Sharp-Line Donor-Acceptor Pair Spectra in AlSb

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We have observed sharp-line donor-acceptor pair spectra (type I) in Se-doped AlSb. We analyze the spectra quantitatively by using a known solution of the Schrödinger equation for an electron bound to a dipole of finite charge separation. Excellent agreement is obtained between the theoretically predicted and experimentally observed spectra for the parameters $E_g = 1.69$ eV, $E_D = 0.15$ eV, $E_A = 0.04$ eV, and an electron Bohr radius $a_e = 4.28$ Å.

INTRODUCTION

DONOR–ACCEPTOR (D-A) pair line spectra seen in photoluminescence were first positively identified in 1963 in GaP.[1] They have since been observed and identified in BP,[2] and spectra attributed to such pairs have been reported in SiC.[3] We wish to report here the observation of a series of sharp lines in AlSb which we identify as D-A pair spectra. The spectra resemble those observed in GaP and BP, but the sharp lines extend to a much closer pair spacing, i.e., $R = 7.5$ Å at $m = 3$. A quantitative analysis, based on a solution of the Schrodinger equation for an electron bound to a dipole of finite charge separation,[4] leads to nearly complete agreement between the theoretically predicted and experimentally observed spectra.

AlSb has the zinc-blende structure with a lattice constant $a = 6.125$ Å, and a low-frequency dielectric constant $K = 11.2$.[5] The optical transition at the energy gap is believed to be indirect, with the conduction-band minima at the (100) zone boundary.[6] Undoped crystals are normally p type and have a hole concentration between 10^{16} and 10^{17} cm^{-3}. Se introduces a donor level of binding energy $E_D \approx 0.16$ eV.[7]

EXPERIMENT

The samples were cut from single crystals of Se-doped AlSb having an electron concentration at 300°K of 8×10^{15} cm^{-3} and were heavily etched immediately before being measured. The fluorescence was excited with a Hg arc lamp and studied with a grating spectrometer. A typical line spectrum taken in liquid helium below the lambda point is shown in Fig. 1. The spectrum contains two series of lines only one of which we discuss in this paper. The lines of this series are identified by shell number[1] in the figure. The relative intensities of the lines, and in particular the absence of lines at

$m = 14$ and 30, indicate that the members of each D-A pair occur on the same type of substitutional lattice site. Since the donor is known to be Se on an Sb site, the acceptor must also be located on the Sb site. An important feature of the spectrum is the appearance of lines corresponding to close-pair spacings including the third-nearest-neighbor pair $m = 3$. This fact requires that one of the binding energies, in our case E_D, be large. Since the spectrum also extends to pairs of larger separation, the other (acceptor) binding energy E_A must be relatively small to produce the required overlap of wave functions. A large ratio E_D/E_A simplifies the calculation of the energy radiated by a given pair.

THEORY OF PAIR SPECTRA

Consider a D-A pair of separation R. The energy radiated by such a complex equals the energy needed to create the excited (neutral) state from the ground (ionized) state. This is the energy E_g needed to create an electron-hole pair reduced by the binding energy of the electron and hole in the field of the ions and of each other. This may be written

$$h\nu(R) = E_g - E_D'(R) - E_A''(R), \tag{1}$$

where $E_D'(R)$ is the binding energy of the electron (assumed to be captured first) in the field of the ionized donor and acceptor ions, and $E_A''(R)$ is the additional binding energy of a hole to this complex. For the most distant pairs which can be resolved, R is larger than both Bohr radii a_e and a_h of the isolated donor and acceptor. Equation (1) then reduces to

$$h\nu(R) \approx E_g - E_D - E_A + E_C, \tag{2}$$

where E_D and E_A are the binding energies of the isolated centers and $E_C = e^2/KR$. This omits the overlap correction[8] and the van der Waals term.[9]

For the closest-spaced pairs the hole cannot be captured alone, since its binding energy is vanishingly small (it has no bound state for $R < 0.64 a_h$),[10] and the electron must be captured first. Its binding energy $E_D'(R)$ is known from the calculation by Wallis *et al.*[4] of the energy

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FIG. 1. Photoluminescent emission spectrum from AlSb at $T \leq 2.2°K$. Shell numbers label the lines according to the pair separations.
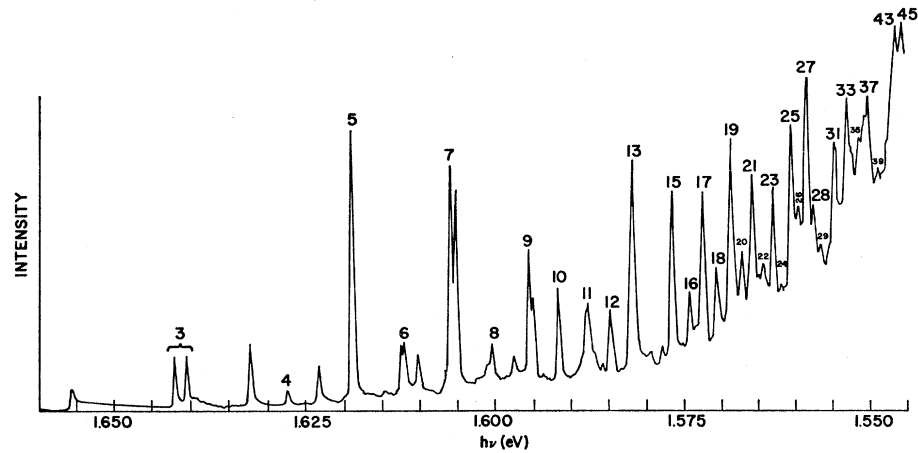
of an electron in the field of a "finite dipole." The energy $E_A''(R)$ for subsequent capture of the hole is not known exactly but is nearly equal to E_A since the hole state is only slightly perturbed by the tightly bound neutral donor while the latter is little influenced by the diffuse charge density of the hole. Thus for close-spaced pairs Eq. (1) becomes

$$h\nu(R) \approx E_g - E_D'(R) - E_A. \qquad (3)$$

As R becomes large, this equation approaches the same limit as Eq. (1), i.e., Eq. (2). For intermediate values of R, Eq. (3) provides a convenient and reasonable interpolation.

ANALYSIS OF THE SPECTRA

In Fig. 2 we compare the R dependence of the experimental energies with that predicted by Eq. (3) using $a_e = 4.28$ Å, $E_D = 0.154$ eV for the determination of $E_D'(R)$, and $E_g - E_D - E_A = 1.501$ eV as obtained from Eq. (2) for pairs of large separation. The agreement is seen to be excellent throughout the entire range $m > 3$.[11] The discrepancy at $m = 3$ is probably due to the failure of the assumption leading to Eq. (3) when $E_D'(R)$ becomes very small (although it may reflect a changing value of K at small R). Above the $m = 3$ doublet (discussed below), weak background emission rises toward higher energy and ends abruptly with a peak at 1.658 eV. In GaP such a high-energy limit is also observed approximately 30 meV below the band gap. If we assume that the highest-energy emission line in AlSb and the high-energy limit in GaP are due to excitons of similar binding energy, we conclude that the AlSb energy gap is $E_g \approx 1.69$ eV and hence that $E_D + E_A \approx 0.19$ eV. Since we have shown that $E_D \approx 0.15$, an acceptor energy of $E_A \approx 0.04$ eV is predicted.

[11] We have also found that a first-order perturbation-theory calculation of E_D' [including the correction for overlap of the donor wave function with the acceptor ion (Ref. 8), but neglecting distortion of the wave function] gives very good agreement with the exact values discussed in the text, if the Bohr radius is taken as $a_e = 6.2$ Å.

In GaP the ratio E_D/E_A is normally between 1 and 2, so that the assumption $E_A''(R) = E_A$ is not justified, and the data cannot be fit with Eq. (3). In this material, however, the band-gap and binding energies are sufficiently well known to permit a determination of $E_A''(R)$ experimentally with the help of Eq. (1). We find from the pair spectra of Zn-S pairs that the difference $E_A - E_A''(R)$ rises by about 14 meV between $m = 32$ and $m = 10$, but is nearly constant between $m = 32$ and $m = 55$.

ANALYSIS OF DOUBLETS

The occurrence of doublets in the lines for $m = 3, 6, 7$, and 9, as seen in Fig. 1, is a prominent feature of type-I spectra—those for which donors and acceptors lie on the same sublattice. This splitting occurs because the A sublattice does not have inversion symmetry about the donor or acceptor located on a B site. In contrast,
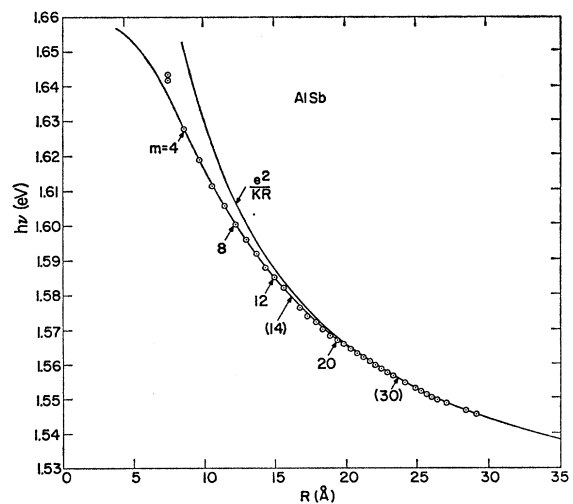

FIG. 2. The energies of the type-I lines plotted against pair separation in A. The experimental points follow Eq. (3)—solid curve—with $E_D = 0.154$ eV, $a_e = 4.28$ Å, and $E_g - E_D - E_A = 1.501$ eV.

TABLE I. Energy splittings in meV of type-I
pair spectra in Se-doped AlSb.

Pair shell m	Localization $\delta E_m/W_A$	Polarization $\delta E_m/S_A$	Experiment δE_m
3	0.06	1.00	1.60
6	0.03	0.73	0.53
7	0.01	0.35	0.76
9	0	0.11	~0.6
11	0	0.28	~0.3

the B sublattice on which the impurity ions lie has the full cubic symmetry. Thus an acceptor at a position R relative to a donor is not necessarily equivalent to the one at $-R$. The inequivalence occurs when all three of the Miller indices describing the D-A separation are nonzero. The splitting is expected to arise mainly from two contributions: (1) the concentration of the wave functions on the ion cores, and (2) the polarization of the individual ions which leads to localized changes in the dielectric constant. We examine the former effect first.

The contribution to E_D' made by the electronic charge concentrated on a given lattice site can be calculated if we know the complete (envelope-plus-core) wave function and hence the distribution of charge of the conduction electrons within each unit cell. We can approximate this distribution by assuming that all of the charge is concentrated at the lattice sites with the amount of charge at an A (or B) site given by the product of the square of an envelope wave function $F^2(r)$ at that point and a weighting factor W_A (or W_B). The latter equals the integral of the core wave function squared $|u(r)|^2$ over the appropriate half of the unit cell (of volume $\frac{1}{8}a^3$) and is normalized so that

$$W_A + W_B = 2 .$$

Since only the A (Al) sublattice, which lacks inversion symmetry about an impurity on a B (Sb) site, can make a contribution to the splitting, the effect is proportional to W_A.

The second, polarization, contribution to E_D' depends on the electrostatic field ε and the polarization produced by this field at the A (Al) lattice sites. It is proportional to the polarizability α_A of the A ions and hence to the atom refraction of the aluminum,

$$S_A = \tfrac{4}{3}\pi N_{Av}\alpha_A ,$$

where N_{Av} is Avogadro's number.

Both of the above effects—that proportional to W_A and that proportional to S_A—have been calculated and the results are shown in Table I.

When an isotropic hydrogenlike wave function is used for the envelope function $F(r)$, the contribution of the first (W_A) effect is found to be negligible. The second (S_A) effect gives agreement within about a factor of 2 for the first five doublets when the atom refraction is chosen to be $S_A = 2$. This is in reasonable agreement with the value $S \approx 3$ deduced for aluminum in Al_2O_3 (corundum) when the atom refraction of oxygen is subtracted.[12]

The neglect of the distortion of the electron wave function cannot properly be justified here and possibly accounts for the observed discrepancies. This distortion produces a concentration of the electron's charge on the side of the donor opposite to the acceptor which can make a significant contribution to the effect of localization. This correction is most important for tightly bound states for which the distorted wave function overlaps only the four nearest neighbors.

An interesting consequence of this analysis is that for donors and acceptors on the A sublattice the polarization effect should be proportional to S_B which, by comparison of the atom refractions of Sb in Sb_2O_3 with that of Al, is larger by a factor of 4.[12] Hence the splittings should be approximately four times as large.

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[12] The molar refraction of an ionic compound A_xB_y depends only on the dielectric constant and the unit-cell volume V and is equal to the sum of the atom refractions: $S = N_{Av}V(K-1)/(K+2) = xS_A + yS_B$. The additivity property does not hold in valence crystals where the bonding electrons are not localized near the ions. The values of the index of refraction $n = \sqrt{K}$ for the compounds of interest—1.768 for Al_2O_3 and 2.35 for Sb_2O_3—and the atom refraction of oxygen, $S = 1.5$, were taken from N. A. Lange, *Handbook of Chemistry* (Handbook Publishers, Sandusky, Ohio, 1949), 7th ed.