Energy of an Interstitial Donor in ZnSe from Pair Spectra

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We report donor-acceptor-pair line luminescence from Na-doped ZnSe. The luminescence is "type II," and analysis gives an energy of 20 ± 2 meV for the donor. From the spectrum type and the energy value we conclude that the donor must be an alkali-metal (Na or Li) interstitial ion. Prior evidence for such species in II-VI compounds has been circumstantial, and no reliable energy values have been available. Moreover, the magnitude of the energy value raises serious questions on the theory of shallow levels in compound semiconductors.

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Interstitial alkali-metal ions have often been implicated in various puzzling electronic and luminescence properties of II-VI compounds. It is, for instance, well known[1-4] that it is difficult to obtain well conducting *p*-type wide-band-gap II-VI semiconductors. Such alkali-metal interstitials would act as donors in these materials; thus if they are present, even if only as contaminants,[5] this difficulty is understandable.[1-5] However, unambiguous evidence for these interstitial species has been elusive. Mostly, their presence is inferred circumstantially, for example, from drift in an electric field[2,4,6] or from the appearance of a luminescence line (for Li) appearing together with a line identified as due to substitutional Li.[7] Moreover, experiments of this type have not yielded any reliable values for the energy levels of such donor species.

In the present paper we show unambiguously, from the observation of type-II donor-acceptor pair spectra,[8] the presence of an interstitial donor in Na-doped ZnSe, and evaluate its energy level as 20 ± 2 meV. As far as we know, this is the first definitive report of type-II pair spectra in a II-VI compound. Moreover, the 20-meV level is well below the prediction of simple effective-mass theory, which gives a 28-meV value; since effective-mass theory is expected to be best for shallow levels, this disagreement is disconcerting.

We have prepared Na-doped ZnSe by adding Na_2Se and Se to a Bi melt, and heating ZnSe crystalline wafers in contact with this melt.[9] The luminescence spectrum, measured with a photon counting modification to a previously[5] described system, for a sample heated at 830 °C for 1 h, is shown in Fig. 1. One can identify two I_1 lines (at 2.7929 and 2.7937 eV), an I_2 line (at 2.7976 eV), a phonon replica of the I_1 lines (the notation is standard,[1,8] where I_1 refers to recombination of excitons bound to acceptors, and I_2 to those bound to donors), as well as a pair peak (at 2.68 eV) with phonon replicas. The energies of the I_1 lines agree with other identifications[5,10,11] of such lines as due to Na. In addition, there is structure indicative of pair lines, on which we will now focus.

It is well established[8] that because of the discrete positions of impurities in a lattice, there are discrete values for the separations between a donor and its nearest acceptor (the *D*-*A* pair), and resultant line luminescence. The luminescence energy ($h\nu$)

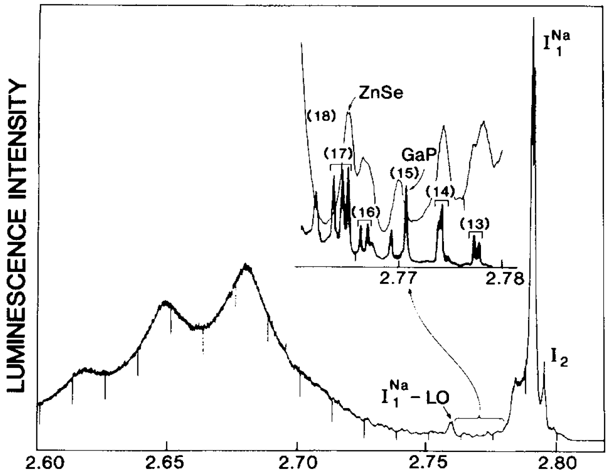

FIG. 1. Photoluminescence from Na-doped ZnSe sample at 5 K. The I_1 and I_2 lines are indicated [the notation is standard (Refs. 1 and 8)], as well as the LO-phonon replica of the I_1 lines. The pair structure can be discerned from about 2.78 eV down to 2.71 eV. The peaks from 2.68 eV down are the distant donor-acceptor peak and its LO-phonon replicas. The inset shows the pair lines from the close pairs (those whose energies are between the shoulder on the I_1 peak and the I_1 phonon replica) on an expanded scale, together with a match to appropriately scaled results (Ref. 13) for GaP(Zn,O); the energy scale on the inset refers to the ZnSe, and the numbers in parenthesis are the shell numbers of the GaP.

from a pair at a distance R is given by[8]

$$h\nu = h\nu_\infty + e^2/\epsilon_0 R - \Delta E, \qquad (1)$$

$$h\nu_\infty = E_g - (E_D + E_A). \qquad (2)$$

Here, $h\nu_\infty$ is the emitted energy for pairs at infinite separation, and is given by the band gap (E_g) minus the sum of energies of the isolated donor (E_D) and acceptor (E_A), e is the electronic charge, ϵ_0 is the static dielectric constant, and ΔE is a correction term resulting from additional interactions for close pairs (ΔE goes to zero as $R \rightarrow \infty$). Each set of lattice positions at a given R is referred to as a "shell." Moreover, there is a given number of sites associated with a particular shell, resulting in a corresponding intensity distribution of the luminescence lines.[8] This intensity distribution is different for donors and acceptors on the same type of lattice site (e.g., both on the Zn site) as against location on opposite types of lattice sites.[8,12] The former is referred to[8,12] as type I, the latter as type II.

In general, it is not always easy to decide whether a spectrum is type I or type II, especially if the lines are not very sharp; the problem is that $E_D + E_A$ is not known *a priori*, but instead is obtained from fitting to the spectra once the type has been established. As a first step, we tried to superimpose, with an appropriate energy displacement, the present spectrum on known type-I spectra in ZnSe with Li acceptors.[10] This was not successful. Thus, assuming a type-II spectrum, we compared the present results with this type in GaP.[13] The inset of Fig. 1 shows this comparison (appropriately scaled[14]) between our close pairs and very similarly structured lines in GaP(Zn,O), as given by Dean, Henry, and Frosch.[13] The similarity appears satisfactory. As a further check we then compared more distant pair lines with the theoretical predictions. Since the observed lines were rather broad, the theoretical spectrum was generated with a computer program which includes line broadening, following Vink, van der Heyden, and van der Does de Bye.[15] The resultant fit is shown in Fig. 2, and uses the following parameter values: $h\nu_\infty = 2.676$ eV, $\epsilon_0 = 8.8$,[16] the donor radius $a_B = 24$ Å, a half-width Gaussian $\sigma = 0.0012$, and the correction factor $C = 650$, where we use the assumption of Vink, van der Heyden, and van der Does de Bye[15] that $\Delta E \approx C/R^4$. (It was not possible to fit to type I by use of the same fitting procedure.) In Fig. 2 we also indicate the energies where one expects the second phonon replicas of the I_1 lines. It can be seen that good agreement is obtained between the data and theory except in the phonon-replica region. With use of $E_g = 2.822$ eV,[17] our value of $h\nu_\infty$ leads to $E_D + E_A = 146$ meV.

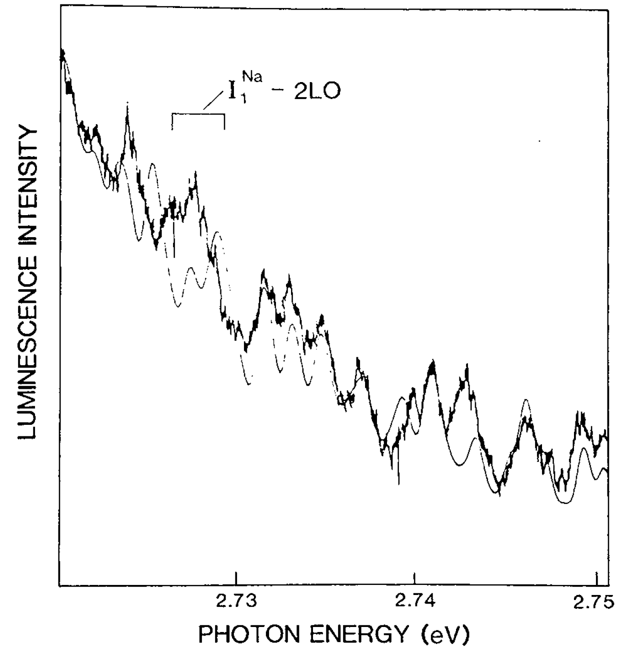

FIG. 2. Photoluminescence, at 5 K, from the ZnSe(Na) sample of Fig. 1 on an expanded scale. Shown are the more distant pair lines (those whose energy is on the low-energy side of the first LO replica of the I_1 peak and its shoulder) together with a computer generated fit (see text), shown as the thin line. The fit can be seen to be good except in the region of the second phonon replica of the I_1 peak, i.e., this replica is of sufficient magnitude to distort the pair luminescence. (The indicated width of the replica corresponds to the half-width of the first phonon replica. It neglects the shoulder on the I_1 peak, whose first phonon replica we have clearly observed; this shoulder may well be affecting the luminescence on the low-energy side of the indicated width.)

A remaining question is identification of the donor and acceptor species. Regarding the latter, the only sensible assumption is Na on zinc sites (Na_{Zn}) in view of the doping and of the Na I_1 lines. Thus, based on the type-II spectra, the donors must be halide ions on the Se site, or interstitials. To eliminate the halide ions, we first consider the value obtained for E_D. Recent results for the ionization energy of Na_{Zn} range from 124 meV (Ref. 5) to 128 meV,[18] and the use of $E_A = 126 \pm 2$ meV gives $E_D = 20 \pm 2$ meV. This value is well below the known[19] values for Cl (27 meV) and F (29 meV). Thus neither Cl nor F can be involved. As to Br and I, *deliberate* attempts to introduce these into ZnSe, as reported by Merz *et al.*,[19] as well as by Nassau and Shiever,[7] were unsuccessful. Thus these can also be ruled out. We conclude that an interstitial metal ion must be providing the donor. The prime possibility, of course, is the dopant itself, i.e., Na_I. Nevertheless, contamination is always a problem[1,4,5,20]; since Li is a common contaminant,[1,5] Li_I cannot, as yet, be ruled out.[21]

Given an interstitial donor with an energy of 20 meV, it remains to examine implications of this result for the theory of shallow levels in compound semiconductors. An energy of 20 meV is relatively shallow, and one would thus expect that simple effective-mass theory (energy $= e^4 m^* / 2\hbar^2 \epsilon_0^2$) would apply relatively well.[22] This turns out not to be the case: using $m^+ = 0.16$ (Ref. 17) and $\epsilon_0 = 8.8$ (Ref. 16), one obtains an effective-mass energy of 28 meV. The observed energy is thus appreciably more shallow. It is by now well established that improved energy values require various corrections to simple effective-mass theory.[22] It is generally believed[22] that the most important are the following four: (1) inclusion of other bands[22,23] (or extrema); (2) inclusion of q-dependent electronic screening[22,23]; (3) polaron effects[22,24]; (4) central-cell effects.[22,24] The first three effects are unlikely to play a role here. As regards effect (1), higher bands and extrema are fairly far removed[25] in ZnSe; as regards effect (2) and (3), both would be expected to give basically the same energy[24] value for an interstitial donor as for a substitutional donor, where values for the latter[1,17] are in the 26-29-meV range. This leaves the central-cell correction[26] as the remaining possibility; however, we here require a correction of about −8 meV (i.e., −30%), and large negative central-cell effects[26] would be unusual.[22] At this point we have no other ready explanation; however it does appear that either the theory of central-cell effects and/or the theory of shallow levels in compound semiconductors requires further examination. We still wish to point out that no comparable check on interstitial donors can be carried out for GaAs, the most extensively studied direct-gap III-V semiconductor, since no interstitial donor levels appear known.[27]

In conclusion, we report type-II pair spectra from a ZnSe(Na) sample, and show that this spectrum results from an interstitial metal ion (probably Na_I, also possibly Li_I) as donor. We believe that this is the first unambiguous observation of a type-II spectrum in II-VI semiconductors. The ionization energy of the interstitial donor is 20 ± 2 meV. This energy value raises questions regarding the theory of shallow levels in compound semiconductors.

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[9] Our procedure is similar to that used for growth of liquid-phase epitaxy (LPE) layers in ZnSe, except that Zn is omitted from the melt. This was done in order to encourage the Na to be incorporated on substitutional Zn sites. The LPE method is described, for example, by B. J. Fitzpatrick, C. J. Werkhoven, T. F. McGee, III, P. M. Harnack, S. P. Herko, R. N. Bhargava, and P. J. Dean, IEEE Trans. Electron Devices **28**, 440 (1981).

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[27] Levels due to alkali-metal impurities in GaAs are reviewed, for example, by A. G. Milnes, in *Advances in Electronics and Electron Physics,* edited by P. W. Hawkes (Academic, New York, 1983), Vol. 61, p. 63.