ca^{2+}. They observed that the initial decay of dielectric loss was governed by a third-order process, which implies that the first stage of aggregation is the simultaneous union of three dipoles forming a trimer. This was a surprising result since the probability of a random encounter of a pair of dipoles should be much larger than for the simultaneous encounter of three dipoles. Further, rough calculations have shown that the planar quadrupole configuration of two dipoles has only slightly less

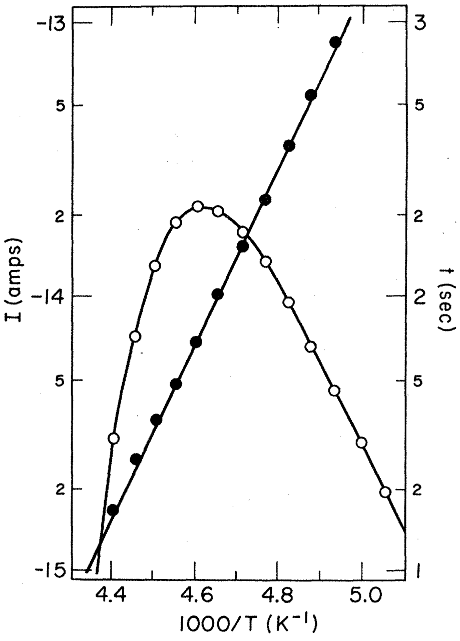

FIG. 1. ITC curve and the variation of relaxation time with temperature for NaCl : Pb.

TABLE I. Parameters for Pb^{2+}-vacancy reorientation, aggregation, and diffusion.

	τ_0 (sec)	E_{rot} (eV)	τ_0 (sec)	E_{ag} (eV)	E_{dif} (eV)
NaCl : Pb	5×10^{-14}	0.66[a]		0.80[b]	0.98[c,d]
KCl : Pb	2×10^{-14}	0.68[a]		0.80[b]	1.01[e]
	7.3×10^{-14}	0.66[f]	2×10^{-14}	0.74[a]	0.91[d]
	2×10^{-13}	0.65[g]			

[a] Values obtained in this work.

[b] The value for NaCl was obtained from Ref. 9. The value for KCl has been corrected by J. S. Dryden (private communication).

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binding energy per dipole than the hexagonal arrangement of three, and thus the dimer should have comparable stability. Therefore, one would expect the initial decay to be second order rather than third. However, measurements of aggregation behavior in other systems verified the third-order process. Cappelletti and DeBenedetti *et al.*[3] did report an early-stage second-order reaction in NaCl : Sr followed by a third-order reaction. An explanation for these observations has been offered by Crawford[11] based on electrostatic constraints which tend to inhibit the formation of the planar quadrupole. This model involves the assumption that loosely bound pairs of dipoles are the precursor to trimer formation. Provided that a quasiequilibrium between dipoles and the precursor is rapidly and readily established, the rate of trimer formation will still be proportional to the third power of the dipole concentration. Thus the very early stage of the process would be second order, switching over to apparent third order when equilibrium is established. The early process may be obscured since the loosely bound dimer is expected to have a residual dipole moment; thus its formation would not markedly decrease the dielectric loss. A significant consequence of this two-step model is that the observed activation energy for the aggregation should be smaller than the activation energy for impurity diffusion by the binding energy of the dimer, which is on the order of 0.2 eV. Indeed, in almost every case the observed energy of diffusion is larger than that obtained from aggregation studies, although the magnitude of the difference varies widely.[11]

This paper describes a study of the aggregation of Pb-vacancy dipoles in KCl and NaCl which uses both dielectric loss and ITC as well as the decay of luminescence in NaCl : Pb. The crystals were initially given a "solution" quench from a temperature sufficiently high to put the Pb into solution. The quenched crystals were isothermally annealed in the range 50–115 °C. The kinetics of the early

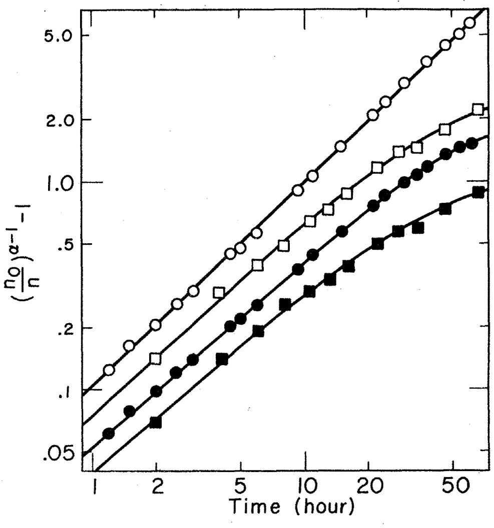

FIG. 2. Decay of dielectric loss and ITC during aging near room temperature. KCl : Pb (100 ppm): ○, α = 3; ●, α = 2. NaCl : Pb (20 ppm): □, α = 3; ■, α = 2.

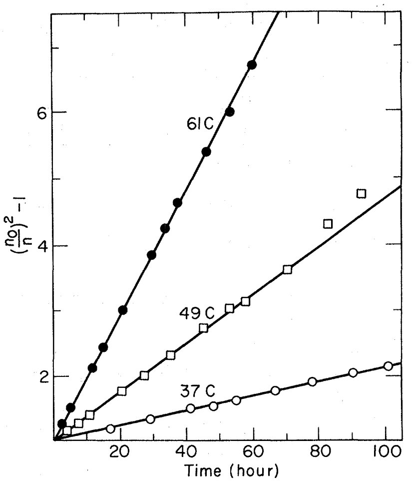

FIG. 3. Third-order plot of dielectric loss decay in KCl : Pb (100 ppm) at various annealing temperatures.

stages of the process were extensively investigated for both dilute (10–20 ppm) and concentrated (100–200 ppm) Pb-doped crystals using both dielectric loss and ITC to monitor the dipole density. Although less convenient to use than dielectric loss, ITC is two orders of magnitude more sensitive and thus was used for study of the dilute specimens. The ITC peaks occur at 223 and 219 °K in KCl and NaCl, respectively. The reorientation activation energy E and the relaxation time τ_0 can be obtained from the shape of the depolarization curve. Such a curve for NaCl : Pb is shown in Fig. 1. The parameters for reorientation are listed in Table I. The area under the ITC peak is proportional to the concentration as is the height of the dielectric loss peak. For the high-concentration crystals the best fit to the initial decay was third order. This is shown in Fig. 2 by a log-log plot of $(n_0/n)^{\alpha-1}-1$ vs time, where for $\alpha=2$ or 3 a slope of unity gives the order of the reaction as 2 or 3, respectively. Here n_0 and n are the concentrations of dipoles at time zero and t, respectively. The fractional decrease in dielectric loss or ITC (or luminescence) is assumed to be equal to n/n_0. The third-order decay for the concentrated crystals is also shown by a linear plot of $(n_0/n)^2-1$ vs decay time as given in Fig. 3 for several annealing temperatures. An Arrhenius plot of the slope of these curves gives the activation energy for the process. The value obtained for KCl : Pb is listed in Table I with results of Dryden and Harvey.[9] The results for dilute crystals also appear in Fig. 2, where it can be seen that there is a deviation from both third and second order.

The values obtained in this work and those reported in Ref. f of Table I were obtained in the same laboratory. In the present work, calculations involving ratio of areas under the ITC curve as determined by hand were used, while in Ref. f the energy and τ_0 were obtained as parameters in a computer least-squares fit to the theoretical expression for the ITC curve. The latter parameters tend to fluctuate more than the hand calculations for low peak heights in the dilute specimens and hence we feel that the former are more reliable.

If the model proposed by Cook and Dryden[1] of direct trimer formation were valid, then initially when the concentration is highest the third-order reaction would be favored. As Wintle[12] has shown, if the precipitation involves competition between second- and third-order processes, the third order can never be observed to follow second order, only to precede it. On the other hand, the difference in behavior between the high- and low-concentration specimens supports the two-stage model. In crystals with high Pb content, the initial equilibrium between monomers and dimers would be rapidly established and third-order kinetics should dominate, while in dilute crystals the early state requires a much longer time to establish itself and a deviation from third order would be expected. The kinetics were also studied using the 315-nm emission band in dilute NaCl : Pb. The data were not precise enough to definitely establish the kinetics but the decay was faster than the electrical decay obtained on the same crystals. This result has also been observed by Dryden and Harvey.[9] Such a behavior would be expected if the luminescence is quenched upon dimer formation but the ITC is decreased only upon trimer formation. This difference between optical and electrical responses is consistent with the assumption that the precursor to trimer formation is a loosely bound dipole pair. Clearly there are other possible explanations for the disparity between the kinetics as revealed by optical and electrical means. For example, the dipolar complexes may migrate to trapping sites where the quenching of luminescence may occur more readily than the inhibition of reorientability, e.g., near a charged dislocation.

Finally, we note that, if one uses the best and most recent value for the diffusion activation energy for Pb^{2+} in the high-concentration limit[13] as listed in Table I, the difference between this and that for aggregation is in good agreement with the difference expected from the two-step aggregation model.[11] Therefore, we conclude that the work reported here supports the mechanism of aggregation in which a loose dipole pair is the precursor of the stable trimer rather than one in which three dipoles simultaneously combine.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 10 15 NOVEMBER 1971

Force-Constant Changes and the Crystal Impurity Problem

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We study the crystal impurity problem for the case of nearest-neighbor force-constant changes around the defect site of body-centered and face-centered cubic crystals. We discuss general group-theoretical techniques for determining the dynamics of the system and also its response to an external optical probe. We provide closed-form expressions for all the necessary dynamical quantities, and show that their determination only requires knowledge of the pure-crystal density of states in cases where there are only central forces. We apply our results to the absorption spectra of xenon and of krypton in solid argon, to obtain good agreement with the observed data.

I. INTRODUCTION

This paper is a direct continuation of an analysis previously carried out by one of the authors.[1] Some of the results presented in this work have already been provided in Ref. 1, and we present them here only so that this paper may be self-contained. As well as providing some new results on the response of an impure system to an optical probe, we have also found what we regard as simpler derivations of some of the results of Ref. 1. The literature on the crystal impurity problem is expanding at an enormous rate and we suspect that some of our observations have already been reported, though unknown to us. We refer the reader to Ref. 2 and references cited in Refs. 1 and 2 for a more comprehensive review of the field. The notation we use throughout is the same as given in Ref. 1.

For studies of the lattice dynamics of both pure and impure crystal systems the three essential theoretical quantities are $\nu(\omega)$, $|\chi^2(l, \omega^2)|$, and $K(\omega)$. $\nu(\omega)$ is the density of states at a frequency ω. $|\chi^2(l, \omega^2)|$ is the amplitude of vibration of the atom at site l in the lattice mode of frequency ω, and $K(\omega)$ is the linear-response function of the system to an external probe. The physical observables of experiments such as optical absorption, Mössbauer effect, and neutron scattering may be expressed in terms of these quantities, and hence their determination is paramount. In the impure system in particular these quantities show radical departures from their pure-crystal values, and since we have added a source term to the pure-crystal equations of motion, we may solve for them using the lattice-Green's-function technique.

All of the qualitative features of the problem, such as the presence and properties of localized and resonance modes, were established by a study of the isotopic impurity.[2,3] Using group-theoretical techniques which exploit the high (O_h) symmetry at the defect site,[2,4] it is possible to extend the analysis to incorporate force-constant changes as well. Though conceptually the extension is direct, in practice the work is laborious as there are a large number of degrees of freedom (the coordinates of the atoms in the near-neighbor cluster), and hence a large number of lattice Green's functions are required. Since the defect displacement transforms