

Optically Induced Migration of Interstitial Zinc in ZnSe: Caught in the Act

K. H. Chow and G. D. Watkins

Department of Physics, Lehigh University, 16 Memorial Drive East, Bethlehem, Pennsylvania 18015

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Optically detected EPR studies of zinc-vacancy–zinc-interstitial Frenkel pairs produced by 2.5 MeV electron irradiation at 4.2 K in ZnSe reveal transformations between pairs of differing separations induced by optical excitation at cryogenic temperatures. The interstitial is identified as the mobile constituent by directly observing its conversion between T_d sites surrounded by four Se atoms and those surrounded by four Zn atoms. The interstitials, therefore, have been caught in the act of a single recombination-enhanced diffusion *half jump*, uniquely revealing the exact path taken in the one-jump diffusion process. [S0031-9007(98)07029-X]

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Blue-green laser ZnSe-based diodes are highly efficient but have been found to deteriorate rapidly under cw operation at room temperature. It is generally accepted that, similar to the problem originally encountered but ultimately solved, in GaAs-based lasers, the primary degradation mechanism results from dislocation climb into the active region from stacking faults at the lattice mismatched device interfaces [1,2]. For dislocation climb to occur, mass must diffuse into or out from the dislocation cores. This, in turn, suggests that one or more of the intrinsic defects (lattice vacancies and/or interstitials) normally required for diffusion must become mobile in the presence of the large concentration of injected electrons and holes required for laser action. Substantial improvements in device lifetime recently have been achieved by successful reduction in stacking fault densities, but it appears that similar degradation processes continue to be important, occurring at point defects in the bulk of the active layer [3].

In addition to its technological importance, this remarkable phenomenon, called recombination-enhanced migration (REM) [4], is also of strong current scientific interest. Several possible mechanisms have been suggested for the phenomenon [4–6], the most commonly discussed being an *energy-release* mechanism where the electronic excitation energy supplied to a defect, either optically or by electron and/or hole capture, is nonradiatively converted into the kinetic energy necessary to assist it over its migration barrier [7–9]. Only a very few well-established examples of REM for *identified* defects exist [10–13], and in no case has the detailed mechanism been firmly established. In the present Letter, we demonstrate that interstitial zinc can be made to migrate in ZnSe under optical excitation even at 1.5 K. In addition, we demonstrate that we can trap it in its intermediate diffusion position, revealing the exact path taken in the one jump diffusion process.

For this experiment we take advantage of a truly unique situation in ZnSe. It has been demonstrated that in this material 1.5–2.5 MeV electron irradiation at cryogenic temperatures produces a variety of zinc-interstitial–zinc-vacancy Frenkel pairs frozen into the lattice, some of

which were first observed directly by electron paramagnetic resonance (EPR) [14], and many more of which have been more recently observed by optically detected EPR (ODEPR) via their photoluminescence (PL) [15–18]. Up to ~ 25 distinct pairs of different separations in the lattice have been resolved in the ODEPR studies, as well as interstitial zinc atoms sufficiently separated from their partner vacancies to behave as truly isolated ones [19].

In the early EPR studies [14], it was noticed that for 1.5 MeV irradiation at 20.4 K the closest pair was formed linearly vs dose, as expected, but more distant “isolated” vacancies were also being produced, in that case roughly quadratically vs dose. Already at this time, this was cited as evidence that separation of the pairs was occurring after their initial production and that it was being stimulated by the ionization accompanying the irradiation. In the present study, we take advantage of the many discrete pairs seen in the ODEPR studies to probe the phenomenon in detail, monitoring some of the individual pairs to help unravel the process.

The setup for the experiments to be described was identical to that of the earlier ODEPR work [17], which should be referred to for details. Briefly, a 20 GHz EPR spectrometer, capable of *in situ* 4.2 K electron irradiation, was modified for ODEPR by inserting into the TE₀₁₁ microwave cavity a capillary tube, which served as a light pipe to extract the photoluminescence, and within which was threaded an optical fiber through which the sample could be photoexcited. To monitor the ODEPR signals, the luminescence was detected with either a silicon (EG&G 250UV) or cooled germanium (North Coast EO-817S) diode detector, and excitation (≤ 6 mW) was supplied by the 458 or 476 nm line of an argon ion laser. The sample was immersed in pumped liquid helium (~ 1.5 K). The microwave power was on-off modulated at various audio frequencies, and synchronous changes in the luminescence were detected via lock-in detection. The enhanced migration studies were performed with 458 nm excitation (2.707 eV, just below the ZnSe band gap of 2.818 eV, to allow bulk penetration) and at a power

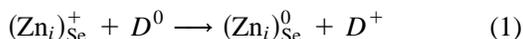
level of ≤ 50 mW, still well below what might produce significant heating of the sample. The sample studied was a high resistivity *n*-type single crystal grown by Brian Fitzpatrick at Philips Laboratory.

Immediately after *in situ* 2.5 MeV electron irradiation at 4.2 K, the PL-ODEPR spectra of the many distinct pairs observed in the previous studies were reproduced. Small changes were observed in the relative amplitudes of the different pairs after prolonged illumination with 458 nm light at 1.5 K. However, upon raising the temperature to 25 K under illumination, the changes were observed to occur much more rapidly, the intensities of the intermediate pairs rapidly decreasing by a factor of 2–5, depending upon the particular pair, while the most distant pairs first increased then decreased. Only minor changes were observed in the closest pairs.

These results clearly confirm that optically induced rearrangements are occurring between the pairs and migration of at least one of the constituents must therefore be occurring. The greatly increased rate at 25 K serves also to explain the clear evidence of the process in the early EPR studies, where the samples were electron irradiated at 20.4 K, but not in the more recent ODEPR studies which utilized 4.2 K irradiations. In order to help unravel the detailed process involved, we have investigated more closely two specific reactions, which we now describe.

(1) The strongest ODEPR signals arise from four very close pairs, labeled A–D, for which the exchange interaction between the spins on the separated interstitial and vacancy significantly exceeds the Zeeman interaction of either. For them, therefore, only the characteristically stronger ODEPR transitions within their $S = 1$ manifolds are observed. Upon annealing to 150 K in the dark, first the A and then the C spectrum disappears, presumably by annihilation, leaving B and D plus all of the more distant pairs unchanged. In Fig. 1 we show the result of prolonged 458 nm optical excitation at 1.5 K after this annealing step. A is clearly regenerated by conversion from B. The conversion is not complete, saturating at a fixed ratio, revealing that the conversion process goes in both directions, as indicated in the figure. Here we are therefore monitoring the one-jump process directly between the two configurations, which is occurring even at 1.5 K. The additional jump required for annihilation is apparently occurring much more slowly, if at all, however. At this stage, we have no direct evidence as to which—the interstitial or the vacancy—is the mobile species.

(2) As mentioned above, interstitials that are sufficiently separated from their companion vacancies to be for all practical purposes isolated can also be observed by ODEPR [19]. This is illustrated in Fig. 2, where the competing spin dependent process



produces the negative $(\text{Zn}_i)_{\text{Se}}^+$ EPR signal on the ODEPR spectrum of the 625 nm “self-activated” luminescence

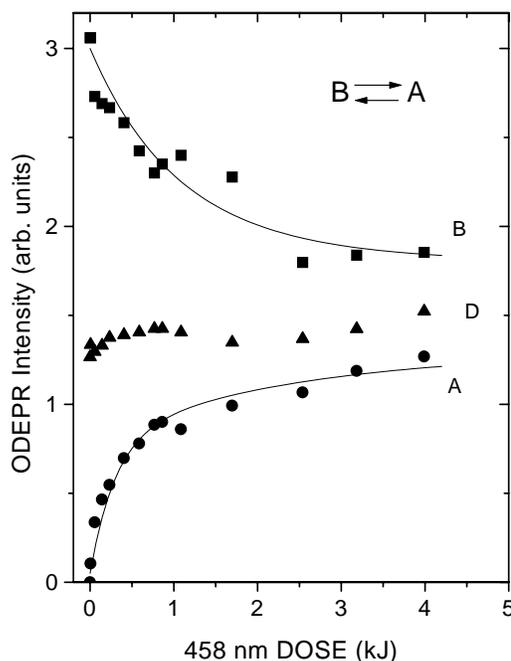


FIG. 1. Intensity of the ODEPR signals for three of the closer Frenkel pairs vs accumulated dose of 458 nm excitation at 1.5 K, after 150 K anneal in the dark.

originally present in the material



Here $(\text{Zn}_i)_{\text{Se}}$ denotes the interstitial zinc atom in the high symmetry T_d interstitial site surrounded by four Se atoms, A is the particular vacancy-donor complex responsible for the self-activated luminescence in the material, and D is the shallow donor. The identification of $(\text{Zn}_i)_{\text{Se}}^+$ was unambiguously demonstrated in the early studies [19] by the observation of the central isotropic hyperfine interaction of ^{67}Zn ($I = 5/2$, 4.1% abundant) and ^{77}Se ($I = 1/2$, 7.6% abundant) hyperfine interactions with the four nearest (indicated in the figure) and twelve third-nearest neighbors.

Shown also in the figure is a weaker negative signal, labeled $(\text{Zn}_i)_{\text{Zn}}^+$. This isotropic signal was also noted in the early study (originally denoted “X”) and speculated to possibly arise from zinc in the other high symmetry T_d site surrounded by four Zn atoms [19]. Consistent with this identification, partially resolved satellites on the line (also evident in Fig. 2) were argued to be similar to that expected for ^{77}Se hyperfine interaction with its six next-nearest neighbors. It was assumed to be the less stable site, but frozen in after an initial displacement collision that accidentally brought it there. We will now present strong evidence that it is indeed $(\text{Zn}_i)_{\text{Zn}}^+$ and, therefore, have labeled it accordingly in the figure.

In Fig. 3, we show the result of several sequential annealing and illumination steps on the two centers. First, annealing in the dark at 25 K completely removes the $(\text{Zn}_i)_{\text{Zn}}^+$ spectrum. A subsequent 458 nm illumination at

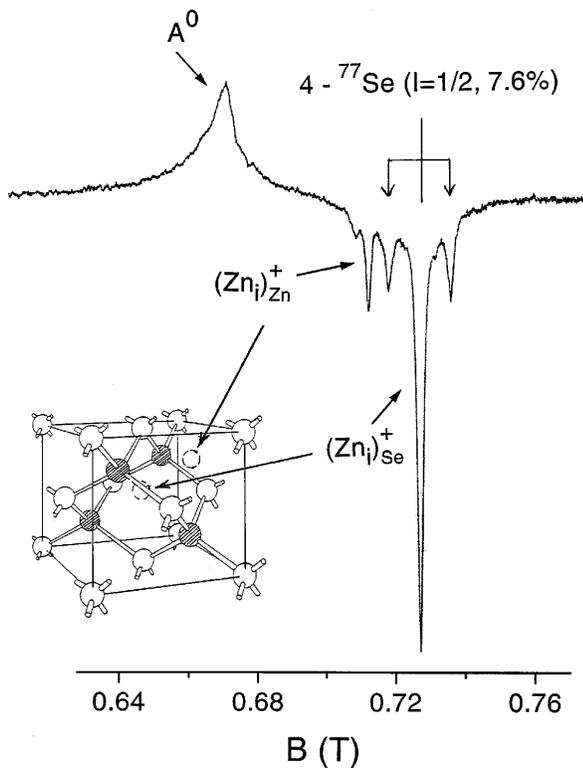


FIG. 2. Interstitial zinc ODEPR signals observed in the 625 nm DA self-activated luminescence after 4.2 K electron irradiation. (The D^0 shallow donor resonance is off scale at 1.29 T.) In the inset, the two interstitial positions are indicated, the crosshatched atoms representing Se atoms.

25 K with rapid cooldown strongly regenerates the signal so that it is now, for the first time, *actually the dominant one*, with a correspondingly strong decrease in the $(Zn_i)_{Se}^+$ signal. With this increased intensity for the signal, now we have been able to confirm in detail its six next-nearest neighbor ^{77}Se hyperfine structures and also detect its isotropic central ^{67}Zn hyperfine interaction. Upon subsequent excitation at 1.5 K, slow partial return conversion is observed demonstrating that optically induced conversion occurs in both directions even at this low temperature.

These results demonstrate several important facts: First, the detection of the resolved isotropic central ^{67}Zn and the next-nearest neighbor ^{77}Se hyperfine structure for the X spectrum provides direct confirmation of its identity as $(Zn_i)_{Zn}^+$, i.e., that of the zinc atom in the other available high symmetry T_d site. Second, the close one-to-one conversion between these two sites and back constitutes a *single diffusion jump*, each site representing an intermediate position from which a return jump carries the atom to four possible choices of the other. We have unambiguously identified, therefore, the interstitial as the mobile species and have a method of directly measuring its single diffusion jump rate. We note that the rates for the conversion at 1.5 K in Figs. 1 and 3 are comparable. Third, we have inadvertently caught the interstitial in its

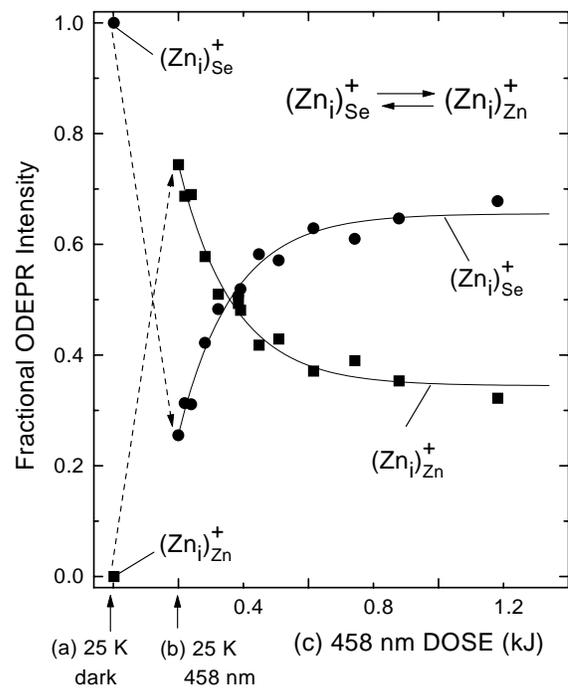


FIG. 3. Interstitial zinc ODEPR signal intensities (a) after 25 K anneal in the dark, (b) after subsequent 25 K anneal with 458 nm excitation, and (c) vs subsequent accumulated dose of 458 nm excitation at 1.5 K.

half jump position, which serves unambiguously to determine the mechanism of its diffusion, in this case as moving between the two T_d sites (as opposed to the various possible interstitialcy mechanisms, evidence for one of which having been proposed for a lower temperature Frenkel pair thermal annealing process at 60 K [14]).

Preliminary studies of the temperature dependence for the isolated interstitial conversion process indicate little change in the rate at 4.2 K, but several orders of magnitude increase in the rate already at ~ 10 K. Such behavior suggests a thermally assisted process that changes over to an athermal tunneling-assisted one at the lowest temperatures. The difference in the saturation ratios indicated in Fig. 3 for the two spectra at 1.5 vs 25 K reveals further that the forward and backward rates have different temperature dependences.

The fact that the zinc interstitial is the mobile species could not have been easily predicted. On the one hand, it is perhaps not too surprising, its barrier for thermally activated diffusion having been estimated experimentally to be ~ 0.6 – 0.7 eV [17], compared to that for the zinc vacancy of 1.25 eV [20]. The energy required from the recombination event is therefore less. On the other hand, for an energy release mechanism, it is less obvious how the recombination energy is able to assist its migration since, in either T_d site, it is expected to stay on center for each of its neutral ($4s^2$), singly ($4s^1$), and doubly ($4s^0$) ionized nondegenerate A_1 -symmetry states [21], and receive, therefore, no “kick” in a diffusive direction upon

electron or hole capture. There could well be substantial breathing mode relaxational changes, but in the notation of Stoneham [6], the “accepting” and “promoting” modes are orthogonal [9]. The vacancy, on the other hand, undergoes a strong symmetry-lowering Jahn-Teller distortion upon hole capture [22], providing selectively more appropriate kicks to its neighbors.

But our results show that it *is* the interstitial, and understanding the detailed mechanism for its optically induced enhancement therefore becomes an important challenge. Another previously considered mechanism involves simply a reduced or vanishing diffusion barrier in a different charge state for the defect [4–6], and this remains a possibility. Alternatively, capture or direct optical excitation into an excited atomic p -like state for any of its charge states could initiate a symmetry-lowering Jahn-Teller distortion to supply the necessary kick. And, of course, we cannot rule out DX -like behavior, where an additional negative charged state ($4s^2 4p^1$) is available which goes off center [23].

Some of these issues can hopefully be addressed experimentally, and we plan to continue these studies to explore the effects of defect charge states (zinc-fired samples for low resistivity n -type, changes vs irradiation dose in high resistivity as-grown samples, etc.). Hopefully, theory can also play a role. Already, important theoretical contributions have been made concerning the interstitial in recent *ab initio* local density calculations [24]. In particular, they predicted the two T_d sites to be energetically very close in stability, even reversing as to which is lowest vs charge state, fully consistent with the ease with which we are able to convert between them. It would be highly desirable to explore in similar theoretical calculations the energy contours between the two configurations and their dependence upon charge state, as well as explore the question of excited p states or possible DX behavior.

To summarize, this system is truly unique. In the first place, it remains still the only case where an isolated host interstitial atom has been unambiguously identified and can be directly monitored experimentally in a semiconductor. Taking advantage of this, we have shown that it can be made to migrate at cryogenic temperatures by optical excitation, and the process can be followed in microscopic detail by freezing it in after a one-half diffusion jump. To our knowledge this represents the first case in any diffusion process where the intermediate diffusion configuration has been caught and identified. In its two configurations it has been established to be on center in a high symmetry T_d configuration for the paramagnetic singly ionized charge state, as predicted also for its neutral and doubly ionized states as well. We, therefore, have also the first demonstration that an interstitial defect can execute recombination-enhanced migration even from simple on-center T_d to on-center T_d sites. This latter fact poses a new challenge for understanding the mechanism for the phenomenon.

Finally, the demonstration of efficient recombination-enhanced motion for interstitial zinc supplies one of the elements necessary to explain the degradation of ZnSe-based laser devices.

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