Optical Properties of Cd-O and Zn-O Complexes in GaP†

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We report sharp line spectra, due to Cd and O impurities in GaP, which show that the red luminescence previously attributed to recombination between distant donor-acceptor pairs arises instead from nearest-neighbor Cd-O complexes. The binding energy of isolated O donors is thus shown to be ~1 eV. The energy levels and the optical selection rules for the complexes are found to be consistent with the C_{3v} symmetry of these centers. The spectra reveal three local phonon modes which we identify with the symmetric modes of vibration of the O atom and its four nearest neighbors. We show that the broad red emission band from Zn- and O-doped GaP is attributable to similar complexes having a strongly damped local vibrational mode.

ELECTRON–HOLE recombination in Zn- or Cd-doped GaP containing O has been shown to produce efficient broad-band luminescence in the red region of the spectrum.[1–3] This emission has been attributed to acceptor-oxygen pair recombination[1–3] in analogy with the green pair spectra also observed in GaP.[4] The line shape has been interpreted in terms of the coupling of the deep O donor state with local vibrational modes in the crystal.[5]

We report here low-temperature photoluminescence and excitation spectra from GaP crystals containing Cd and O which show sharp lines not attributable to distant pairs. These spectra indicate that the luminescence is produced by a Cd-O complex having a single (nearest-neighbor) interion separation. Studies of Zn- and O-doped material indicate that the red emission from these crystals is associated with similar Zn-O complexes, but that the spectra are broadened by a strongly damped local vibrational mode.

Cd-doped platelets were grown by cooling slowly from about 1100°C a GaP-saturated Ga solution containing 2.5 at.% Cd and 0.07 at.% O. The room-temperature hole concentration was 7×10^{16} cm^{-3} in a typical sample. The O concentration was estimated to be $\sim10^{17}$ cm^{-3}. In one experiment Ga_2O_3 enriched to 76% O^{18} was used. Photoemission in the green consisted largely of Cd-shallow donor pair spectra.

Figure 1 shows typical red emission and excitation spectra. Both the excitation spectrum and the emission spectrum at 10°K, which we refer to as "A" spectra, consist of a zero-phonon line A at 1.907 eV and phonon replicas of A involving local and lattice phonon modes. Gershenzon *et al.*[1,3] have established that the red emission in Cd-O doped GaP involves both Cd and O impurities, in agreement with our findings. However, the sharp line spectra of Fig. 1 are inconsistent with the proposed pair model and thus force us to conclude that the Cd and O occur in a complex at a *single* interimpurity distance, presumably as nearest neighbors. Such complexes involving close-spaced ion pairs are energetically favored, as discussed by Prener and Williams,[6] and can bind electron-hole pairs if one of the states is deep and highly localized. We shall summarize our experimental results and then interpret them in terms of this model.

In the A emission spectrum ($T=10$°K) of Fig. 1, four discrete phonons are evident. These are a sharp 50.1-meV phonon corresponding to the longitudinal optic (LO) mode energy near the zone center, a sharp 48.5-meV local mode X_3, and a diffuse 24.5-meV local mode X_2. Throughout, the 7.2-meV local mode X_1 converts each line into a series of lines which reaches a maximum at the third or fourth replica. In excitation, however, only the LO lattice phonon appears at the same energy, while the three others appear at new energies, thus confirming that they are local modes. These energies are X_1' at 7.4 meV, X_2' at 9.0 meV, and X_3' at 37 meV.

As the temperature is reduced below 4°K, the intensity of A decreases in emission as $\exp(-\delta E/kT)$ with $\delta E\approx2$ meV and is replaced by a weak zero-phonon line B and its phonon replicas, the B spectrum. Line B is found to lie 2.3 meV below line A. Both no-phonon lines appear with a halfwidth of 0.75 meV. However, this was found to be at the resolution limit of the spectrometer. The spectra are found to be independent of the polarization of both the emitted and exciting light.

Our results confirm that the oxygen donor in GaP occurs substitutionally on a P site and binds an electron in a deep state. (Note the discussion of the low-energy mode X_1 below.) Consequently, in p-type material the O^+ and Cd^- ions form complexes in which the latter occupy Ga sites adjacent to the former. The energy of the associated donor state relative to the isolated one is raised by

$$E_c=e^2/KR_1\approx0.7\text{ eV},$$

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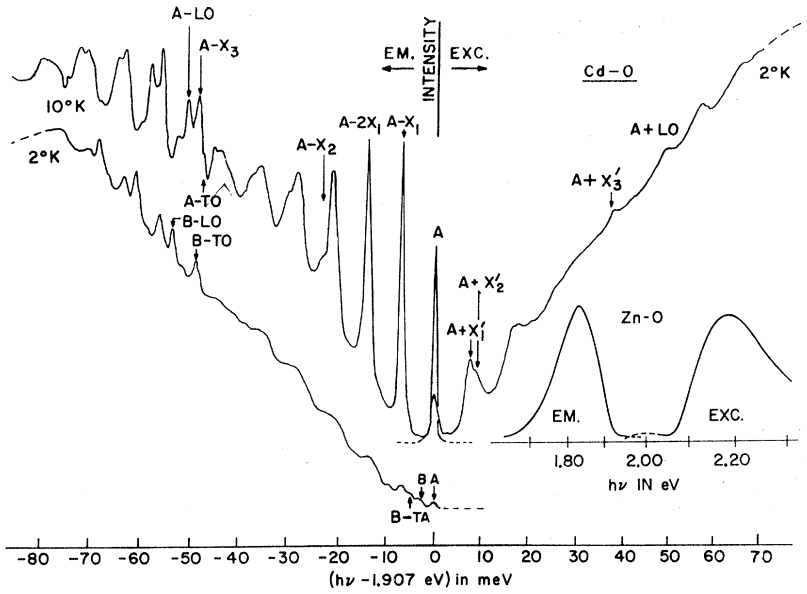

FIG. 1. A typical set of emission (em.) and excitation (exc.) spectra from a Cd-O-doped GaP crystal. The excitation spectrum represents the intensity of red luminescence as a function of the exciting photon energy and is temperature-independent for $T \lesssim 20$°K. This and the emission spectrum at 10°K consist of a zero-phonon line A and its phonon replicas. Both lattice (LO and TO) and local (X_1, X_2, and X_3) modes appear. At the lower temperature in emission the no-phonon line B and its lattice phonon replicas replace the A spectrum. The insert on the right shows a similar set of spectra from a Zn-O-doped crystal at 10°K.

based on a value of the optical dielectric constant of $K=8.46$ and an unperturbed nearest-neighbor distance of $R_1=2.36$ Å. The Cd acceptor state, being shallow, is not appreciably perturbed by the neutral oxygen and lies approximately 95 meV above the valence band edge.[7] Combining these energies with a band gap of 2.338 eV[8] and the no-phonon transition energy of $h\nu=1.907$ eV places the energy of an electron bound to a Cd-O pair at $E_D=336$ meV below the (100) conduction-band minima and the energy of the isolated oxygen level near midgap about 1 eV from the conduction-band minima.

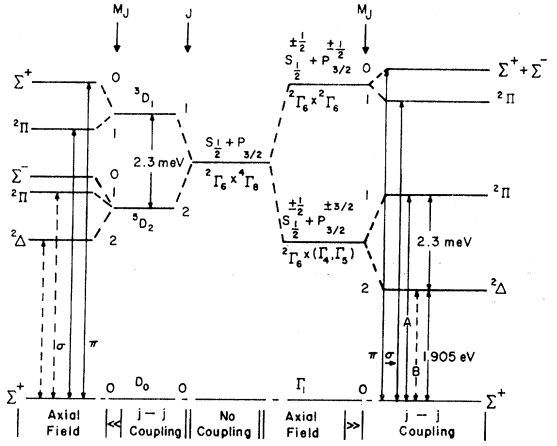

FIG. 2. Energy levels of an exciton in axial symmetry for the two cases: $\delta E_{j-j} \gg \delta E_{Ax}$ (left side) and $\delta E_{j-j} \ll \delta E_{Ax}$ (right side) (see *note added in proof*). The coupling scheme is indicated at the bottom of the figure. The uncoupled electron $S_{1/2}{}^{me}$ and hole $P_{3/2}{}^{mh}$ states which produce the levels are indicated together with the corresponding irreducible representations of the appropriate crystal-field groups. Total angular-momentum values J and their components M_J along the symmetry axis are given where they are defined. The resulting states on the far right and left resemble states of a diatomic molecule and are labeled similarly. Superscripts to the left of a symbol are used to denote the degeneracy of all but nondegenerate states. Strong allowed dipole transitions with the ground state are marked by solid vertical lines, while dashed lines indicate those transitions which are allowed by virtue of the perturbing fields. The polarization of the emitted photons relative to the symmetry axis is indicated by π or σ adjacent to the lines.

The above model is consistent with the anomalous pressure dependence of the red emission in Zn-O-doped GaP reported by Zallen and Paul,[9] and with the annealing effects reported by Logan *et al.* in GaP diodes.[10] In addition, the infrared emission at about 1.4 eV,[5] which often accompanies the red emission, could arise from a similar complex involving an acceptor on a second nearest-neighbor site. The shift to lower energy is consistent with the increased ion spacing.

The excited states of the nearest-neighbor Cd-O complex resemble other bound exciton states involving one electron and one hole[11] except for the lowered (C_{3v}) symmetry of the center.[12] Thus the electron occurs in an S-like state of spin $\frac{1}{2}$ and the hole in a $P_{3/2}$ state. In the energy-level diagram, Fig. 2, we classify the degenerate electronic states according to their total angular momentum J and the irreducible representa-

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[12] A similar analysis of pairs in SiC has been given by L. Patrick, Phys. Rev. **117**, 1439 (1960).

tions of the appropriate point groups.[13,14] Transitions between the $J=1$ state and the $J=0$ ground state produce the A spectra. Transitions from the slightly lower $J=2$ states to the ground state produce the B spectrum. The A-B splitting of 2.3 meV is consistent with the thermal depopulation of the higher state at low temperatures. The phonon energies are characteristic of the ground state in emission and of the excited state in absorption. [*Note added in proof.* The model originally proposed (shown on the left side of Fig. 2) depicts the case $\delta E_{j-j} \gg \delta E_{Ax}$, where δE_{j-j} (2.3 meV) is the separation of the $J=1$ and the $J=2$ exciton states and δE_{Ax} is the splitting in the axial crystal field between the $m_j=\pm\frac{1}{2}$ and $\pm\frac{3}{2}$ levels of the $P_{3/2}$ hole state. Its use was prompted by an estimate of the magnitude of the axial Stark field acting on the hole. The Zeeman splitting of the A and B lines into doublets reported by C. H. Henry, P. J. Dean, and J. D. Cuthbert [following paper, Phys. Rev. **166**, 754 (1968)] indicate that the opposite case—$\delta E_{j-j} \ll \delta E_{Ax}$—applies. (The large axial splitting is presumably produced by the distortion of the lattice near the acceptor.) This model, as proposed by Henry *et al.*, has been added on the right side of Fig. 2 with the symmetries of the levels and the transitions between them indicated. The resulting states on both sides of the figure are labeled according to their M_J values using the notation of molecular spectra [see G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., New York, 1950), 2nd ed.]. On both sides of the wave functions transform as the spherical harmonics $Y_J^{\pm M}$ except that on the right the $^2\Pi$ states are mixtures of the $Y_1^{\pm 1}$ and the $Y_2^{\pm 1}$ harmonics. Note that the weakness of the B transition (dashed in the figure) requires that the trigonal part of the crystal field be very small. We wish to thank C. H. Henry and P. J. Dean for sending us a preprint of their paper reporting the Zeeman studies.] Dipole transitions from the $^2\Delta$ level to the ground state are forbidden and appear mainly with phonon cooperation as observed at the lowest temperatures. Both acoustical and optical phonons appear. The active phonons in the B spectrum may belong to any Λ (or Γ) type representation except the symmetric Λ_1 (or Γ_1). The phonon spectrum of A thus differs from that of B by the appearance in A of Λ_1 phonons. The cubic symmetry and effects of transitions between the excited states produce complete depolarization of the emitted light.

In the excitation spectra of Fig. 1 only allowed transitions between the $J=0$ ground state and the $J=1$ excited state appear strongly. The phonon spectrum, which is characteristic of the latter, reveals that the local modes differ in energy from those of the ground state. These energy differences reflect changes in the stiffness coefficients of the oscillators between the neutral excited state and the ionized ground state and account for the appearance of a 0.6-meV isotope shift of line A toward higher energy when O^{18} replaces O^{16}. By assuming that the zero-point mode energies depend on only the O mass, we deduce from this shift a lower limit of 20 meV for the total energy change of the participating modes, in agreement with the experimental value of 27 meV.

The local phonons X_2 and X_3 appear only in the A spectrum, while the X_1 mode produces replicas of more fundamental lines in all spectra, but does not reduce the forbiddenness of any of the transitions. Hence we assign all three to the symmetric (Λ_1) representation of the C_{3v} group. The data can be interpreted qualitatively in terms of the three symmetric modes of a 5-atom molecule[15] if the decrease in the stiffness coefficients k_i with increasing bond length is considered. In this model, X_1 consists of a breathing type mode involving mainly the heavy Ga and Cd ions, while X_2 and X_3 are dominated by motion of the O relative to the Cd. The value of k_i required for the Ga-O bond is about 10% of the normal GaP lattice value and thus provides confirmation that O replaces a larger (P) ion. In the ionized (ground) state the displacement of the O^+ ion toward the Cd^- ion increases k_i for the Cd-O bond and raises the energies of the modes X_2 and X_3, while the lengthened Ga-O bonds cause a slight reduction in the X_1 mode energy.

Although the local modes have energies lying within the lattice phonon bands, the spectra show that all but X_2 are sufficiently weakly coupled to the lattice to remain relatively sharp. For other deep centers, the local modes may be strongly coupled to the lattice and cause the emission to appear in broad bands with little or no structure. This is found to be the case in Zn-O-doped GaP.

Emission and excitation spectra of a Zn-O-doped sample are shown in the insert in Fig. 1. The absence of the phonon structure, so prominent in Cd-doped material, suggests that at least one of the local modes is strongly coupled to the lattice. The weakness of both emission and absorption in the middle 100-meV (no-phonon) region indicates that for one mode of energy near 50 meV the overlap of the zero-point vibrational wave functions in the ground and excited states is negligible. With these two changes the model developed above for the Cd-O spectra also explains the Zn-O spectra.

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