for the terms associated with the two-center Coulomb integrals is the same for the nearly empty and the nearly full bands, positive for the nonmagnetic state, zero for the ferromagnetic state.

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PAIR SPECTRA IN GaP

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Recent reports of the fluorescence in GaP have described amazingly complicated spectra with at least 100 sharp lines near the band gap energy.[1-3] The present Letter reports three quite distinct types of spectra in which a total of about 300 lines have been counted, and shows that the vast majority of these lines arise from the recombination of electrons and holes which are trapped on distant donor-acceptor pairs. By the use of the intensity patterns of the spectra, particular lines may be identified with known donor-acceptor separations, and from their energy positions the sum of the isolated donor and acceptor binding energies is obtained. The observation of such lines should be useful in the chemical analysis of crystals and in the study of donor and acceptor wave functions.

The sharp lines considered here fall in the green, between 2.317 eV and about 2.2 eV at 1.6°K, and appear to be independent of other broad emission bands, one of which lies at 2.22 eV.[2,3] The lines have a half-width of about 3×10^{-4} eV and occur without phonon cooperation. All the crystals which display the spectra have been grown from Ga solutions. Type I spectra were obtained from "undoped" crystals, type II from crystals grown from a solution containing Zn (an acceptor), and type O from a run in which air entered the system. Type II spectra often include weak type I lines. The spectra do not depend strongly on the thermal history of the sample. The spectra were recorded photographically using a grating spectrograph giving a dispersion of 2 Å/mm.

Donor-acceptor pairs have been suggested as an explanation of different fluorescent effects in SiC- and ZnS-type phosphors.[4,5] It has been dif-

ficult to identify conclusively pair effects, chiefly because it has been believed that the important pairs are only very closely spaced pairs, or excited states of pairs with larger internuclear separations, and the precise conclusions which can be drawn from the experimentally observed broad bands are few.

Distant donor-acceptor pairs are, in comparison, simple. By considering a Born cycle the energy of an electron and a hole (i.e., the energy of fluorescence) on an isolated distant donor and acceptor separated by a distance r is

$$E(r) = E_{gap} - E_D - E_A + e^2/\epsilon r - (e^2/\epsilon)(a/r)^6 \cdots, \quad (1)$$

where E_D and E_A are the isolated donor and acceptor binding energies, ϵ the static dielectric constant, and a the effective van der Waals coefficient for the interaction between a neutral donor and a neutral acceptor. For an isolated pair [typically a pair separated by a distance less than r_0, where $r_0 =$ (donor or acceptor concentration)$^{-1/3}$] and a given type of donor and acceptor, the possible values of r are discretely distributed. A spectrum of discrete lines will result. [When the distance between donor and acceptor becomes small, there will also be angular dependencies of $E(r)$ for fixed $|r|$ which will be related to the donor and acceptor wave functions, and the spectrum will become more complex, but remain discrete.]

It is expected that the fluorescent intensity from isolated pairs at large separation r will be proportional to the number of pairs, N_r, at that distance multiplied by a smooth and fairly slowly varying function of r. This function is controlled by the

dependence of capture cross section and fluorescent efficiency on r. For separations less than r_0, the relative numbers of isolated pairs of separation r is proportional to the number of lattice positions with this separation, is independent of concentration, and is also proportional to a slowly varying function of r determined by the thermal history of the sample and the diffusivities of the donors and acceptors. The only rapidly varying number on which the intensity depends is N_r. Thus for comparing nearly adjacent lines, N_r should give a good description of the spectral intensity distribution.

There are four possible positions for donors and acceptors; two are substitutional and two interstitial. Any combination of donor-acceptor pairs among these sites will produce one of three possible geometries. Each one of these three geometries have different characteristic intensity patterns.

Figure 1(a) shows schematically the main experimental sharp fluorescent lines for type I crystals, after subtraction of broad background fluorescence. The heights of the vertical lines indicate the intensities of the fluorescence. The lines A, B, and C have been shown to be of an entirely different origin from the pair lines being discussed

here and will be treated elsewhere. The spectra are taken at $1.6°K$. It is important to compare theory with spectra taken at low temperatures because each pair has several low-lying states. These arise from (a) the strain around a pair splitting the valence band, (b) valley-orbit effects, and (c) electron-hole spin-spin interactions. The patterns in the spectra become clear only when the temperature is sufficiently low that fluorescence has to take place from the lowest states as a result of thermalization effects. For simplicity, some of the lower energy, very closely spaced multiplets have been combined in the figure (these multiplets result from crystallographically inequivalent pairs with the same separation). Above the experimental results, lines have been drawn which indicate the calculated N_r values. The N_r values were calculated on the assumption that the donor and acceptor were both on gallium sites (for instance, Si and Zn), or both on phosphorus sites (for instance, S and C), the relative geometry therefore being fcc. For this geometry r has the values $(\frac{1}{2}m)^{1/2}a_0$, where a_0 is the lattice constant and m is an integer. The values $m = 1, 2, \cdots,$ $12, 13, 15, 16, \cdots$ actually occur. But there are no atoms for shells with m equal to 14, and also 30, $46, 56, 62, \cdots$.[6] As $E(r)$ is a smooth function of r,
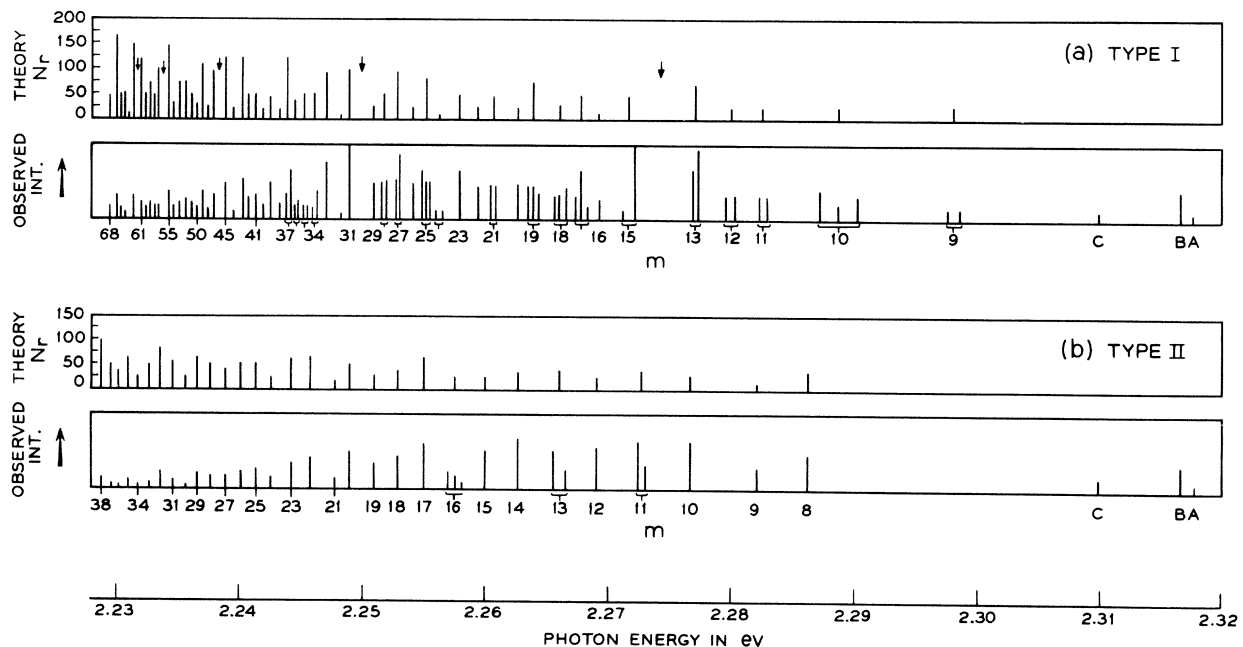

FIG. 1. A schematic drawing of the intensities and positions of the observed lines in type I and type II spectra at $1.6°K$, together with the corresponding N_r values. Multiplets in the observed spectra which all have the same m values have been bracketed together. For clarity, broad background fluorescence has been omitted, and also several lines occurring at lower energies. The arrows mark the missing lines for the type I spectrum.
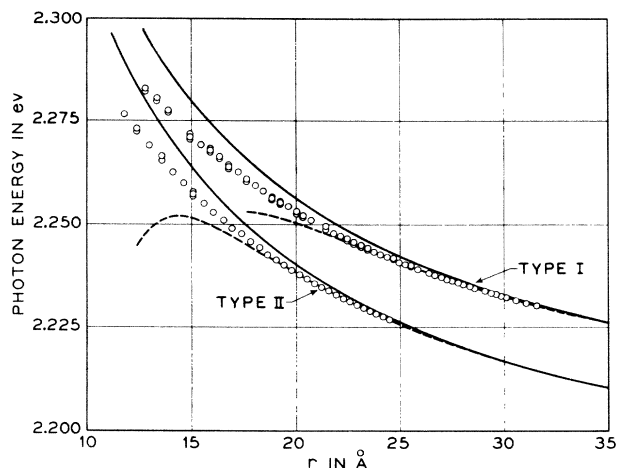
FIG. 2. The energy of the lines in type I and type II spectra plotted against the pair separation in Å. The solid lines follow Eq. (1) with $a = 0$; the dashed lines follow Eq. (1) with $a = 11.1$ Å for type I, and $a = 9.45$ Å for type II. The limiting values of $E(r)$ for $r = \infty$ are 2.18567 eV and 2.16960 eV for types I and II, respectively. Assuming a band gap of 2.325 eV,[3] we have $(E_A + E_D)$ equal to 0.140 eV and 0.155 eV for types I and II, respectively.

the absence of $m = 14$ will cause a gap in the spectrum. To facilitate counting, this situation is described as $N_\gamma = 0$ for the $m = 14$ multiplet. It is seen that there is an unambiguous match between theory and experiment, the latter values being modified by a slowly varying factor.

Figure 1(b) is analogous to Fig. 1(a), but for type II crystals. In this case the N_γ values which matched the experimental intensities were obtained from the geometry in which a donor is on one lattice site and the acceptor on another [for instance, S on a P site and Zn on a Ga site, or Si on both sites; the pattern could also arise from an interstitial atom surrounded by Ga (or P) atoms, and the other atom at a Ga (or P) site]. r now becomes $[(8m - 5)/16]^{1/2} a_0$. It should be noticed that the intensity pattern for this geometry is quite different from that for the fcc geometry. (The third type of donor-acceptor intensity pattern has not yet been seen.)

Figure 2 shows a comparison between observed line energies and the predictions of Eq. (1) for type I and type II crystals. A lattice constant of 5.45 Å

and a dielectric constant[7] of 10.18 have been used. The two spectra differ chiefly by an energy displacement. They can both be approximately described by Eq. (1) without the van der Waals term. However, the inclusion of a van der Waals radius, a [comparable to the radii of donors or acceptors of binding energy $\frac{1}{2}(E_D + E_A)$], provides a very precise fit to the data for the larger values of r.

The type O crystals show the A, B, and C lines and associated phonon effects, and several other miscellaneous sharp lines, but the pair spectra are quite absent. These might be crystals of high purity, or with no compensation, or with one or both of the impurities with an abnormally large binding energy, so that radiation occurs far from the band edge and will then probably be broadened by phonon effects. The observation of a sharp line spectrum out to pair separations of 30 Å seems possible only if the concentration of neutral centers is less than 5×10^{19}/cc, and the concentration of charged centers (during fluorescence) is less than 10^{16}/cc.

Prolonged annealing of the crystals at comparatively low temperatures should produce changes in the intensity ratios of the pair spectra, which will lead to information concerning low temperature diffusion and pairing phenomena.

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