TWO-ELECTRON TRANSITIONS IN THE LUMINESCENCE OF EXCITONS BOUND TO NEUTRAL DONORS IN GALLIUM PHOSPHIDE

P. J. Dean*
Bell Telephone Laboratories, Murray Hill, New Jersey

and

J. D. Cuthbert
Bell Telephone Laboratories, Whippany, New Jersey

and

D. G. Thomas and R. T. Lynch
Bell Telephone Laboratories, Murray Hill, New Jersey
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We describe spectra in which excitons bound to neutral donors in gallium phosphide decay radiatively leaving the donor in an excited state. These two-electron transitions provide a convenient way of studying the donor energy levels and, together with the results of donor-acceptor pair spectra, have given many donor and acceptor binding energies in gallium phosphide.

In gallium phosphide, excitons, or hole-electron pairs, may bind to neutral donors such as sulfur, selenium, or tellurium to form molecularlike complexes. For sulfur the simple radiative decay of these complexes leads to a sharp zero-phonon line, S_0, at energy $(E_0)_S = 2.3095$ eV (4.2°).[1] This line has weak phonon replicas, the total strength of which is about 6% of that of S_0.[2] The sulfur-exciton complex decays predominantly (99.8%) by a nonradiative Auger mechanism[3] in which most of the recombination energy is given to the second electron, which is ejected deep into the conduction band. We report here a third partially radiative decay mechanism with a total efficiency comparable with or less than that of S_0,[3] in which a photon is emitted but the second electron is left in bound or continuum states of the donor. There result novel "two-electron" luminescence spectra with structure corresponding to the bound and continuum states of the donors.

The discrete two-electron luminescence lines are weak, and for them to be seen, crystals must be prepared in which other luminescence, particularly donor-acceptor pair radiation, and recombination at nitrogen atoms,[4] must be of very low intensity.

The association of the two-electron photoluminescence spectrum of sulfur, shown in Fig. 1(a), with the higher energy S_0 transition (not shown in the figure) is established because the two spectra always occur with the same relative strength, and measurements using pulsed electron-beam excitation show that they have the same radiative decay time (~25 nsec). Its association with transitions in which the donor is left in an excited state is made partly because of the great similarity between the spectrum in Fig. 1(a) and the photoexcitation spectra of donors in silicon.[5]

The differences between the donor binding energies of S, Se, and Te in GaP are accurately known from donor-acceptor pair spectra.[6] If, therefore, the energies of the different donor excited states measured from the ionization limit are nearly the same, as is known to be so for silicon,[7] the shift in energies of the two-electron spectrum lines with respect to the zero-phonon lines should be predictable. The energy separation between corresponding lines of the sulfur and selenium spectrum will approach the difference in their ionization limits given by

$$(\Delta E_{\mathrm{lim}})_{S-Se} = (E_0)_S - (E_0)_{Se} - \{(E_D)_S - (E_D)_{Se}\} \cdots, \quad (1)$$

where $(E_0)_S - (E_0)_{Se}$ is observed to be $+1.6 \pm 0.1$ meV. The pair spectra show that the difference between the donor binding energies $(E_D)_S - (E_D)_{Se}$ is $+1.4 \pm 0.3$ meV. Hence $(\Delta E_{\mathrm{lim}})_{S-Se}$ is 0.2 ± 0.3 meV, or essentially zero. Only the relatively strong lines are clearly seen in the spectrum from a selenium-doped crystal in Fig. 1(b), but, as expected from the identification with "two-electron" transitions,

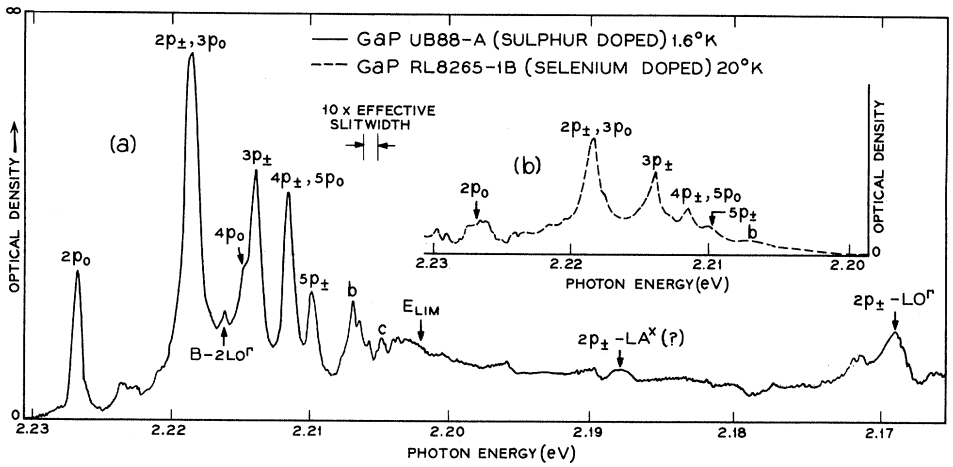

FIG. 1. (a) A "two-electron" photoluminescence spectrum associated with the decay of excitons bound to neutral sulfur donors in gallium phosphide. The lines above 2.205 eV and the continuum below this energy correspond to transitions in which the donor is either left in various excited states or in which the second (donor) electron is ejected into the conduction band. Weak phonon replicas are superimposed on this continuum. The weak component B-2LO$^{\Gamma}$ arises from the presence of nitrogen as a trace impurity. (b) A section of the two-electron photoluminescence spectrum associated with selenium donors in gallium phosphide. Only the discrete lines are shown since the continuum was obscured by an underlying donor-acceptor pair luminescence band. The discrete lines have been labeled in analogy with the photoexcitation spectra of donors in silicon (Ref. 5).

these coincide in energy (to within ~0.2 meV) with the corresponding lines of the sulfur spectrum. The intensity pattern of the two-electron spectra of sulfur and selenium are however quite different.

Figure 2 shows the "two-electron" spectrum derived from the Te donor and, in addition, the Te_0 line and its phonon replicas. Suitably doped Te crystals were hard to prepare, and these fast-time resolved spectra were obtained under high-energy electron-pulse excitation of the crystal. This technique emphasized the fast decaying "two-electron" spectrum and minimized the slow donor-acceptor pair transitions. Donor-acceptor pair spectra show that $(E_D)_S - (E_D)_{Te} = +14.8 \pm 0.2$ meV and this quantity should equal $(\Delta E_{lim})_{Te-S}$ since $(E_0)_S - (E_0)_{Te} = 0.0 \pm 0.1$ meV. Comparison of Figs. 1(a) and 2 shows that the energy separation $Te_{2P\pm} - S_{2P\pm}$ is, in fact, $+14.8 \pm 0.3$ meV. The excellent agreement between the expected and observed values provides strong evidence for the proposed mechanism of decay. The energy separations between the tellurium "two-electron" lines are very similar to those between corresponding lines in the sulfur and selenium two-electron spectra.

Figure 2 also shows that the sulfur and tellurium two-electron lines have comparable decay times.

Somewhat analogous transitions have previously been reported in SiC.[8] In contrast to the present case, only one line displaced from the main line by $\lesssim 5\%$ of E_D is observed for each

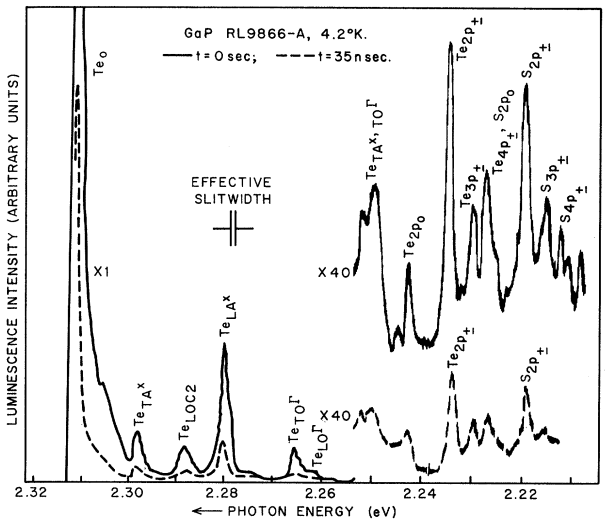

FIG. 2. Time-resolved luminescence spectra excited from a tellurium- and sulfur-doped crystal of gallium phosphide by 10-mA 30-nsec pulses of ~360-keV electrons. The full line and dashed spectra, respectively, were recorded during and 35 nsec after the excitation pulses. Above ~2.25 eV the luminescence is predominantly due to the no-phonon decay of excitons at neutral tellurium donors (Te_0) and the associated phonon replicas. The two-electron transitions at tellurium and sulfur donors appear below 2.25 eV. The notation is discussed in the text.

donor complex. These lines have been tentatively attributed to transitions in which the donor is left in a valley-orbit excited state derived from the $1s$-like hydrogenic ground state.

If the ionization limit E_{lim} of the two-electron spectra can be determined, the donor binding energy follows from the relation $E_D = E_0 - E_{\mathrm{lim}}$. In the absence of a complete theory for effective-masslike excited donor states in GaP and of detailed knowledge of the effective masses, $(E_{\mathrm{lim}})_S$ was determined by scaling the positions of the lowest energy resolved two-electron lines of Fig. 1(a) to the corresponding lines in the spectrum of donors in silicon.[5] The sulfur donor binding energy is thus found to be 107 ± 2 meV. This value, together with values of $E_A + E_D$ determined from pair spectra using a recently determined accurate value of the indirect energy gap,[9] enable other donor and acceptor binding energies to be determined with much greater precision than has hitherto been possible (Table I). These results are consistent with the generally less accurate Hall-effect values.[10]

The assignment of the two-electron lines proposed in Figs. 1 and 2 would be unexpected if p-like states in GaP really had odd parity. Thus, in the transitions, a p-like hole is annihilated by an electron and a photon is created, but, in addition, an electron is elevated from the ground state of the donor to a p-like excited state. However, parity is not a good quantum number here because GaP lacks a center of symmetry.[11]

It seems likely that two-electron spectra of the type discussed here should be seen in other semiconductors provided that they are not obscured by fluorescence from different centers or by normal phonon replicas of the original zero-phonon line. They provide a means of studying the excitation spectra of donors, and presumably also acceptors, that in many ways is easier than normal infrared absorption methods.

Table I. Ionization energies of various shallow donor and acceptor centers in gallium phosphide.

Donor (meV)		Acceptor (meV)	
Sulfur E_D	$= 107 \pm 2$	Silicon E_A	$= 46 \pm 2$
Selenium E_D	$= 105 \pm 2$	Zinc E_A	$= 62 \pm 2$
Tellurium E_D	$= 93 \pm 2$	Cadmium E_A	$= 95 \pm 2$

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*On leave of absence from Wheatstone Laboratory, King's College, Strand, London, England.

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[11]There is a similar nonconservation of parity in the longitudinal-optical (LO) and transverse-optical (TO) zone-center phonon replicas of the normal zero-phonon lines of S and Te. The evidence for this is that the TO-to-LO replica intensities are in the ratio 2.5 ± 0.3 to 1, close to the degeneracy ratio 2:1 for these phonons. Coupling, therefore, occurs through deformation potentials to the p-like zone-center phonons. Frequently in infrared-active crystals, coupling is dominantly to LO phonons by means of the long-wavelength electric field component of these phonons. The phonons involved here have long wavelengths, but are not zone-center phonons, and they have in fact s-like symmetry. An example of this type of coupling is provided by the "A line" in GaP, arising from an exciton bound to the isoelectronic trap nitrogen (Ref. 4).