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Stochastic resonance interpretation of temperature-dependent F-center formation in NaCl

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Experiments by Tanimura and Hess have revealed that the formation of F centers after exciton creation in NaCl appears complete within ∼6 ps, a time too short to be consistent with thermally-activated conversion from self-trapped excitons (STE) in equilibrium. Yet the yield of prompt F centers is temperature-dependent. Molecular dynamics simulations of the relaxation from self-trapped excitons to F centers in NaCl have been performed as a function of modeled temperature, and are found to duplicate the main features of the seemingly paradoxical experimental observation. Additional insight is gained from the MD simulations by being able to observe excitation of a long-lived local vibrational mode on the compacted anion row produced by the off-center STE. The MD results indicate that the defect formation rate increases with temperature from 10 K up to about 100 K, and decreases above about 200 K. This thermal "resonance" in the yield of prompt defect formation, along with the presence of a vibrational soliton forcing motion along the reaction coordinate, are interpreted as an example of stochastic resonance in defect formation. The same explanation may explain the *dynamic interstitial* phenomenon, *i.e.* observation that a freshly created H center has a lower thermal activation energy for transport than an equilibrated H center.

Keywords: F-center formation; NaCl; stochastic resonance; molecular dynamics; self-trapped exciton.

Resultados experimentales de Tanimura y Hess han revelado que en NaCl la formación de centros F después de creación excitónica ocurre completamente en ∼6 ps, un tiempo muy corto e inconsistente con la conversión térmicamente activa de excitones auto atrapados (STE) en equilibrio. Por otro lado es un hecho conocido que la súbita formación de centros F es dependiente de la temperatura. Simulaciones de dinámica molecular (DM) del proceso de relajación de excitones auto atrapados en centros F llevados a cabo en NaCl en función de la temperatura contradicen las observaciones experimentales. La simulación mediante DM permite obtener un conocimiento más profundo debido a que se pueden examinar los modos vibracionales locales de vida media extensa en el arreglo compacto de iones producidos por STE desplazados del centro. Los resultados de DM indican que la rapidez de formación de defectos aumenta conforme aumenta la temperatura en el rango de 10 – 100 K, y disminuye por arriba de los 200 K. Esta "resonancia" térmica en la rapidez de formación repentina de defectos, conjuntamente con movimiento forzado de un solitón vibracional a lo largo de la coordenada reactiva, se interpreta como una resonancia estocástica en la formación de defectos. Una situación similar puede explicar el fenómeno de dinámica intersticial, es decir, la observación de que los centros H recién creados fuera de equilibrio exhiban una energía de activación térmica menor a la de un centro H en equilibrio.

Descriptores: Formación de centros F; resonancia estocástica; NaCl; dinámica molecular; excitones auto atrapados.

PACS: 61.72J; 71.75.Pd; 71.35.Aa

1. Introduction

In 1973, Itoh and Saidoh reported experimental results comparing thermally-activated transport of new and old H centers in KBr[1,2]. New H centers are those whose range of thermally-activated transport was measured within 200 nanoseconds of their creation from the perfect lattice by radiation. The defect pair formation results in a Br^o atom ejected from its lattice site (becoming part of an interstitial Br_2^- molecule ion). An F center (halide vacancy with electron) is left in its place. Using time resolved spectroscopy and pulsed irradiation, the transport of the interstitial Br_2^- molecule (H center) was measured by optically detecting the association of H centers with Na^+ impurity ions doped in the crystal at known concentration,. Doing this as a function of temperature allowed extracting the activation energy for transport of newly created H centers. Similar experiments were done using "old" H centers created by prior irradiation at low temperature and subjecting that population to pulsed thermal annealing to again extract the activation energy for transport to annihilation centers. The somewhat startling result was that new H centers in KBr had an activation energy for transport of 25 meV while old H centers in the same material had an activation energy of 90 meV[1].

This means that for some period shorter than 200 ns after their creation by radiation, H centers retain a memory that they are newly created, and this memory somehow translates into easier *thermally-activated* transport through the lattice. The two possible repositories of such a memory could be an electronic excited state as suggested by Itoh and Saidoh [1],

or a vibrational excited state. In either case the explanation remains rather startling because such an excited state (of the halogen molecular ion interstitial) must be maintained as the hole and its consequent molecular bond are passed from one halide pair to another repeatedly along the transport path, in a *thermally-activated* process. One looks for a memory mechanism that is robust under such thermal interactions and under bond-switching from site to site, and that also carries the means to enhance that bond-switching transport.

More recently in 2004, Tanimura and Hess [3] reported picosecond time-resolved studies of temperature-dependent F center formation in NaCl showing that at various temperatures in the range around 120 K, the F center formation is complete within about 6 ps of electron-hole pair generation, with no evident increase in F center number after that time. Why was that remarkable? It is because in NaCl very few F centers are produced at low temperature such as 10 K; it is only with rising temperature that radiation becomes effective in creating F-H pairs. Thus in NaCl, the F-H pair formation is temperature dependent and had often been described as *thermally-activated* conversion from self-trapped excitons to F-H defect pairs [4], before the 2004 results of Tanimura and Hess. However, thermally-activated conversion in the conventional sense of repeated attempts of an equilibrated system on a barrier with probabilistic success specified by a Boltzmann factor makes predictions of the rate and especially the time span over which the defects should appear, as well as the total yield. Specifically, such a thermal activation model of conversion from STE to F-H pair says that for as long as the equilibrated STE population exists, F centers should continue to be produced. The triplet STE lifetime is well known in NaCl and other alkali halides. At 120 K for the result quoted from Tanimura and Hess [3], the STE triplet population lives for 420 ns, nearly 5 orders of magnitude longer than the 6 ps F-center formation time. There is a lot of strong evidence that F-H pairs generated from excitation of the perfect lattice do result from transformation of self-trapped excitons.[4] Is there a way to reconcile a suddenly-terminated (6-ps) creation of F centers with the observed fact that the yield is temperature–dependent with the generally accepted fact that the defects are coming from self-trapped excitons?

Molecular dynamics simulations of F-H pair formation after introduction of an exciton in NaCl [5,6] were found to duplicate the main aspects of the experimental findings reviewed above. The simulations, including quantum mechanics in the central part of the cluster, show F-H defect pairs coming from self-trapped excitons, the defect yield increasing from negligible at 10K to substantial yield at higher temperature, and the process is complete in a matter of a few picoseconds. Duplication of this combination of properties by the MD simulations is comforting evidence that there is not a fundamental contradiction among the experimental observations as described above, despite the difficulty in applying a conventional picture of thermally-activated conversion from one state to another over an energy barrier in thermal equilibrium. The challenge is to extract a physical picture or sequence of events to explain the unusual combination of parameter values seen in experiment and duplicated in MD simulations. That is the topic of this paper, following earlier works by the authors on this subject[5,6].

It is helpful for development of the following discussion to highlight several additional published observations: An important one is the observation of coherent wavepacket oscillations of the STE on its common potential surface with the F-H pair in NaCl by Tokizaki *et al.* in 1992 [7]. Essentially what was observed is the optical absorption of the (electron + vacancy + H center) combined system as the H center oscillates from being partly in the vacancy to being mostly in the next-neighbor site along the [110] direction. The oscillation was observed to retain good definition persisting through approximately 6 complete cycles amounting to about 6 ps total duration. Please note in the following the recurrence of the time interval 6 ps in our discussions of NaCl phenomena involving the STE and F-H pair formation.

In 2003, Schulman *et al.* presented an explanation of prior observations on optical excitation of Pb^{2+} ions in KBr[8]. In the ground state, Pb^{2+} has the $6s^2$ spherical electron configuration, but in the 6s6p excited state, Jahn-Teller distortion around the quasi-molecular complex $Pb^{2+}[Br^{-}]_6$ compresses a [100] row of host ions in the vicinity. This distinguishes a one-dimensional chain within the otherwise 3-d host lattice, on which a soliton breather mode may exist. Model simulations by Schulman *et al.* [8] explored the expectation for such a mode and its properties. They invoked the soliton breather to explain the experimental observation that the excited Pb^{2+} center remains vibrationally hot as observed via luminescence for the extraordinary time of milliseconds [9].

2. Method of simulations

The method for computing molecular dynamic simulations which include quantum mechanics in the central part of the cluster where the localized exciton relaxation powers lattice atom displacements that can include vacancy-interstitial pair formation has been described previously [5,6,10-13]. The total energy of the system is evaluated as a function of the positions $\mathbf{R}_i$ of all ions in the cluster, of the wavefunction (coordinates **r**) of the single electron excited from a halide ion, and of the hole wavefunction left behind on the halogen atom. The total energy is found by summing E_{el} + E_{cndo} + E_{latt} + E_{pol}. The excited electron is given the privileged status of evaluating E_{el} by a quantum mechanical method, the extended ion approximation also called one-electron Hartree-Fock approximation. The hole occupying ultimately a molecular halogen antibonding orbital in the H center is also treated quantum mechanically, evaluating E_{cndo} with a CNDO quantum-chemical code applied to only a linear row of 5 halide ions extending outward from the site of the initially excited halogen. The H center is constrained to move by bond-switching within this row of 5 halide ions. The energy E_{latt} is evaluated for ground-state ion-ion interactions using Buckingham pair

potentials. The electronic polarization energy E_{pol} is evaluated via a point polarizable model.

Cluster sizes were 149 ions in the earliest simulations, increasing to 621 and now 1055 ions in the results presently reported. From the total energy expression, the gradient defines the force acting on each ion in the cluster and is used to evaluate displacement in the next time step. Time steps are 0.96 fs. At the start of a simulation with all ions at their equilibrium positions, velocities are assigned to each ion using randomized values consistent with the chosen temperature. Then the cluster is equilibrated for approximately 1000 time steps, and three of the resulting position and velocity configurations are chosen as the three "starting conditions" for simulations reported in this paper.

The exciton relaxation imparts about 1 eV of extra energy to the vibrational energy of the cluster, which should be dissipated corresponding to energy diffusion out of the boundaries of the finite cluster. This was done computationally by extracting 1% of the excess kinetic energy above the equilibrium value for the specified temperature, on each time step. For the smaller clusters treated originally, the dissipation rate could affect the results, but in the 1055-atom cluster, no effect of changing the dissipation rate was observed.

3. Simulation results and discussion of experiments

The first application of these simulations was used to compare the result of exciton relaxation at the fixed low temperature of 10 K in the two alkali halides KBr and NaBr[13]. This pair of materials was chosen because of contrasting experimental behavior. KBr is an archetype of the class of alkali halides with large Rabin-Klick ion-size parameter [14,4] in which excitons can transform to F-H defect pairs at temperatures as low as 4.2 K, and in which the defect yield is nearly independent of temperature until much higher T. With changing the alkali ion from K^+ to Na^+, the lattice constant shrinks enough that the Br_2^- molecular ion no longer slips as easily between the adjacent anion pair straddling a [110] row; *i.e.* the Rabin-Klick parameter S/D has assumed a value which correlates experimentally with nearly negligible F-H pair formation yield at low temperature. In such crystals, the F-H yield rises with temperature beginning from moderately low T. The simulation temperature of 10 K qualifies as a low temperature in both cases, so that from experiment one expects to find only the STE resulting from irradiation in NaBr, but a significant yield of conversions from STE to separated F & H center defects in KBr. The simulations, conducted at that time on a small cluster of only 149 atoms, reproduced the findings from experiment quite well. Only the STE was found in NaBr, while in KBr the H center moved as much as 4 lattice spacings from the site of the initial exciton (which is the eventual site of the F center). The entire $\sim$11 Å displacement process took place within a time of 2.2 ps, consistent with the experimental F-center formation time of $\sim$6 ps in KBr and KCl at low temperature [15,16]. The STE resulting in NaBr continued after formation to exhibit large-amplitude oscillation in a particular vibrational mode for the entire time of the simulation (2.2 ps). The mode corresponded to oscillation along [110] of the entire Br_2^- molecular ion within the structure of the off-center STE. As discussed at length in *e.g.* Ref. 4, the STE can be viewed in many regards as a close pair of F center and H center. The Br_2^- molecular ion bearing the hole component of the STE is in those terms an H center in a position that will be subject to electronic recombination with the electron in the similarly nascent F center component of the STE. However, in Ref. 13 no particular significance was attached to this lingering vibrational amplitude mainly because there was greater concern about the large energy deposit represented by the exciton relaxation energy deposited suddenly within the relatively small cluster of 149 ions. Provision was made in the simulations to remove different amounts of the excess energy in each time step, and indeed the chosen dissipation rate affected the occurrence of F-H pair generation in KBr. Against this background, it was not clear how much significance should be attached to lingering vibrational energy in a particular H-center mode.

In 2003-2004, the same simulation method was used while varying the starting temperature of the cluster, to look for temperature-dependence of F-H pair formation [17]. These simulations were being conducted simultaneously with receipt of the first report from Tanimura and Hess [18] of 6-ps completion of temperature-dependent F-center formation in NaCl. Thus the temperature-dependent simulations became concentrated mainly on the case of NaCl to compare with experiment. In view of the discussion already given in the Introduction of how startling the Tanimura-Hess results were in the context of expected thermally-activated conversion from STE to F-H pair, it was both startling and confirming to find the same behavior mirrored in the MD simulation results. The cluster size was still only 149 atoms, so three simulations were conducted at each temperature, one for each of 3 fixed rates of energy extraction from the cluster per time step. In NaCl simulated at 10 K, only the STE resulted regardless of the dissipation rate used. When the starting temperature was raised to 80 K and above, a "breakout" of the H center from the STE configuration to a defect configuration with 4 lattice spacings distance between F and H occurred for the lowest two dissipation rates. In all cases when defect formation occurred, it took place quickly, in approximately 0.7 ps according to the simulations. When the H-center "breakout" failed to occur and the system remained in the STE configuration, there was again always found the large-amplitude oscillation of the H center moving as a whole along the [110] direction. This mode is to be contrasted with the "beating mode" of the H center where the two Cl atoms move in opposite phase against each other. This mode is found clearly in more detailed simulations to be discussed below, but its frequency is higher and it never is excited with the large amplitude being seen for the low-frequency translational mode.

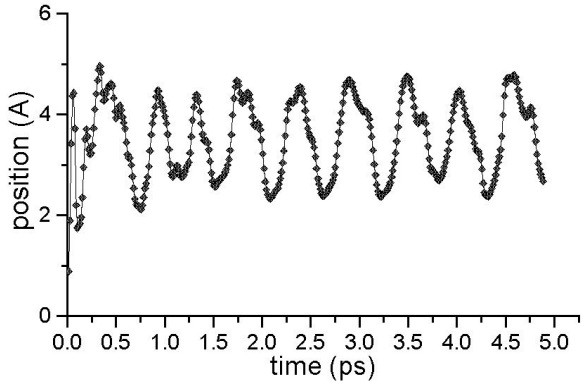

FIGURE 1. Trajectory of the center of hole charge (representing the H-center displacement along a [110] row) measured from the initially excited halide site. The simulation was run for a temperature of 15 K in NaCl, so the H center never gets beyond the displacement consistent with the off-center STE in NaCl. The point of interest is the large amplitude, low frequency vibration of the H center, which does not appear to be damping or dephasing within the 5 ps time scale of this simulation.

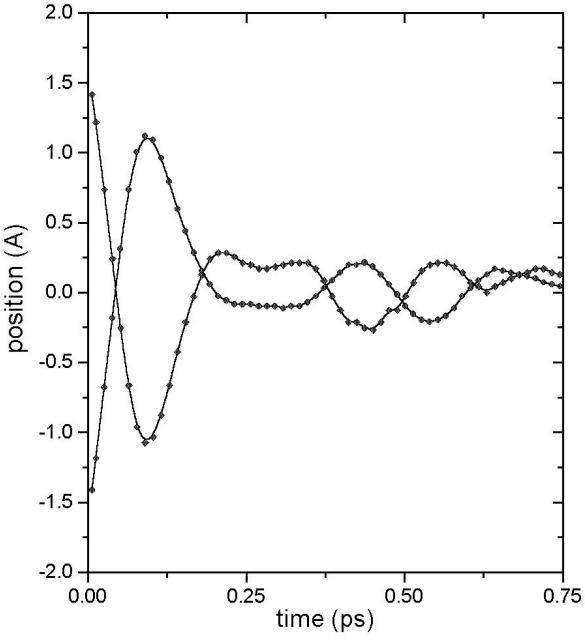

FIGURE 2. Trajectories of two adjacent halide ions started from large displacements in opposite directions without introducing the electronic excited state (electron and hole). The resulting vibration dephases quickly, in approximately 250 fs.

After 2004, the simulations were performed on larger clusters of atoms in NaCl, eventually 1055 atoms. Those large-cluster simulations will be the only ones addressed in further discussion and presentation of results. In the 1055 atom cluster, the vibrational energy accompanying creation and relaxation of an exciton is a small perturbation on the overall cluster temperature.

As a result, it was found that the choice of energy dissipation per time step no longer had an effect on the occurrence of H-center breakout to form a defect in the large cluster. Therefore a fixed dissipation rate of 1% of *excess* energy per time step was applied uniformly in all further results to be presented. It then became notable that the large-amplitude translational mode vibration of the H center remained just as prominent in the STE after formation, even though in the large cluster there is much less excess energy per atom contributed by the exciton relaxation, and whatever excess energy is present should be distributed quickly among the modes of a 1055-atom cluster. So it appears that the prominence of that mode in the simulation results is telling us something about the physical system, and it should at least be examined carefully. Figure 1 plots the position of the center of hole charge (corresponding to the H center) for a long simulation time of 5 ps at 15 K. The vibration has an amplitude of about 2 Å, and it is not attenuated perceptibly within the 5-ps simulation. To be sure that this persistent vibration was not an artifact of the simulation, the test simulation shown in Fig. 2 was run. In that case, the crystal remained in the electronic ground state, *i.e.* no exciton was introduced. But two halide ions were started at t=0 with displacements 1.4 A from their equilibrium positions in opposite directions, or 2.8 A relative displacement. The resulting oscillation de-phased within about 0.25 ps. The persistent vibration mode seems to result from relaxation of the STE. In addition, the same persistent translational vibrational mode was also seen to characterize the H center *after* breakout to form the defect. This became evident in the large cluster simulations carried out to 5 ps, which afforded more opportunity to see vibrations after defect formation.To see just what is moving and what are the phase relations in this prominent mode, refer to Figs. 3 - 7. Figure 3 plots the displacements along [110] of each of 3 adjacent halide ions.

The positions are plotted as departures from the initial starting position for each ion, so all trajectories have a common origin in the plot. The simulation represented in Fig. 3 is one for which there was no breakout of the H center to a distant site. Only the STE configuration is produced. Figure 4 will help with picturing where the ions go in the course of relaxation. The top-most trajectory in Fig. 3 obviously experiences the largest displacement from its starting site, so we can recognize it as the ion that starts at the central site and is converted to a neutral halogen atom in creating the localized exciton at time zero. As already discussed in, *e.g.*, Ref. 4, at that instant the neutral halogen atom finds itself occupying a lattice site of high positive Madelung potential. The excited electron will be energetically happiest (on the order of 1eV lower energy) if occupying the same site as a vacancy rather than sharing the space with a neutral halogen. The latter possibility entails a kinetic energy rise associated with orthogonalization to the halogen valence and core orbitals. The effect on energy of the total system amounts to a strong downhill gradient of potential as the halogen moves away from its initial site. This is the primary sense in which

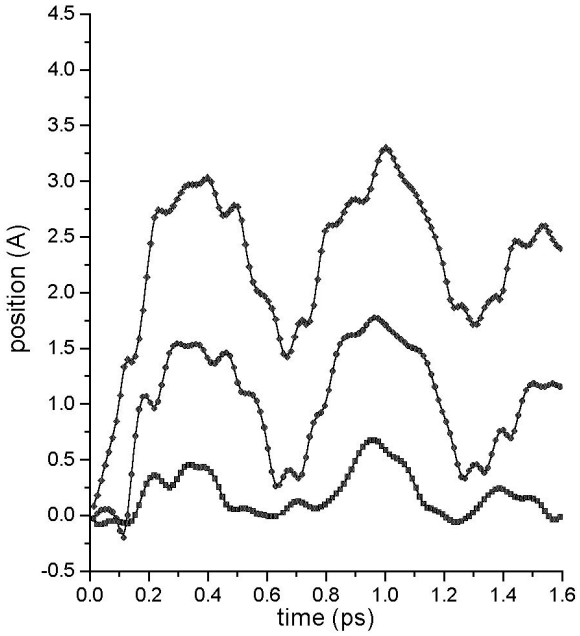

FIGURE 3. Trajectories of three Cl atoms starting from positions (000), (110), and (220), sequentially located along the [110] row, where (000) is the initial site of the exciton. Each atom position is plotted relative to its *own* starting position. Thus an atom with larger displacement than its neighbor will end up closer to that neighbor. In this simulation conducted at 45 K, there was no H-center breakout for the initial cluster conditions chosen. This represents the atom displacements establishing the STE configuration, and shows directly the *in-phase* oscillation of the two Cl atoms which comprise the nascent H center within the STE.

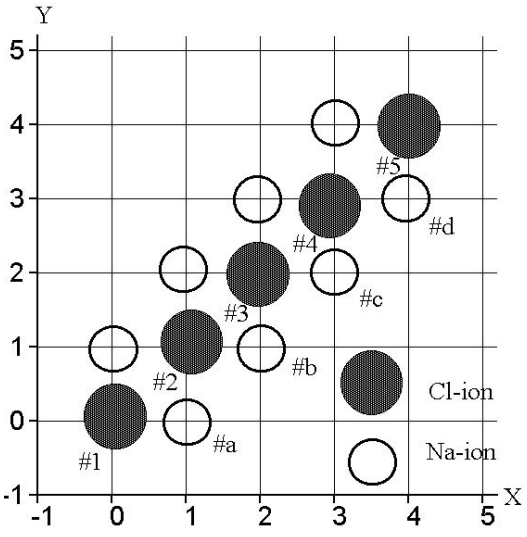

FIGURE 4. This schematic illustration of the 5-chlorine row on which the H center may propagate, starting from the exciton site at lower left, includes numbered labels on the chloride ions and lettered labels on the sodium ions, for reference in discussions.

the localized exciton is the driver of lattice atom displacement in alkali halides. It is why the halogen labeled #1 in the schematic of Fig. 4 (corresponding to the top trajectory in Fig. 3) starts from t=0 accelerating away from the site of excitation at a high rate, covering 1.4 Å in the first 100 fs. Now look at the trajectory of halogen #2 (second trajectory from the top).

It does nothing for the first 80 fs after exciton creation, but then it starts moving backward, toward halogen #1. The reason for this is that the halogen atom #1, missing one electron in its p shell, has approached close enough to halogen #2 that a molecular bond begins to form with the hole occupying the topmost antibonding σ orbital of the resulting Cl_2^- molecular ion. At about 110 fs, the two halogens reach their closest approach and bounce off of each other. This is clearly seen in both trajectories. In fact this persists as a beating mode vibration of the Cl_2^- vibration, superimposed on the larger amplitude slow vibtration to be discussed next. The period of the beating mode is 110 fs, which compares reasonably with the beating mode period of 94 fs for H centers (interstitial Cl_2^-) in NaCl with resonance Raman spectroscopy by Tanimura *et al.*[19] The small-amplitude oscillations of this beating mode produce peaks 180° out of phase with each other in the two halogen trajectories, as expected. In contrast, the much larger amplitude oscillation on which the beats ride has the same phase in both the trajectories for halogens #1 and 2. The motion is that of the entire Cl_2^- molecule ion moving back and forth along the [110] close-packed halogen row. The amplitude of this vibration is 1.5 Å, a substantial fraction of the distance between normal chloride ions along the [110] row.

In this sense the large-amplitude oscillation comes very close to propagating the H center on its own during each oscillation cycle. Figure 5 shows chloride ion trajectories for another simulation at T=45 K; this one for initial conditions that led to "breakout" of the H center from the STE to form a defect pair at 4 lattice spacings separation. Trajectories for Cl ions #1-5 (defined in Fig. 4) are plotted in Fig. 5 taking the "position" axis to be displacement along [110] relative to zero at the respective ion's initial lattice site. The Cl #1 trajectory is at the top, reaching a displacement of about 4 Å, corresponding to one full lattice displacement along [110]. Cl #2 reaches the same final displacement, indicating that both of the first two halogens (including the central one initially bearing the electronic excitation) have simply displaced one lattice spacing and exist as ordinary chloride lattice ions after the H center has passed through. Examining the beating mode vibration of these two ions in the very beginning, we see again the same story as Fig. 3, for the first 0.5 ps. After that, the beating mode period of the pair Cl #1-2 slows from 0.1 to 0.2 ps. This coincides with the loss of the hole from the first halogen pair to be shared in a bond mainly between Cl #3 and Cl #4. The slower 0.2 ps beat period of two adjacent ground-state chloride ions should be compared to 0.185 ps for the period of the zone-boundary LO phonon along [110] in NaCl [20]. Simultaneously with acceptance of the hole, the Cl #3-4 pair picks up the higher-frequency beat of the

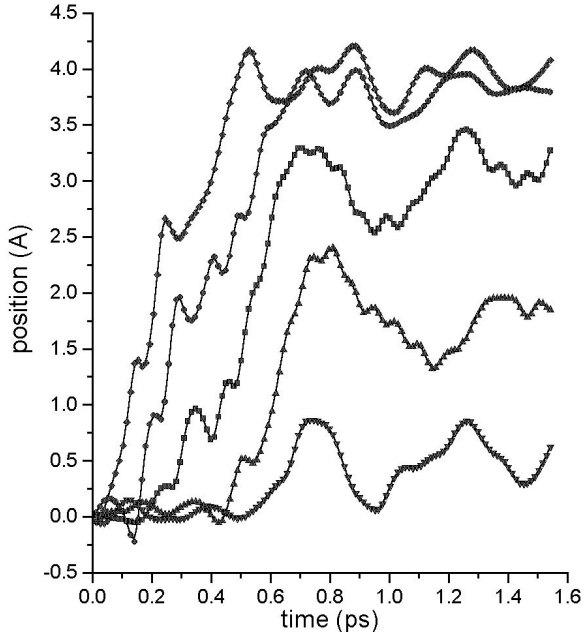

FIGURE 5. Trajectories of five Cl atoms starting from positons (000) through (440) along the [110] row pictured in Fig. 4. Each atom position is plotted relative to its *own* starting position. In this simulation at 45 K, the initial cluster positions and velocities were such that H-center breakout occurred, *i.e.* an F-H pair was created. The H center spreads over the 3^{rd} thru 5^{th} ions, which share in the large-amplitude, mostly in-phase oscillation. The high-frequency beating mode vibration can be seen superimposed.

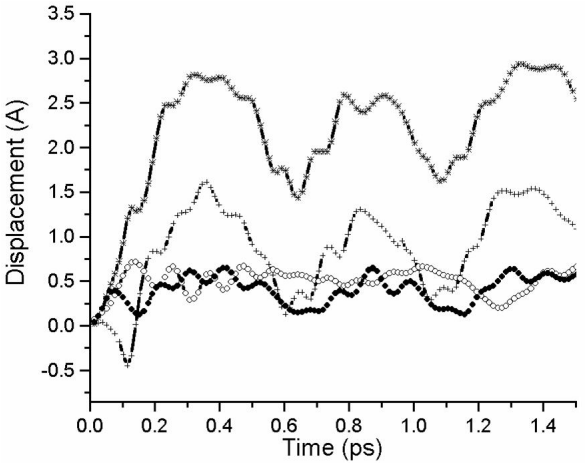

FIGURE 6. For T = 10 K, the open and filled-circle trajectories with smaller excursions plot the displacements parallel to [1,-1,0] (*i.e.* perpendicular to path of the H center) of alkali ions starting at (100) and (210) relative to the origin. The two trajectories at top are displacements along [110] of the Cl atoms starting at (000) and (110) from the origin. This simulation used a 621-atom cluster.

H center as well as the large-amplitude, slow (0.6 ps) soliton vibration of both Cl #3 and Cl #4 moving in phase.It is also worthwhile to have a look at how the several neighboring pairs of Na^+ ions straddling the [110] row of Cl^- ions are moving to accommodate the "H center" within the STE. This gives insight on how far off-center the H center is in the NaCl STE, considered to be Type II or moderately off-center [4]. (Despite our use of the term H center in the context above, the Cl_2^- does not really become an H center until it entirely passes the first Na^+ ion pair barrier and occupies an interstitial site. Even then, it will not be a stable H center against electronic recombination until it moves several more lattice spacings farther from the F center with its electron.) Referring to the [110] line of halogen ions pictured schematically in Fig. 4, the distance from the origin to the intersection with a line drawn through the two Na #a cations is 1.97 Å.The Cl atom initially at the origin would need to have a displacement of 1.97 Å to pass the first so-called "cation barrier". As shown directly in Fig. 3, the Cl #1 atom within the simulated STE in NaCl has a maximum displacement of about 3.0 Å from the origin, at the peaks of its oscillatory motion. The valleys of its oscillatory motion are about 1.6 Å displacement, which would be short of the cation barrier. The average or midline position of Cl #1 in the STE is 2.3 Å, meaning that the STE in NaCl has the trailing ion of the Cl_2^- already through the first cation barrier in its equilibrium configuration, according to this MD simulation. However, the Cl #2 leading ion of the Cl_2^- in the same STE has an average displacement from its initial site of about 0.9 Å according to Fig. 3. This is about 1 Å short of the 5.87 Å distance from the origin of Fig. 4 out to the 2^{nd} cation barrier.

In these terms, the simulated STE in NaCl is comprised of the F center at the origin plus a nearest-neighbor H center sitting off-center in the nearest interstitial site, about 0.35 Å closer to the F-center side. At maximum excursion in its oscillatory motion within the STE, the leading atom Cl #2 of the Cl_2^- molecular ion stops short by about 0.35 Å of passing the second cation barrier! It is therefore the 2^{nd} cation barrier which impedes and controls the further escape of the H center to make a defect. The first barrier has already been passed by the trailing atom of the H center even at the equilibrium STE configuration. The 2^{nd} cation barrier is almost breached on every cycle of the [110] H center oscillation, suggesting that only a modest amount of thermal energy could make a difference. Figure 6 shows the displacement of Na #a (open circles) and Na #b (closed circles) along a line perpendicular to the H-center trajectory while the H center (Cl_2^- molecular ion) is oscillating along its length at large amplitude of about 2 Å peak-to-peak. All trajectories are plotted as displacements relative to their respective ion starting positions. The Na #a cation pair can be seen in Fig. 6 to spread apart in the first 0.17 ps as the Cl_2^- bond forms, and then to maintain that spread nearly constant as the Cl_2^- oscillates along [110]. The Na #b separation at the 2^{nd} cation pair has a weak oscillation *in phase* with the H center vibration depicted in Fig. 6. As the H center rams into the 2^{nd} cation barrier confining it within the STE, the barrier ions spread slightly, but not enough to let it through without further energy supplied.

The crucial threshold displacement of the H center should come after the Na *#b* ion pair has been spread as wide as the

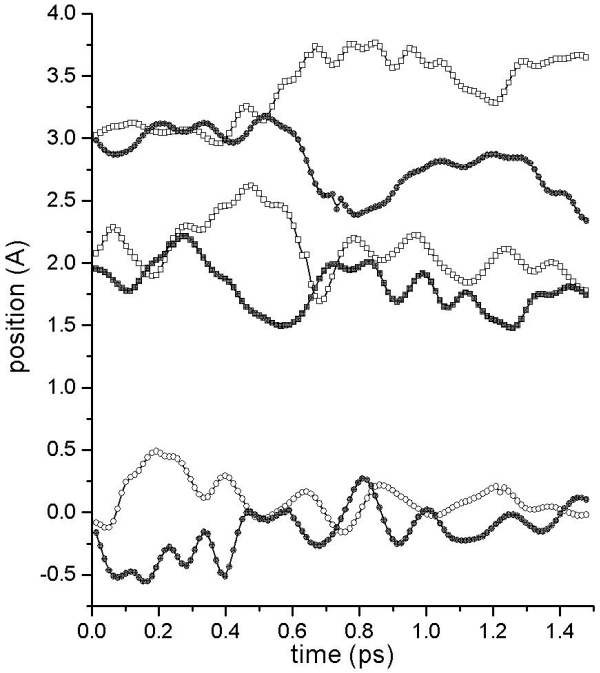

FIGURE 7. Trajectories of the x- (open) and y- (closed circle) displacements of the Na^+ ions at position (100), (320), and (430) relative to the exciton site (000) are plotted for a case (T=55 K) when the H center breaks out to form a separated H and F pair. These plots for the first, third, and fourth "cation barriers" (the second barrier simply is not plotted) show that the cation pairs separate and then close up again as the H center passes through.

Na *#a* ions and when the Na *#a* ion pair will start to close up behind the Cl_2^- pair with farther displacement.

Simply from elastic interactions with the surrounding ground-state ions, the energy cost of any further displacement toward the next interstitial H-center site along [110] will from this point be compensated by energy lowering of the Na *#a* ion pair closing in behind. It's like squeezing an elastic tube to force a couple of balls along its length. An illustration of this is shown in Fig. 7, giving Na trajectories at 45 K when the displacement moves past this threshold point. Instead of staying apart as in Fig. 6, the pair Na *#a* opens briefly and then closes again as the Cl_2^- moves on through. The elastic energy was invested and then withdrawn from the pair Na *#a*, with little net deposit of energy in that ion pair. The same thing happens for the pairs Na #b (not shown), Na *#c* and Na *#d* in Fig. 7 as the H center moves on down the line. The H center finally comes to a stop (still vibrating along [110] in the slow oscillation) at the 4^{th} site from initial excitation. The pair Na *#d* remains spread to accommodate the H center at that site.

Is there experimental evidence for the existence and persistence of the slow translational vibration mode seen in these simulations? Yes. The observation by Tokizaki et al of the coherent oscillation from STE to closest F-H pair in NaCl was a direct demonstration [7]. Slow vibrational cooling of the STE after creation was observed in ps time-resolved spectra of KI [21]. The mode proposed for this in 1992 was the same translational vibration of the entire halogen$_2^-$ molecular ion, the same mode seen in the MD simulations 10 years later.

The data of Tokizaki *et al.* show that the coherent translational vibration of the Cl_2^- within the STE in NaCl lasts about 6 ps. [7]. Recall that Tanimura and Hess found the temperature-dependent production of F centers in NaCl to be complete after about 6 ps. We do not believe that this is a coincidence. Instead it suggests that the large coherent translational oscillation of the H center is used in creating separated F-H pairs within the observed temperature range. Conversely, in absence of this stored energy in one particularly effective mode, F-H separation cannot occur at the same temperature range. Because the very large energy stored in the coherent H-center translational mode of vibration almost succeeds in "breakout" to the next interstitial site on each cycle, only a small amount of random thermal energy is needed to enable the actual jump. The main enabling effect of thermal noise in the system is in random "opening" of the pair of Na^+ ions that inhibits further progress of the H center in its oscillation along [110]. Of course, thermal noise should also add a randomly varying bit to the amplitude of H center oscillation as well. It is doubtful that the roles of these two can actually be separated. The bottom line is that random thermal noise of rather low amplitude can "push or permit" the strongly vibrating H center to pass over the critical amplitude at which the trailing pair of Na^+ ions will begin to close in behind it, regaining invested elastic energy as they help push the H center onward into the next valley. The amplitude of this thermal noise by itself at the experimentally indicated temperatures from 25 K up to 100 K is extremely unlikely to push an equilibrated (no coherent vibration) H center over the threshold for motion in the short time permitted by the Tanimura-Hess measurement [3] and other experiments on NaCl finding the same results [22].

It takes the coherent oscillation and thermal noise together to get past the cation barrier at modest temperature and short times. In the barrier region separating one harmonic well from another, the forces acting on the H center are highly nonlinear. The combination of a signal (coherent vibration in this case) and thermal noise superimposed in a nonlinear system to produce a resulting motion in phase with the signal and of larger amplitude describes a process widely studied and given the name *stochastic resonance*. [23] The term *resonance* in this context refers to a maximum in the signal amplitude (H-center displacement in the present case) versus temperature. This is a distinctly different plot of yield versus temperature than is predicted by activation over a barrier in thermal equilibrium. The STE system is not in thermal equilibrium with the lattice as long as the soliton vibration exists. Conventional thermal activation or Boltzmann statistics predicts a yield increasing monotonically with increasing temperature. Stochastic resonance predicts a decreasing yield in phase with the signal above the resonance temperature. The criterion of being in phase with the signal specifies

among other things that if the signal (soliton oscillation in this case) disappears after 6 ps, the defect yield enabled by stochastic resonance will cease after 6 ps. Such a resonance in prompt defect yield versus temperature was found in our MD simulations on NaCl as discussed in Ref. 5.

The stochastic resonance result refers to the prompt (in-phase) defect formation at moderate temperature. It does not preclude additional defect formation after the soliton dephases and thermal equilibrium is reached. Such a process will be slower, lasting for as long as there are excited states able to convert to defects, *i.e.* the triplet STE lifetime. The thermal equilibrium channel may not produce significant yield until a higher temperature. F center formation in true thermal equilibrium is difficult to observe directly in NaCl because the STE absorption spectrum overlaps the F-center absorption band significantly at low temperature and increasingly so as the bands broaden at higher temperature. Therefore if STE population is converting to F centers, the absorption signal at the F band peak will decrease with STE depletion and increase with F-center growth, both with exactly the same time constant. In that context, the nearly flat F band height as a function of time after 6 ps reported in Ref. 3 is indirect evidence for the additional conversion of equilibrated STEs to F-H pairs.

4. Summary

We propose that two different phenomena of nonlinear systems, a soliton vibration and stochastic resonance, together account for fast, temperature-dependent defect formation and for the property of the *dynamic interstitial* (anomalous thermal diffusion of a fresh H center) as measured and described by Itoh and Saidoh [1]. The key point is that at moderately low temperature where the yield is temperature-dependent and fast, F-H pairs are generated from STE's having a large amount of energy after initial relaxation off-center, organized in a mode which rams the entire mass of the Cl_2^- molecular ion against the restraining barrier posed by the next Na^+ ion pair along the [110] row on every cycle. The amplitude is such that it almost succeeds in breaking through on every cycle. This is distinctly not a situation of thermal equilibrium, but the soliton mode is localized almost entirely to the Cl_2^- molecular ion so that in fact the rest of the lattice including the restraining Na^+ barrier is almost in thermal equilibrium. Then random thermal motions of the Na^+ barrier ions, for example, can have a controlling influence on whether the organized energy of the soliton breaks through to the next harmonic potential well, and so on.

When the soliton dissipates in about 6 ps [7], this particular channel of thermally-activated conversion of a non-equilibrium STE population terminates, also in about 6 ps [3]. There may afterward be additional defects produced by conventional thermal activation of lattice-equilibrated STEs over an energy barrier. The indirect evidence suggesting this was mentioned above. The fast, temperature-independent defect formation in crystals such as KCl and KBr may simply be the fast, thermally-activated soliton-driven process in which the barrier presented by the cations is too small to restrain the soliton vibration from crossing the barrier to the next harmonic well (and so on) even in absence of thermal noise.

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