Optically Detected Magnetic-Resonance Observation of the Isolated Zinc Interstitial in Irradiated ZnSe

F. Rong and G. D. Watkins

Department of Physics, Sherman Fairchild Laboratory, Lehigh University, Bethlehem, Pennsylvania 18015

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Optical detection of magnetic resonance is reported for isolated interstitial Zn_i^+ in ZnSe produced by 2.5-MeV electron irradiation at 4.2 K. It is detected as a reduction of the distant-donor–to–Frenkel-pair recombination luminescence at 625 nm. Resolved hyperfine interaction with the central zinc ion and two shells of Se neighbors reveals a highly localized "deep" state for the paramagnetic electron. It is stable only to ~220 K.

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The elemental intrinsic lattice defects of a semiconductor are isolated vacancies, self-interstitials, and, in the case of a compound semiconductor, antisites. Although a great deal of information has been accumulated about vacancies, and more recently antisites, very little is known about the structure and properties of isolated self-interstitials. In a few cases indirect information has been obtained about interstitials trapped next to impurities or other defects,[1-6] but their structure is often altered considerably in the trapped state. In a recent Letter,[7] optical detection of magnetic resonance was reported for Ga interstitials in $Al_{0.26}Ga_{0.74}As$ grown by molecular-beam epitaxy at 620 °C. Again, asymmetry in the spectrum lead these authors to suggest that the defect may be paired with a second unknown defect. A similar spectrum has also been reported by Lee in GaP.[8]

In this Letter we report optically detected magnetic resonance (ODMR) of the isolated zinc interstitial in ZnSe. We believe that this is the first direct unambiguous observation of an *isolated* self-interstitial in any semiconductor.

Some of the properties of the interstitial zinc atom have previously been inferred from studies of zinc Frenkel pairs in ZnSe. In early EPR studies,[1] several Frenkel pairs were observed in the $V_{Zn}^{-}\cdot Zn_i^{++}$ charge state with a hole ($S=\frac{1}{2}$) residing primarily on the zinc vacancy. From the symmetry of the spectra, the Zn_i^{++} ion was deduced to reside in a tetrahedral site but at different distinct separations from the zinc vacancy. In recent ODMR studies,[5] two of the Frenkel pairs were observed in an exchange-coupled excitonic triplet state of $V_{Zn}^{-}\cdot Zn_i^{+}$. With knowledge of the EPR parameters for the isolated zinc vacancy V_{Zn}^{-},[1] it was possible to deduce those for the neighboring interstitial Zn_i^+. In this Letter, we describe for the first time the direct observation of the *isolated* zinc interstitial Zn_i^+ by ODMR. Its isotropic g value and the hyperfine interaction from its four nearest-neighbor selenium atoms agree well with those predicted from the Frenkel pairs. In addition, the central-ion hyperfine interaction from ^{67}Zn ($I=\frac{5}{2}$, 4.11% abundant) and ^{77}Se hyperfine interaction from the third nearest-neighbor (nn) shell of twelve equivalent selenium atoms are resolved, confirming the identification.

The ZnSe samples studied were single crystals grown by vapor transport in a sealed quartz ampoule in which 10^{-3} mole fraction of $SrCl_2$ was added to the charge. The as-grown samples were high-resistivity n type. The samples were irradiated *in situ* along the [111] direction at 4.2 K by 2.5-MeV electrons to a fluence of 2.5×10^{16} e^-/cm^2 in a 20-GHz EPR spectrometer cryostat which has been modified for ODMR measurements.[5,6] Optical excitation of 5 mW was provided by the 476-nm line of an argon-ion laser. The microwave power was on-off modulated at 1 kHz and resulting changes in the photoluminescence intensity were phase sensitively detected in the direction perpendicular to the static magnetic field by means of a silicon photodiode (EG&G 250UV). Before *in situ* irradiation, ODMR of the as-grown sample revealed positive resonance signals (increase in intensity with microwaves on) from the shallow donor and the self-activated acceptor $A3$, in donor-acceptor recombination luminescence at ~600 nm. (The $A3$ center has been identified as a zinc vacancy paired with a donor of unknown chemical identity.[9])

Figure 1 shows the luminescence spectrum (1.5 K, 476-nm excitation) in as-grown ZnSe after *in situ* irradiation and after correction for monochromator and detector response. The broad bands at ~625 nm and ~800 nm are the sane bands that were previously reported in irradiated "zinc fired" ZnSe.[5,6] In this earlier work, it was demonstrated that the 625-nm band arises from radiative recombination between a distant donor D^0 and the nearest (V^I) Frenkel pair $V_{Zn}^{-}\cdot Zn_i^{++}$, while the 800-nm luminescence band arises from a localized excitonic transition at two neutral Frenkel pairs of increased separation.

Figure 2(a) shows the observed ODMR spectrum at 1.5 K, monitoring only the 625-nm band (500–650 nm) by use of color filters. For this orientation, $\mathbf{B}\parallel\langle100\rangle$, four groups of lines can be observed: one (positive) arising from the V^I Frenkel pair, $V_{Zn}^{-}\cdot Zn_i^{++}$; the shallow-

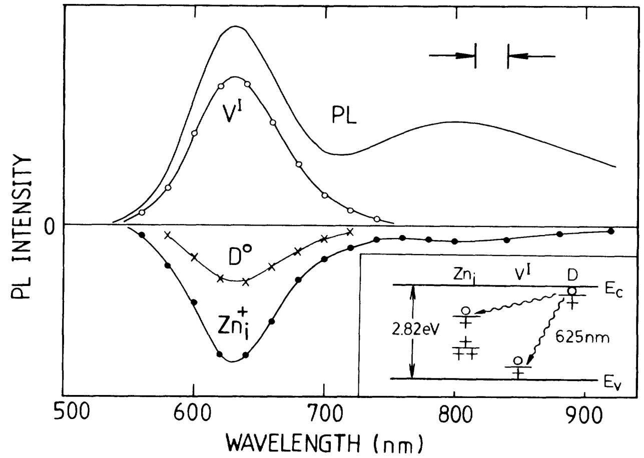

FIG. 1. Photoluminescence spectrum (PL) and spectral dependence of ODMR intensity for the Frenkel pair (V^I), the distant shallow donor (D^0), and the zinc interstitial (Zn_i^+) for irradiated ZnSe at 1.5 K with 5 mW of 476-nm excitation. The inset illustrates the recombination processes involved in the ODMR detection.

donor electron resonance (negative) labeled D^0 at $g = 1.109$[10]; a new spectrum (negative) labeled Zn_i^+; and a weaker new (negative) resonance line marked X at $g = -2.0064(5)$.

The spectrum labeled Zn_i^+ consists of a strong isotropic central line at 7279 G ($g = 1.9664$) with three sets of resolved satellite structures. These are shown in Figs. 2(b) and 2(c). The positions of all of the lines can be fitted by the single-spin Hamiltonian

$$H = g\mu_{\mathrm{B}}\mathbf{B}\cdot\mathbf{S} + \textstyle\sum_j \mathbf{I}_j\cdot\mathbf{A}_j\cdot\mathbf{S}, \tag{1}$$

with the parameters given in Table I. The first term describes the electronic Zeeman interaction with $S = \frac{1}{2}$, the second term, hyperfine interactions with nuclei on the central and neighboring sites.

Hyperfine interaction with the central $^{67}\mathrm{Zn}$ nucleus ($I = \frac{5}{2}$, 4.11% abundance) produces six ($2I+1$) satellites, four of which can be seen in Fig. 2(b). (The remaining two are obscured by the strong V^I and central Zn_i^+ resonances.) The interaction is isotropic ($\mathbf{A}_0 = a_0 \cdot \mathbf{I}$).

The resolved structure on the shoulders of the central line matches well that predicted for hyperfine interaction with $^{77}\mathrm{Se}$ ($I = \frac{1}{2}$, 7.58% abundance) at four equivalent sites, as shown in the figure. Angular dependence studies reveal partially resolved anisotropy with $(\mathbf{A}_1)_{\parallel}$ along a different $\langle 111\rangle$ axis for each of the four Se nuclei. We identify these, therefore, as arising from the first nearest Se shell.

Additional structure is also evident on the central line itself, as shown in Fig. 2(c). It is greatly enhanced by our taking the second derivative of the spectrum, which is also shown.[11] The match to the predicted intensity ratios shown for twelve equivalent $^{77}\mathrm{Se}$ nuclei is very good.[12] The structure shows no detectable anisotropy and we extract therefore only the isotropic part of the

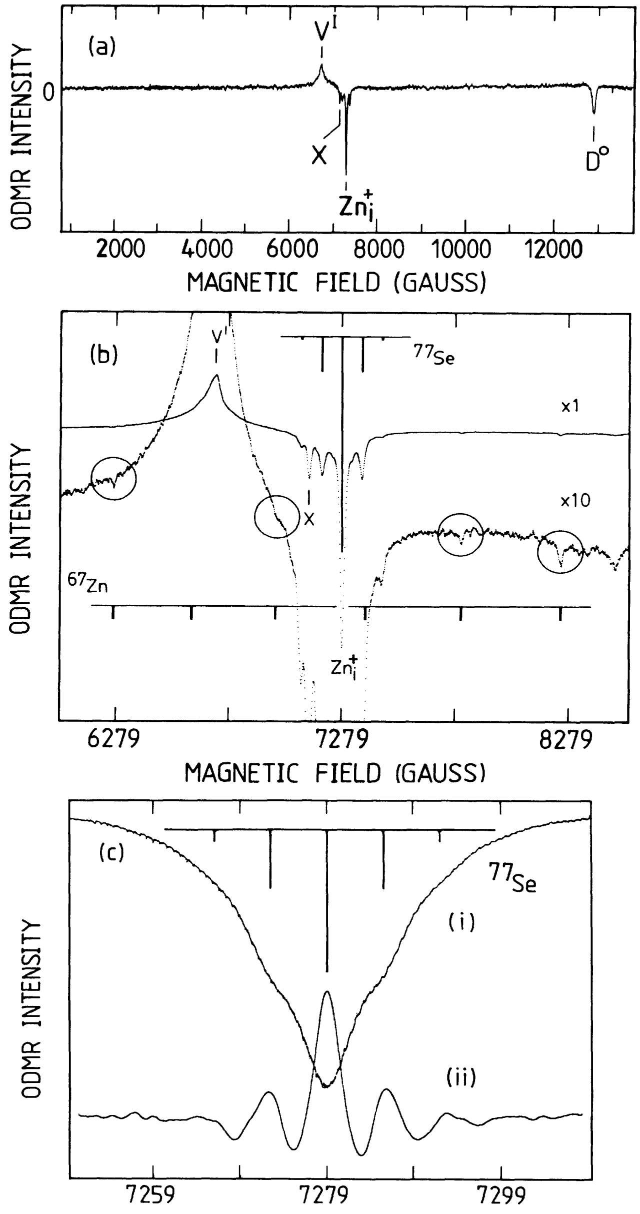

FIG. 2. (a) ODMR spectrum detected from the 625-nm luminescence band in irradiated ZnSe at 1.5 K with $\mathbf{B}\parallel\langle 100\rangle$ and $\nu = 20.033$ GHz. (b) ODMR spectrum with higher sensitivity and expanded magnetic field scale, revealing satellites associated with the central line of Zn_i^+ at $B = 7279$ G, which arise from hyperfine interaction with the central ion ($^{67}\mathrm{Zn}$) and the first-nearest-neighbor shell ($^{77}\mathrm{Se}$). (c) The central Zn_i^+ ODMR signal with further expanded magnetic field scale revealing (i) partially resolved hyperfine structure from the third-nearest-neighbor shell ($^{77}\mathrm{Se}$), and being greatly enhanced (ii) by second-derivative processing.

TABLE I. Spin-Hamiltonian parameters for isolated interstitial Zn_i^+ compared to those deduced from the Frenkel-pair systems, and the unpaired electron wave-function distribution. ($\mathbf{A}$ and a in units of 10^{-4} cm^{-1}.)

Zn_i^+	Zn_i^+ in $V_{\mathrm{Zn}}^- \cdot \mathrm{Zn}_i^+$	Identity	Localization per shell (%)
$g = 1.9664(4)$	1.95^a	...	...
$a_0 = 363 \pm 5$	360 ± 10	$\mathrm{Zn}_{\mathrm{central}}$	60
$(\mathbf{A}_1)_{\parallel} = 171.5 \pm 1.0$	150 ± 10^a	$(\mathrm{Se})_{1\mathrm{nn}}$	20
$(\mathbf{A}_1)_{\perp} = 154.7 \pm 1.0$			
$a_3 = 12.5 \pm 1.0$	...	$(\mathrm{Se})_{3\mathrm{nn}}$	3

[a] Reference 5.

hyperfine tensor a_3.

In Table I we compare these parameters to those previously inferred for Zn_i^+ (g, $\mathbf{A}_1$) from the ODMR studies of the Frenkel-pair triplet ($S=1$). We see that the agreement is very good. Knowing now the central $^{67}\mathrm{Zn}$ hyperfine interaction, we have reinvestigated the Frenkel-pair luminescence ODMR. By carefully filtering out background luminescence, we have now also identified the weak $^{67}\mathrm{Zn}$ interaction of the pairs, giving $a = (180 \pm 5) \times 10^{-4}$ cm^{-1}. This corresponds to $a_0 = (360 \pm 10) \times 10^{-4}$ cm^{-1} for the unpaired electron on Zn_i^+ and this value has also been included in the table. Again the agreement is very good.

We conclude, therefore, that the spectrum arises from interstitial Zn_i^+ and that it resides in the T_d interstitial site surrounded by four Se nearest neighbors.[13] The good agreement between the two sets of results confirms, in turn, the highly localized character for the electron (on the zinc) and the hole (on the vacancy) for $S=1$ excitonic state of the Frenkel pairs, as was inferred previously.[5,6]

The central hyperfine interaction is ∼60% of that predicted from Hartree-Fock calculations for the free Zn^+ ion (622×10^{-4} cm^{-1}).[14] Comparison with correspondingly determined values[14] for neutral Se provides for the nearest-neighbor shell an estimate of ∼3.1% $4s$ and ∼1.8% $4p$ on each atom, and for the third-neighbor shell containing twelve atoms ∼0.25% $4s$ on each. Viewed, therefore, as a linear combination of atomic orbitals centered on the atoms near the defect, the unpaired electron wave function is ∼60% on the central Zn_i ∼20% on the first Se shell, and ∼3% on the next. The wave function is therefore highly localized ("deep") with ∼83% apparently accounted for.

In a 15-min isochronal annealing sequence, the V^I nearest Frenkel pair ODMR disappears at ∼80 K along with its associated 625-nm luminescence. The Zn_i^+ ODMR signal remains, however, until ∼220 K, being detected as a negative signal on the remaining 600-nm luminescence. This is a higher temperature than that for the disappearance of the various Frenkel close pairs (80, 140, 180 K),[5,6] consistent with the many diffusional jumps required for an interstitial well separated from its vacancy before annihilation or trapping.

The spectral dependence of ODMR for the Frenkel pair V^I, the distant shallow donor D^0, and the zinc interstitial Zn_i^+ are shown in Fig. 1, revealing that all three are being detected in the shallow-donor-to-V^I Frenkel-pair band at 625 nm, with differing signs. We find that in various samples, V^I is always positive, Zn_i^+ always negative, but the sign of D^0 depends upon the relative intensities of the V^I and Zn_i^+ ODMR signals. In particular, the Zn_i^+ signal appears to grow superlinearly with irradiation fluence so that at low doses V^I dominates and D^0 is a positive signal. For higher fluences, Zn_i^+ dominates and D^0 is negative. We conclude, therefore, that the ODMR of Zn_i^+ arises from spin-dependent electron capture from the shallow D^0 donor,

$$\mathrm{Zn}_i^+ + D^0 \rightarrow \mathrm{Zn}_i^0 + D^+ (+h\nu?), \qquad (2)$$

in *competition* with the radiative D^0 donor to V^I acceptor recombination

$$(V_{\mathrm{Zn}}^- \cdot \mathrm{Zn}_i^{++})^+ + D^0 \rightarrow (V_{\mathrm{Zn}}^{--} \cdot \mathrm{Zn}_i^{++})^0 + D^+ + h\nu. \qquad (3)$$

This is illustrated in the inset of Fig. 1.

A search from 500 to 1350 nm and from 1400 to 1900 nm using a cooled Ge detector reveals no region where the Zn_i^+ ODMR signal is positive. The region 1350–1400-nm is excluded because of the characteristic water absorption band in our long quartz light pipe. We can conclude therefore either that (1) the D^0 to Zn_i^+ recombination is nonradiative, (2) it is radiative with $h\nu < 0.65$ eV, or (3) it is radiative in the 1350–1400-nm blind region. It is important to mention this third possibility because in a separate luminescence study with thin optical windows, a luminescence band with a strong zero-phonon line at 1365 nm (Huang-Rhys factor $S \sim 1$) has been detected after electron irradiation at 30 K.[15] It disappears upon annealing at ∼220 K (15 min), the same temperature region where the Zn_i^+ ODMR signal disappears. Its possible connection with the Zn_i is currently being investigated.

In conclusion, we have identified by ODMR the interstitial zinc ion Zn_i^+ residing in the tetrahedral site surrounded by four selenium nearest neighbors in electron-irradiated ZnSe. We conclude that it is, for all practical purposes, an *isolated* interstitial for the following reasons: (1) It displays no evidence of lowered symmetry through its third-neighbor shell; (2) its higher annealing temperature (220 K) than the Frenkel close pairs (80, 140, 180 K)[5,6] is consistent with many diffusional jumps before annihilation or trapping; (3) its superlinear production is similar to that reported for isolated zinc vacancies,[1] confirming that the initially produced close pairs can indeed separate during the 4.2-K irradiation, presumably as a result of ionizationenhanced processes. The observation of instability for the isolated zinc interstitial at $T > 220$ K gives us the first direct indication of the diffusional mobility of an interstitial in a compound semiconductor. With this as a guide, it seems unlikely that the corresponding interstitials in III-V materials would be stable at room temperature after high-temperature processing, unless as trapped by another defect.[7,8]

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[11] The computer-stored spectrum was first Gaussian smoothed (standard deviation $\sigma = 0.1$ G), then the second derivative was taken, and the resultant curve was again Gaussian smoothed ($\sigma = 0.8$ G).

[12] A very good fit to the line shape can be made with a Lorentzian shape function centered at each of the hyperfine satellite positions. From this fit, which reflects primarily the amplitude ratios of the central three components, the number of equivalent sites can be determined to be 12 ± 2.

[13] There is an alternative available T_d site surrounded by four zinc atoms. The spectrum labeled X in Figs. 2(a) and 2(b) is a good candidate for Zn_i in this site, its resolved satellite structure appearing consistent with six ^{77}Se nuclei of the next-nearest shell.

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