EPR Observation of Close Frenkel Pairs in Irradiated ZnSe†

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Four distinct EPR spectra observed in ZnSe irradiated by 1.5-MeV electrons at 20.4°K are identified as simple zinc-vacancy, zinc-interstitial close pairs of different microscopic configuration. Correlation of defect alignment with incident-electron-beam direction confirms the identification. Isolated zinc vacancies are also produced but with zero initial production rate, suggesting that their production is a two-step process, the first being the formation of close pairs.

In this Letter I report the EPR observation of several discrete zinc-vacancy, zinc-interstitial close pairs in ZnSe. Although such Frenkel pairs have often been called upon to explain radiation-damage behavior in solids, I believe this is the first direct unambiguous observation of these simple fundamental defects in a solid.[1]

Irradiation of ZnSe with 1.5-MeV electrons at 20.4°K produces two prominent well-resolved anisotropic EPR spectra, with $S=\frac{1}{2}$. One, labeled V, has been previously identified as arising from the isolated zinc lattice vacancy.[2,3] Its spectrum is axially symmetric along a ⟨111⟩ axis of the crystal with $g_{\parallel}=1.9548$, $g_{\perp}=2.2085$. This, coupled with the analysis of resolved Se^{77} hyperfine interactions, has revealed that the spectrum arises from a hole primarily located in the $4p$ shell of a single selenium neighbor to a zinc vacancy. The defects align under externally applied stress at cryogenic temperatures (i.e., the hole can "hop" between the four equivalent selenium neighbors of the vacancy and seeks out the lowest-energy one under stress). This establishes that the reduced local symmetry of the vacancy results from a trigonal ⟨111⟩ Jahn-Teller distortion and that otherwise the vacancy has the full tetrahedral symmetry (T_d) of the zinc lattice site, with no defect close enough nearby to produce a strain field comparable to that which can be applied externally.

The second spectrum, V^{I}, also has ⟨111⟩ axial symmetry. Its g tensor and Se^{77} hyperfine interactions differ only slightly from those for V, indicating that it also results from a zinc vacancy. Uniaxial stress does not produce measurable alignment,[3] however, suggesting that here the vacancy is in the strain field of a nearby defect located in a ⟨111⟩ direction from the vacancy.

Figure 1 shows the results of annealing. There are several discrete stages between 60 and 180°K at which other well-resolved EPR centers, V^{II}, V^{III}, V^{IV}, grow and disappear. These additional centers show small departures from axial symmetry but are otherwise very similar to V and V^{I}, indicating that they too are perturbed zinc vacancies. For V^{II} and V^{III}, uniaxial stress produces partial alignment revealing a restricted type of reorientational motion available to each. For V^{II}, the hole can hop between three of the four selenium neighbors which suggests the presence of a nearby defect in the ⟨111⟩ direction of the fourth selenium neighbor. For V^{III}, the hole motion is between two of the selenium neighbors indicating a defect in a ⟨100⟩ direction from the vacancy. The intensity of V^{IV} is too weak to make reliable stress measurements on it.

This Letter establishes that the defects V^{I}, V^{II}, V^{III}, and V^{IV} are zinc lattice vacancies which are perturbed by the presence of the nearby interstitial produced in the damage event. As such, they are simple zinc-vacancy, zinc-interstitial

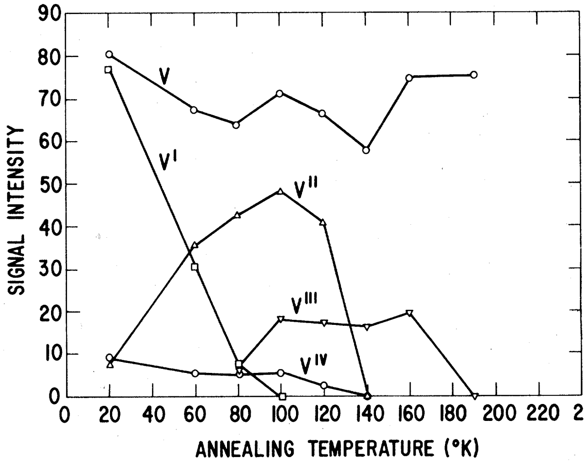

FIG. 1. Intensities of EPR spectra observed at 20.4°K in irradiated ZnSe after 15-min isochronal anneals. The sample was irradiated at 20.4°K with 1.5-MeV electrons to a fluence of 4×10^{17} electrons/cm^2.

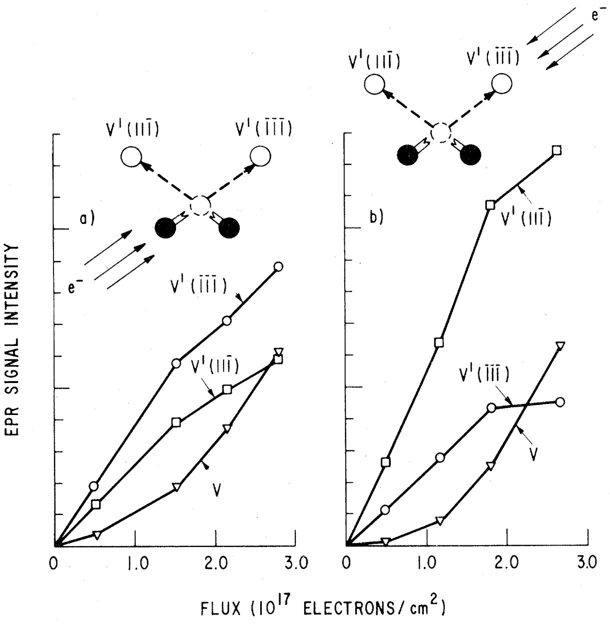

FIG. 2. Production of V and oriented V^{I} centers versus 1.5-MeV-electron fluence at 20.4°K for two different beam directions: (a) $e^- \parallel [\bar{1}\bar{1}\bar{1}]$; (b) $e^- \parallel [111]$.

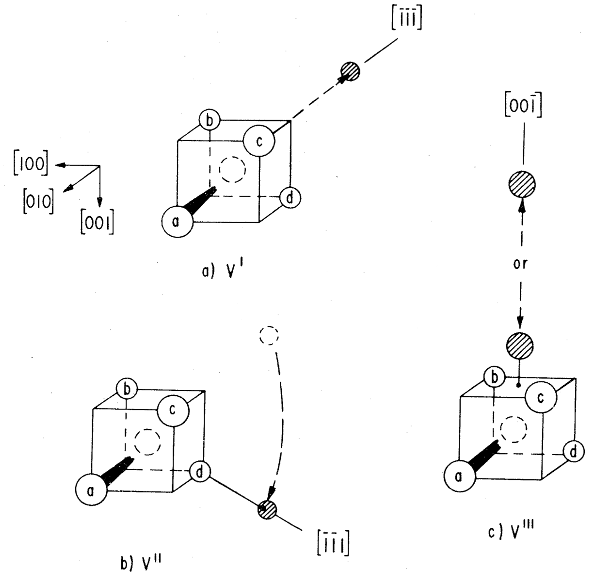

FIG. 3. Models for the Frenkel close pairs. The open circles represent selenium ions, the cross-hatched ones, the interstitial zinc. For each, the hole is on atom a, as indicated by the black orbital.

close pairs of different microscopic configurations. In this model V^{I} is formed as a primary damage event when the zinc atom is knocked out of its lattice site into a nearby interstitial site by the incoming electron. The other spectra result from different microscopic arrangements for the pair. Some of these may also be produced directly as a primary event (Fig. 1) but for the most part they appear to arise from annealing.

A direct test of this identification is possible as follows: In the primary damage event the incoming electron transmits the maximum recoil energy to a zinc atom when it recoils in the direction of the bombarding electron. There should, therefore, be a strong correlation between the orientation of interstitial-vacancy close pairs and the bombarding beam direction.

Figures 2(a) and 2(b) show the results for electron irradiation along the $[\bar{1}\bar{1}\bar{1}]$ and $[111]$ directions, respectively. For the $[\bar{1}\bar{1}\bar{1}]$ irradiation, Fig. 2(a), the production rate for V^{I} defects aligned along the beam direction, $V^{\mathrm{I}}[\bar{1}\bar{1}\bar{1}]$, is 50% greater than that for those oriented along the other $\langle 111\rangle$ directions, as monitored by $V^{\mathrm{I}}[11\bar{1}]$. Radiation along the $[111]$ direction, Fig. 2(b), reverses the effect, the $V^{\mathrm{I}}[\bar{1}\bar{1}\bar{1}]$ production rate now being less than half that for $V^{\mathrm{I}}[11\bar{1}]$. For these studies the sample thickness along the beam direction was ~0.017 in which leads to a mean square scattering angle of the beam of ~55° upon emerging from the other side of the crystal.[4] The electron beam in the sample is, therefore, described by a diffuse cone along the beam direction and the true anisotropy must be considerably larger than that observed in Fig. 2.

I interpret this anisotropy, representing unambiguous memory of the damage event, as convincing evidence of the close-pair identification for V^{I}. At the same time, the *sense* of the anisotropy confirms that the defect is being produced on the zinc lattice, the $[\bar{1}\bar{1}\bar{1}]$ recoil direction [see insets in Figs. 2(a) and 2(b)] being into an accessible interstitial space for the zinc atom. From the $\langle 111\rangle$ axial symmetry of the V^{I} center I tentatively identify V^{I} as a zinc-vacancy, zinc-interstitial close pair with the interstitial in the nearest available site in the $[\bar{1}\bar{1}\bar{1}]$ direction ($\frac{1}{2}\sqrt{3}a$ distant from the vacancy, with $a = 5.65$ Å), as shown in Fig. 3(a). Here the hole is Coulombically repelled from the positively charged interstitial zinc ion and locates on the selenium ion opposite the vacancy, as shown.

Starting with the preferential alignment of $V^{\mathrm{I}}[\bar{1}\bar{1}\bar{1}]$ after $[\bar{1}\bar{1}\bar{1}]$ irradiation of ~1.5:1, Fig. 2(a), one finds after annealing that V^{II}, V^{III}, and V^{IV} also display substantial correlated alignment. The V^{II} alignment, as measured by the $\langle 111\rangle$ axis around which stress alignment reorientation is detected, is of opposite sense and smaller in magnitude than that for V^{I}, the $[\bar{1}\bar{1}\bar{1}]/[11\bar{1}]$ ratio being ~1.0:1.2. This suggests the model of Fig. 3(b). Here in the $V^{\mathrm{I}} \rightarrow V^{\mathrm{II}}$ conversion the interstitial moves to a position equidistant from the vacancy but behind selenium atom d (or b or c, which are equivalent). These three equivalent choices reduce the net alignment by a factor of 3 and result in a net *depletion* of the $[\bar{1}\bar{1}\bar{1}]$ alignment, as observed. In this model, Coulomb repulsion again forces the hole to the other side of the vacancy. In this case there are three equivalent atoms for the hole [a, b, or c, for the configuration of Fig. 3(b)] and a Jahn-Teller distortion localizes it on one (a as shown in the figure). On physical grounds V^{II} might be expected to have a lower energy than V^{I} because of the added binding energy resulting from the polarizable Se^{--} ion between the defects.

The alignment observed for V^{III} is best described in terms of the model in Fig. 3(c). The interstitial is located in a $\langle 100 \rangle$ direction from the vacancy and the preferred direction is equally distributed between $[\bar{1}00]$, $[0\bar{1}0]$, and $[00\bar{1}]$. The observed alignment ratio $[00\bar{1}]/[001]$ is $\gtrsim 2.0$. (The zinc site is not a site of inversion symmetry and the $[00\bar{1}]$ and $[001]$ spectra are distinct.) The three preferred positions, $[\bar{1}00]$, $[0\bar{1}0]$, and $[00\bar{1}]$, lie on the surfaces enclosing the $[\bar{1}\bar{1}\bar{1}]$ octant and reflect the strong correlation of these defects with the initial $[\bar{1}\bar{1}\bar{1}]$ irradiation direction. The large alignment observed reveals that these cannot be derived solely from the annealing of V^{I}. (As for V^{II}, the three choices would reduce the net alignment to ~1.2.) They must, therefore, derive primarily from other more distant pairs, not being initially resolved, which have higher anisotropy of damage production. As shown in the figure, the interstitial could be in the nearest position, $\frac{1}{2}a$ away from the vacancy, or in the next position, $\frac{3}{2}a$ away. The hole is localized on one of the two equivalent selenium atoms on the opposite side of the vacancy, again associated with a Jahn-Teller distortion.

V^{IV} also displays a strong alignment correlated with the $[\bar{1}\bar{1}\bar{1}]$ beam direction of $\gtrsim 2.0$. A detailed model is not possible but the symmetry of the spectrum indicates an interstitial in a low-symmetry direction in the $[\bar{1}\bar{1}\bar{1}]$ octant.

Figure 2 reveals another interesting result. We note that the "isolated" vacancy, V, is not produced linearly versus dose (φ). The initial production rate is zero, the centers growing in as $\sim \varphi^n$, where n appears to be between 2 and 3. This reveals that the vacancy production is at least a two-step process and suggests that the first step is the close-pair production.

In summary, several discrete zinc-vacancy, zinc-interstitial close pairs have been identified by EPR in irradiated ZnSe. Correlation with initial electron-beam direction and stress alignment studies have allowed detailed models to be proposed for the defects. At 20.4°K, with 1.5-MeV irradiation, the primary damage process on the zinc lattice appears to be the production of Frenkel close pairs. Isolated zinc vacancies are also produced but involve at least one other step in the process.

Frenkel close pairs might be expected to be good luminescent centers, the nearby positively charged, interstitial zinc-atom "donor" serving to activate the vacancy double acceptor in a manner similar to that performed by chemical donors for the self-activated luminescent center in II-VI materials.[5] The possibility that the close pairs observed here are responsible for the luminescence reported by Detweiler and Kulp[6] in low-temperature irradiated ZnSe is currently being investigated.

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[1] Hayes and co-workers [W. Hayes and R. F. Lambourn, J. Phys. C: Proc. Phys. Soc., London 6, 11 (1973); W. Hayes, R. F. Lambourn, G. Rangarajan, and I. M. Ritchie, J. Phys. C: Proc. Phys. Soc., London 6, 27 (1973); W. Hayes and R. F. Lambourn, Phys. Status Solidi (b) 57, 693 (1973)] have recently presented optical, EPR, and electron-nuclear double-resonance evidence of F centers perturbed by nearby interstitial halogen ions in alkaline earth halides. These centers, produced by x irradiation at low temperatures, therefore involve Frenkel pairs, but the possible additional involvement of an impurity as well has not been ruled out [P. J. Call, W. Hayes, J. P. Stott, and A. E. Hughes, to be published].

[2] G. D. Watkins, Bull. Amer. Phys. Soc. 14, 312 (1969).

[3] G. D. Watkins, in *Radiation Effects in Semiconductors*, edited by J. W. Corbett and G. D. Watkins (Gordon and Breach, London, 1971), p. 301.

[4] J. W. Corbett, *Electron Radiation Damage in Semiconductors and Metals* (Academic, New York, 1966), p. 30 ff.

[5] See, for instance, D. Curie and J. S. Prener, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland, Amsterdam, 1967), p. 445 ff.

[6] R. M. Detweiler and B. A. Kulp, Phys. Rev. 146, 513 (1966).