PHOTOLUMINESCENCE OF DEFECT-EXCITON COMPLEXES IN II-VI COMPOUNDS*

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We have examined band-edge fluorescent emission spectra in various II-VI compounds at 4°K with the objective of establishing correlations between the presence of specific spectra and the presence of specific defects. The basis for such correlations is the proven existence of radiative recombination from excitons bound to defects,[1-3] and the expectation that such mechanisms can account for much of the plethora of band-edge spectra observed. We have found evidence for a simple relationship governing such correlations for this family of compounds—a significant extension of Haynes's observations[1] in silicon.

Figure 1 (insert) illustrates the procedure employed for acceptor defects. We have attempted, by purification and subsequent introduction of acceptor defects, to obtain samples which exhibit a dominant emission process of near-band-gap energy at 4°K correlated with the presence of a dominant emission process of substantially less than band-gap energy. Attributing the edge emission to transitions involving excitons bound to acceptors, we define as the dissociation energy, E_D, of this complex the energy difference between the zero-phonon peak of the emission series and the reflectivity minimum due to exciton absorption. We assume the lower energy emission results from transitions to an acceptor level from the conduction band or shallow donor states close to the conduction band. For an estimate of the ionization energy, E_i, of the defect, we have taken the energy difference between the band gap, E_g, and either the first peak of this lower energy emission series or the high-energy half-maximum point if a structureless emission band is observed. For this discussion it is useful to plot exciton-defect dissociation energies versus defect ionization energies, each point giving E_D and E_i for one correlated pair of spectra.

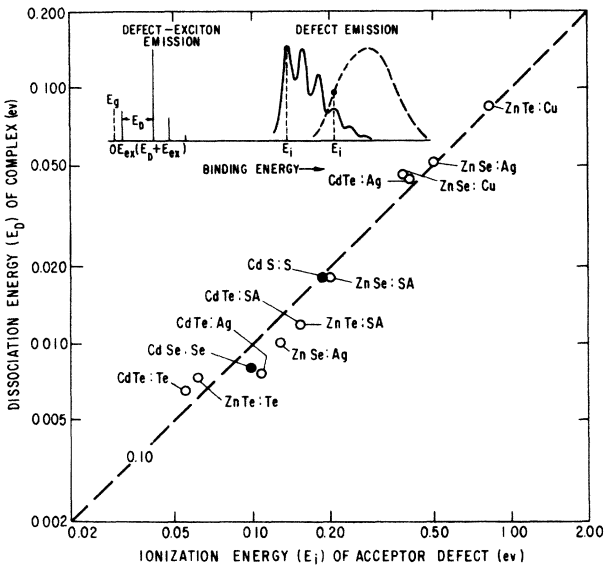

FIG. 1. E_D versus E_i for correlated pairs of fluorescent emission spectra at 4°K in acceptor-doped II-VI compounds. Definitions employed for E_D and E_i are illustrated in insert. Proximity of ratio E_D/E_i to 0.10 is emphasized. Dopants employed are noted. *SA* (self-activation) is believed to involve cation vacancy-donor complexes. Firing conditions favoring anion excess in otherwise undoped material are also indicated (e.g., CdTe:Te).

Figure 1 presents data points involving acceptor defects in ZnSe, ZnTe, CdS, CdSe, and CdTe. The presence of the band-edge spectra in all these cases is enhanced by preparation conditions favoring a low Fermi level. In two cases indicated by filled circles in Fig. 1 (CdS, $E_D = 0.017$ eV; CdSe, $E_D = 0.008$ eV), the transitions have been established by magneto-optical measurements as due to an exciton bound to a neutral acceptor.[2,3] Within the precision of our present measurements and criteria for determining E_D and E_i, a ratio of $E_D/E_i \approx 0.10$ is the rule, even for E_i as great as 0.8 eV. This conclusion appears valid even when more precise definitions of E_i are considered.[4]

A transition due to an exciton bound to a neutral donor has been identified in CdS.[2] We have observed that this is the dominant emission close to the band edge in low-resistivity donor-doped crystals. Figure 2 presents data obtained by assuming that the dominant band-edge emission in donor-doped n-type crystals of other II-VI compounds has similar origin. E_D is defined as before. The values of E_i employed for donor levels represent a composite of optical measurements (CdS),[2] Hall-effect measurements, and estimates based on experimen-

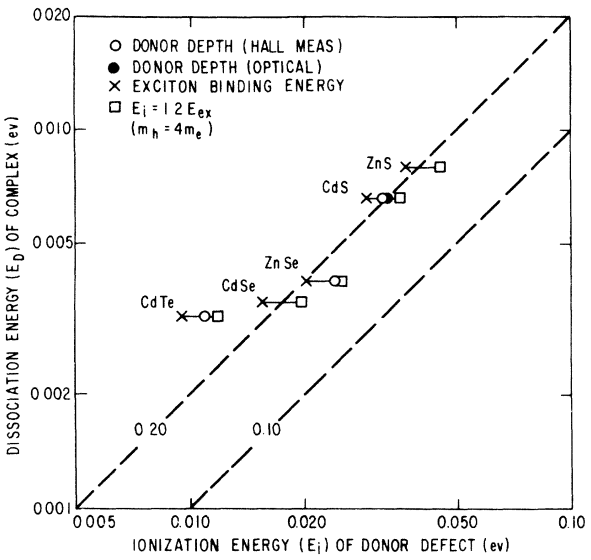

FIG. 2. E_D versus E_i for dominant band-edge fluorescent emission spectra at 4°K in donor-doped II-VI compounds. E_i is estimated by noted methods. Proximity of ratio E_D/E_i to 0.20 rather than 0.10 is illustrated.

tally determined exciton binding energies, E_{ex}. For the latter case, $E_i \approx E_{ex}(1+m_e/m_h)$, where m_e/m_h is the ratio of electron and hole effective masses. Values of E_i for the low-energy limit $m_e/m_h = 0$ ($E_i = E_{ex}$) and for a representative ratio $m_e/m_h = 0.25$ are plotted. The ratio E_D/E_i is of the order of 0.20 for the band-edge spectra in donor-doped n-type II-VI compounds.

Haynes has reported evidence in silicon for radiative recombination from four-particle analogs of the hydrogen molecule.[1] These he identified as the exciton–neutral-donor and exciton–neutral-acceptor complexes whose existence was previously predicted by Lampert.[5] Haynes found a ratio of E_D/E_i of approximately 0.10 applicable for both types of complexes. He presented an argument, attributed to Kohn, which showed that this ratio was reasonable in magnitude from the point of view of hydrogen-molecule and hydrogen-ion approximations applicable for extremes in the ratio of m_e/m_h. The fact that the "average" electron and hole effective masses are approximately equal in silicon would give a similar ratio of E_D/E_i for both types of complexes. In II-VI compounds where $m_e < m_h$, similar considerations would predict a difference for E_D/E_i for exciton–neutral-donor and exciton–neutral-acceptor complexes in the direction experimentally observed. It is surprising, however, that E_D/E_i is approximately constant for a wide range of acceptor ionization energies.

The existence of a simple ratio of E_D/E_i for a given type of exciton-defect complex should provide a useful aid in the identification of spectra. On this basis, Figs. 1 and 2 attribute a number of previously unidentified spectra to transitions involving either donor or acceptor defects. With the noted exceptions, these assignments remain to be verified by other methods. Indications of variability of E_D/E_i within each group are difficult to confirm without a more precise measure of E_i.

Evidence that an analog of the hydrogen ion fairly quantitatively predicts E_D for excitons bound to deep neutral-acceptor levels is of further interest since it also would support the predicted existence[5] of trapping states arising from holes bound to neutral acceptors and, similarly, electrons bound to neutral donors. The binding energy involved is analogous to the attachment energy of an electron to a hydrogen atom. The existence of such trapping states is currently under investigation.

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[3]D. C. Reynolds and C. W. Litton, Bull. Am. Phys. Soc. 9, 224 (1964).

[4]In the case of pair spectra, for example, E_i(true) $< E_i$ as defined for this paper. See D. G. Thomas, J. J. Hopfield, and K. Colbow, Proceedings of the International Conference on Semiconductor Physics, Paris, 1964 (to be published).

[5]M. A. Lampert, Phys. Rev. Letters 1, 450 (1958).