

Impurity radii: Evaluation from donor-acceptor pair luminescence and comparison to effective-mass values

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We have determined the effective radii of donors (interstitial Na) and of acceptors (Na on a Zn substitutional site) in ZnSe:Na. These were determined from the time decay of relatively close pairs. We feel prior determinations of such impurity radii, generally done by using the decay of the distant-pair peak, are mostly inaccurate, due to neglect of excitation transfer; the effect of such transfer is minimized by use of the decay of the close pairs. Our results agree closely with the values obtained from scaled effective-mass theory.

The radii of impurities in semiconductors (and other materials) are of considerable interest, and importance, since they determine most transition probabilities, both radiative and nonradiative. However, there are relatively few techniques which can be used to obtain these radii. One such technique is measurement of the decay of donor-acceptor pair (DAP) photoluminescence (PL); this is particularly appropriate for relatively shallow impurities. We here report such measurements on ZnSe:Na, and obtain the radii for both the donor (interstitial Na, Na_i) and the acceptor (Na on the Zn site, Na_{Zn}) species. We also argue that our method, use of the decay of close pairs, is more likely to give reliable values than the more commonly used decay of the peak due to more distant pairs. In addition, we also show that the radii we obtain agree well with those given by scaled effective-mass theory. This increases our confidence in our values, and also suggests that this theory is useful as a check on values obtained by other techniques.

The evaluation of the radii from DAP PL depends critically on the fact that such PL is a function of the pair separation (R). Thus, the energy ($h\nu$) of DAP luminescence for a donor and acceptor at a distance R is well approximated by¹

$$h\nu = h\nu_\infty + e^2/\epsilon_0 R, \quad (1)$$

$$h\nu_\infty = E_G - (E_D + E_A), \quad (2)$$

where $h\nu_\infty$ is the luminescence energy for pairs at infinite separation, and is given by the band gap (E_G) minus the binding energies of the isolated donor (E_D) and acceptor (E_A), e is the electronic charge, and ϵ_0 is the static dielectric constant. The distribution of R 's is not continuous but is given by discrete numbers corresponding to the lattice site configuration of donor and acceptor, which is usually represented by shell numbers. For example, the nearest neighbor is assigned shell 1, the second-nearest neighbor is assigned shell 2, and so on.

DAP luminescence¹ can be separated into two parts depending on the pair separations (R) between donors and acceptors. For close pairs (small R), the energy separations between neighboring shells are large due to a

large Coulomb interaction term $e^2/\epsilon_0 R$ in Eq. (1), and the pair spectra show a series of sharp peaks; each peak corresponds to a specific shell number. For distant pairs (large R), neighboring shells are energetically close (due to small Coulomb interaction) and are usually unresolvable. The distant DAP's typically give a broad zero-phonon peak, together with several phonon replicas; these peaks are composites of pairs of a range of R 's.

The pair decay rate [$W(R)$], provided that the pair is a sufficiently isolated entity so that the DAP radiative recombination dominates over other pair decay paths (such as excitation transfer, Ref. 2), is given by³

$$W(R) = \frac{4e^2\mu h\nu_\infty}{m_0^2\hbar^2c^3} |M_{DA}|^2, \quad (3)$$

where μ is the index of refraction (for which we used the room-temperature value at 460 nm, $\mu = 2.842$, as given by Marple⁴), m_0 is the electron mass, c is the velocity of light, and M_{DA} is the matrix element of the momentum operator between the donor and the acceptor, and is given as a product of a matrix element between the conduction and the valence band (M_{cv}) and an overlap integral between the envelope functions of a donor and an acceptor [$I(R)$]³,

$$|M_{DA}| = |M_{cv}| |I(R)|. \quad (4)$$

The $|M_{cv}|^2$ given in Ref. 3 is best represented by $m_0 E_p / 6$, where E_p is a band parameter which has been calculated by Lawaetz⁵ using a five-level $\mathbf{k}\cdot\mathbf{p}$ analysis, and the result for ZnSe is 24.2 eV. For unequal donor and acceptor radii, $I(R)$ is given as⁶

$$I(R) = \frac{8(\alpha\beta)^{3/2}}{(\alpha^2 - \beta^2)^3 R} \{ [4\alpha\beta + (\alpha^2 - \beta^2)\beta R] e^{-\alpha R} - [4\alpha\beta - (\alpha^2 - \beta^2)\alpha R] e^{-\beta R} \}, \quad (5)$$

where $\alpha = (1/a_D)$, with a_D the donor radius, and $\beta = (1/a_A)$, with a_A the acceptor radius. For $a_D \gg a_A$, which is the case in ZnSe, where the donors are appreciably more shallow than the acceptors, and provided R is

not too small ($R \gg 4\alpha/\beta^2$), $I(R)$ reduces to

$$I(R) = 8 \left(\frac{\alpha}{\beta} \right)^{3/2} e^{-\alpha R}. \quad (6)$$

Under this condition $W(R)$ reduces to the well-known¹ form

$$W(R) = W_0 \exp(-2R/a_D), \quad (7)$$

where

$$W_0 = \frac{128}{3} \frac{e^2 \mu h \nu_\infty E_p}{m_0 \hbar^2 c^3} \left(\frac{a_A}{a_D} \right)^3 \quad (8)$$

and represents the strength of the recombination. We note that a_D is here the larger radius. We shall, henceforth, carry out the analysis under this condition; however, we note that if the acceptor radius were larger, the subsequent equations would still apply, but with a_A used instead of a_D .

In principle, a_D as well as W_0 and, consequently a_A , can be determined either from the decay of the PL of close pairs or that of the distant pair peak. However, in practice, most⁷ determinations have used the distant peak, because of the higher PL intensity here. The analysis in this case includes the pair distribution (e.g., Ref. 8), and has been carried out only with neglect of excitation transfer (i.e., assuming noninteracting pairs). As we have previously discussed,² literature results, however, show puzzling order-of-magnitude disagreements, which we believe are due to neglect of excitation transfer.

To evaluate the parameters from the close pairs, the spectrally resolved decay of a number of pairs is measured, and a_D and W_0 can then be conveniently obtained by a plot of $\log_{10} W$ vs R [Eq. (7)]. This approach will minimize the effects of excitation transfer, for two reasons. First, the energies from different shells are relatively well separated [small R , Eq. (1)], and thus only one shell, or at most a few shells, is involved; thus it is not necessary to use a pair distribution function, where this function would be modified by excitation transfer. Second, the decay of the close pairs is considerably faster than that at the distant pair peak, so that there is less time for energy transfer. We have carried out such measurements on a sample of Na-doped ZnSe, where it was shown previously⁹ that the luminescence of the close pairs is due to Na_i as donor and Na_{Zn} as acceptor.

Because the recombination rate increases exponentially with decreasing R , our present instrumentation cannot resolve the decay of the really close pairs ($R \leq 27 \text{ \AA}$) [where R is determined from Eq. (1) with $h\nu_\infty = 2.676 \text{ eV}$ as given in Ref. 9] and we therefore concentrate on the pairs near the tail of the distant DAP peak. Several examples at different luminescence energies are shown in Fig. 1. Notice that, for the closer pairs, a fairly good initial exponential decay is obtained together with a small but observable nonexponential tail. This nonexponential component presumably originates from more distant DAP's, whose decay may be introduced by the low spectral resolution of our $\frac{1}{4}$ -meter monochromator; this nonexponential tail increases as the luminescence energy

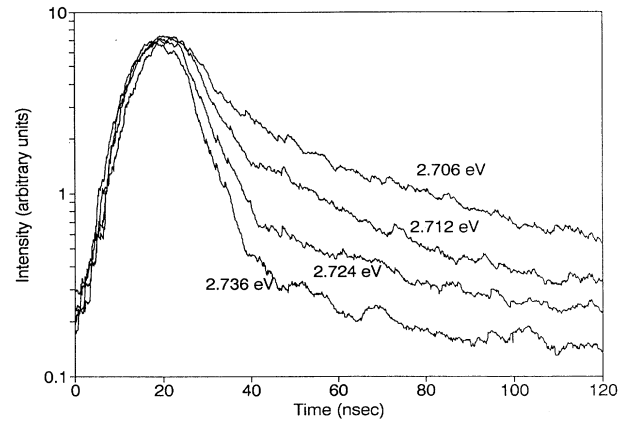


FIG. 1. Time-decay curves of a few close pair lines. The emission at 2.73 eV corresponds to an average R of 27 \AA , with 2.724, 2.712, and 2.706 eV corresponding to R 's of 34, 45, and 54 \AA , respectively.

approaches the distant DAP peak. The initial exponential decay was shown by pairs up to R of about 40 \AA . The overall results are plotted in Fig. 2. Evaluation, using only the points up to $R = 40 \text{ \AA}$, gave $a_D = 37 \text{ \AA}$ from the slope and $W_0 = 6 \times 10^8$ /sec from the intersection. These two values, via Eq. (8) with use of $h\nu_\infty = 2.676 \text{ eV}$, give $a_A = 5.6 \text{ \AA}$.

It is to be noted that the value of $a_D = 37 \text{ \AA}$ which we obtain here is in disagreement with an earlier estimate⁹ of 24 \AA for this donor. This earlier value was obtained from an analysis of the spectral intensity. We believe the discrepancy is due to preferential pairing in this sample;¹⁰ such pairing would impact the spectral intensity, and was not taken into account in the earlier⁹ work.

In view of the concern we have expressed above regarding the role of excitation transfer, it remains to assess the reliability of the present values. We feel they are reliable. This is partly for the reasons given above. In addi-

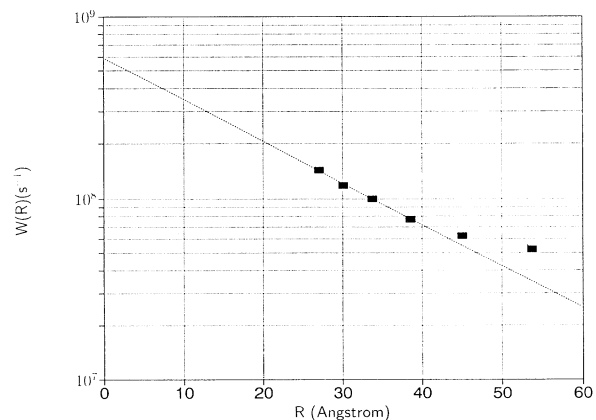


FIG. 2. Semilogarithmic plot of $W(R)$ as a function of R . The intersection at the y axis gives $W_0 \approx 6 \times 10^8$ /sec, and the slope gives $a_D \approx 37 \text{ \AA}$; these two values via Eq. (8) give $a_A \approx 5.6 \text{ \AA}$.

tion, for the close pairs the decay is exponential, as expected [Eq. (7)] and, moreover, the results also obey Eq. (7) as a function of R (Fig. 2). A further reason for our confidence in these values is that they are in quite good agreement with scaled effective-mass theory, and we discuss this theory next.

Effective-mass theory has been used extensively to obtain the activation energies (E_{Ac}) and effective Bohr radii (a_B) of shallow impurities in semiconductors. In the simplest form of this theory¹¹ the results are given by

$$E_{Ac}^* = \frac{m^*}{m_0} \frac{1}{\epsilon_0^2} E_H \quad (9)$$

$$a_B^* = \frac{\hbar^2 \epsilon_0}{m^* e^2} = \frac{m_0}{m^*} \epsilon_0 a_0, \quad (10)$$

where $E_{Ac}^* = E_D^*$ (E_A^*), for donors (acceptors), and correspondingly for a_B^* , and where m^* is the effective mass, a_0 is the Bohr radius of the hydrogen atom (0.529 Å), and E_H is the energy of the hydrogen atom (13.6 eV).

However, despite the considerable success of this theory, it is by now also well known that there are many underlying approximations. One important factor is the contributions due to nearby bands, which is particularly important for acceptors, in view of the degenerate valence-band structure. A convenient formulation for this case was given by Baldereschi and Lipari,¹² where their results are expressed in terms of the valence-band parameters γ_1 , γ_2 , and γ_3 . Other important corrections are due to the wave-vector dependence of the dielectric constant and due to central-cell effects (a review is given, for example, by Pantelides¹³). These latter corrections apply to both donors and acceptors; here, a convenient approach to treating them is the so-called scaled

effective-mass theory, where it is assumed that the radii scale with the impurity energy (which can be determined more easily than the radii) via an effective dielectric constant, i.e., the scaling assumes a constant effective mass. Specifically, this gives

$$a_B = a_B^* \left[\frac{E_{Ac}^*}{E_{Ac}} \right]^{1/2}, \quad (11)$$

where a_B is the scaled Bohr radius corresponding to the actual energy level.

We have evaluated the effective-mass energies for both donors and acceptors (E_D^* and E_A^*), and the corresponding radii (a_D^* and a_A^*), where we have used the Baldereschi and Lipari¹² approach for the acceptors. We have used $\epsilon_0 = 8.8$ (Ref. 14), $m_e^*/m_0 = 0.145$ (Ref. 15), and the valence-band parameters $\gamma_1 = 2.45$, $\gamma_2 = 0.61$, and $\gamma_3 = 1.11$ (Ref. 16). We obtain $E_D^* = 25.2$ meV, $a_D^* = 32.2$ Å, $E_A^* = 151$ meV, and $a_A^* = 4.6$ Å. Scaling the radii to the energy of Na_i of 20 meV (Ref. 9) and to the average of Na_{Zn} values of 124 meV (Ref. 17) and 128 meV (Ref. 18) gives $a_D = 36.1$ Å, and $a_A = 5.0$ Å. Both these values are in quite satisfactory agreement with the values obtained from the decay.

In conclusion, we have obtained the Bohr radii a_D of interstitial Na donors and a_A for substitutional Na acceptors in ZnSe from the decay of a number of relatively close pair lines, where the effect of excitation transfer on the decay is likely to be insignificant. The results of $a_D \approx 37$ Å and $a_A \approx 5.6$ Å are in very good agreement with the values of 36.1 and 5.0 Å derived from scaled effective-mass theory.

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