Electron-Capture ("Internal") Luminescence from the Oxygen Donor in Gallium Phosphide

P. J. DEAN AND C. H. HENRY

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 2 July 1968)

We report the infrared radiative capture of electrons at ionized oxygen donors in gallium phosphide. The radiative transition occurs between a shallow excited state (ionization energy 51.5 ± 2 meV) and the deep $1s(A_1)$ ground state (ionization energy 893 ± 2 meV) of the donor. The uniaxial stress dependence of this transition suggests that the excited state is the doublet $1s(E)$. The luminescence is predominantly due to phonon-assisted transitions. Appreciable fine structure has been resolved in the vibronic sideband. Some of this structure involves phonons characteristic of pure gallium phosphide, but strong replicas associated with in-band-resonance modes of the oxygen impurity atom are also seen. The energies of the local modes are appreciably reduced when O^{16} is replaced by O^{18}. In addition, the no-phonon transition energy decreases slightly by an amount anticipated from the no-phonon shift of donor-acceptor pair spectra involving the oxygen donor. The oxygen electron-capture luminescence is quenched in crystals containing $\gtrsim 5\times10^{15}$ cm^{-3} neutral acceptors and does not saturate as rapidly as the donor-acceptor pair luminescence. Two Auger transitions are suggested to account for these properties. Weak absorption lines due to no-phonon and phonon-assisted interbound-state excitations within the oxygen donor have been detected through measurements of the excitation spectrum of the oxygen luminescence in n-type crystals. A tentative assignment of the principal no-phonon absorption lines is given.

I. INTRODUCTION

THE ionization energy of the deep donor oxygen in gallium phosphide has recently been determined from an analysis of the many sharp near infrared ($\sim$1.4 → 1.6 eV) luminescence lines due to no-phonon radiative recombination between electrons bound to oxygen donors and holes bound to shallow acceptors.[1] The resulting value for the ionization energy of the oxygen donor was 893 ± 2 meV. This ionization energy is some 18 times larger than the effective-mass binding energy of donors in gallium phosphide.[2] Deviations from predictions of the effective-mass theory of the energy states of donors in semiconductors are anticipated to be very large only for states with even envelope functions, which have an antinode in the central cell containing the substitutional donor impurity.[3] Interactions with the short-range components of the donor impurity potential are responsible for the deviations (central cell corrections) from the predictions of the effective-mass theory. This theory assumes a simple Coulomb interaction potential screened by the polarization of the lattice due to the charged impurity ion, calculated assuming the lattice to be a dielectric continuum. The central cell correction, or chemical shift, is largest for the state with the greatest proportion of its wave function within the central lattice cell occupied by the impurity atom, namely, for the ground state with $1s$ envelope function on the hydrogenic approximation to the donor ionization energy.

Kohn and Luttinger[4] have shown that the N-fold degeneracy of each effective-mass donor state due to the existence of N equivalent conduction band minima[5] is lifted by central cell effects which produce the so-called valley-orbit interaction. The N-fold degenerate (neglecting spin) levels are split by this interaction into a number of states whose irreducible degeneracy may be predicted from group theory.[3] Thus the $1s$-like donor ground state in gallium phosphide is expected to split into a symmetric singlet (A_1) state which possesses the full tetrahedral symmetry of the donor site and a doublet (E) state, assuming that $N=3$. Experience with a number of shallow donors in germanium[6] and silicon[7,8] has shown that only the symmetric singlet state is strongly perturbed by the valley-orbit interaction. The remaining degenerate components of the $1s$-like donor ground state lie relatively close to the energy of the donor ground state calculated from the simple effective-mass theory. This is also true even for very deep donors such as those due to bismuth,[9]

[1] P. J. Dean, C. H. Henry, and C. J. Frosch, Phys. Rev. **168**, 812 (1968).

[2] We assume that $(E_D)_{EM}=39\pm1$ meV in gallium phosphide, which corresponds to present best estimates of the effective masses m_l and m_t in the $\langle100\rangle$-type conduction band minima according to a reanalysis of the "two-electron" spectra reported by P. J. Dean, J. D. Cuthbert, D. G. Thomas, and R. T. Lynch [Phys. Rev. Letters **18**, 122 (1967)] and the Faraday rotation electron effective mass of 0.35 ± 0.02 reported by T. S. Moss, A. K. Walton, and B. Ellis [in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962* (The Institute of Physics and The Physical Society, London, 1962), p. 295]—R. A. Faulkner (private communication).

[3] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 257.

[4] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1957).

[5] We assume that $N=3$ for gallium phosphide in the notation used in the present paper. The possible location of the absolute band extrema *within* the zone can be ignored for the present purposes provided that these minima lie below the conduction band at X_1 by an energy small compared with the ionization energies of the bound states considered. This assumption is certainly valid for the deep oxygen donor.

[6] J. H. Reuszer and P. Fisher, Phys. Rev. **135**, A1125 (1964).

[7] F. P. Ottensmeyer, J. C. Giles, and J. W. Bichard, Can. J. Phys. **42**, 1826 (1964).

[8] R. L. Aggarwal and A. K. Ramdas, Phys. Rev. **140**, A1246 (1965).

[9] H. J. Hrostowski and R. H. Kaiser, J. Phys. Chem. Solids **4**, 315 (1958).

magnesium,[10] and sulphur[11,12] in silicon. The s-like states with higher principal quantum number will also be split by the valley-orbit interaction, but the magnitude of this effect should be much less than for the $1s$ state.[4]

In view of the above discussion, we conclude that the $1s(A_1)$ ground state of the oxygen donor may lie $\sim$850 meV below the next lowest bound state if the effective-mass donor ground-state ionization energy is $\sim$40 meV in gallium phosphide.[2] Thus an energy equivalent to $\sim$17 zone center optical phonons, energy $\hbar\omega_{OPT}$, of the gallium phosphide lattice must be liberated in the final stage of electron capture by the ionized donor. The probability of this multiphonon transition should be negligible compared with the radiative transition probability.[13] These considerations suggest that the luminescence from this final stage in the electron-capture (EC) process should be efficient, unlike the initial stages which involve the liberation of amounts of energy small compared with $\hbar\omega_{OPT}$ between high-lying effective–mass-like donor bound states. The initial stage of electron capture by the deep oxygen donor in gallium phosphide is presumably describable by the cascade capture theory due to Lax.[14]

These expectations have been fulfilled. The present paper describes the near infrared luminescence spectrum due to electron transitions between a shallow excited state and the deep ground state of the oxygen donor in gallium phosphide. The no-phonon line of this spectrum occurs at 0.8414 eV. Sharp, but weak, absorption lines lying slightly to higher energy have been observed in the photoexcitation spectrum of this luminesence. Tentative identifications of the transitions responsible for the principal absorption lines have been made.

II. CRYSTAL PREPARATION

The majority of the gallium phosphide crystals used in these experiments were regrown from gallium solution in sealed fused silica capsules.[15] Oxygen was usually added as Ga_2O_3, although the isotope O^{18} was added as O_2 gas in the capsule void space which was otherwise evacuated. The crystals were sometimes also doped with the acceptor zinc and the donor tellurium through the addition of these metallic elements to the gallium solution. Some crystals were also grown

[10] R. K. Franks and J. B. Robertson, Solid State Commun. **5**, 479 (1967).

[11] W. E. Krag and H. J. Zeiger, Phys. Rev. Letters **8**, 485 (1962).

[12] W. E. Krag, W. H. Kleiner, H. J. Zeiger, and S. Fishler, Phys. Soc. Japan Suppl. **21**, 230 (1966).

[13] Recent measurements on the luminescence of rare-earth ions show that multiphonon radiationless transition rates of $\gtrsim 10^5$ sec^{-1} are obtained between electronic states which can be connected by a transition involving the simultaneous emission of $\lesssim 4$ optical phonons—L. A. Riseberg and H. W. Moos, Phys. Rev. Letters **19**, 1423 (1967).

[14] M. Lax, Phys. Rev. **119**, 1502 (1960).

[15] C. J. Frosch and L. Derick, J. Electrochem. Soc. **108**, 251 (1961).

with especially low concentrations of unwanted impurities such as carbon, silicon, and sulphur using open tube furnace systems designed by Frosch.[16]

III. EXPERIMENTAL

The optical spectra reported in this paper were measured with the freely suspended crystals immersed in liquid helium, often pumped below the λ point. The luminescence was excited by 4880 or 5145 Å light from an Ar$^+$ laser. The luminescence was analyzed by a Perkin-Elmer Model 112 spectrometer equipped with a Bausch and Lomb 600 line/mm grating and a cooled lead-sulphide photodetector. A Corning 7.57 filter was often used at the entrance slit of the monochromator to absorb the green and near-infrared donor-acceptor pair luminescence which could be recorded, respectively, in third or second order within the spectral range of the oxygen-capture luminescence.

Photoexcitation spectra for the oxygen-capture luminescence were recorded by passing light from a 625-W tungsten-iodine lamp through the Perkin-Elmer monochromator and focusing it onto the crystals in the helium immersion Dewar through a Corning 7.57 filter. The resulting luminescence was collimated by a wide aperture lens and passed at normal incidence through a bandpass interference filter possessing strong absorption at the no-phonon line of the luminescence spectrum, but a rapidly increasing transmission at lower energies. The exciting radiation transmitted by the crystal was absorbed by this filter, but an appreciable proportion of the lower-energy oxygen luminescence was transmitted and was focused onto the $\sim$1$\times$5-mm sensitive area of the lead-sulphide photodetector by a second lens of small focal length.

IV. RESULTS AND DISCUSSION

A. Luminescence of Oxygen Donors in Gallium Phosphide

1. Luminescence Spectrum

The luminescence spectrum shown in Fig. 1 was observed from all the gallium phosphide crystals which were studied, but was particularly strong for crystals deliberately doped with oxygen and in the absence of significant concentrations of shallow donors and acceptors (Sec. IV A 4). The spectrum contains a weak but sharp no-phonon line O_0 at $\sim$0.841 eV, together with a relatively strong vibronic sideband. Strong phonon cooperation is anticipated for a transition into the tightly bound ground electronic state of the oxygen donor. The phonon spectrum in Fig. 1 is appreciably different from that observed in the infrared pair spectra involving the oxygen donor,[1] where only two broad phonon replicas were resolved, displaced $\sim$19.5 and $\sim$47.0 meV below the no-phonon distant pair peak.

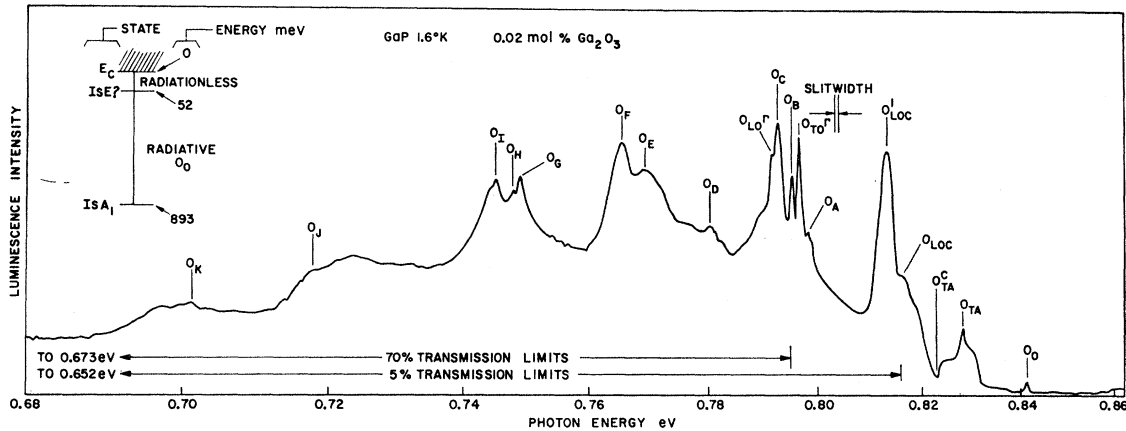[16] P. J. Dean, C. J. Frosch, and C. H. Henry, J. Appl. Phys. **39**, 5631 (1968).

FIG. 1. Infrared photoluminescence due to the radiative capture of electrons by deep oxygen donors in gallium phosphide. The transition occurs from a shallow excited state to the deep ground state, as indicated in the inset. The no-phonon line is O_0. The strong components due to phonon-assisted transitions are labeled according to the nature of the phonon, where known, or by subscript letters in sequence of increasing energy (see Table I). The transmission limits indicated are for the band-pass filter used for the luminescence excitation measurements described in Sec. IVB.

Much more detail is apparent in Fig. 1. This may be because the no-phonon line O_0 is very narrow ($\lesssim 0.7$ meV in the best crystals) compared with the no-phonon donor-acceptor (DA) pair peak, even for distant pairs recorded at very low excitation intensities.

Table I contains a tentative assignment of some of the phonons from Fig. 1, based upon a comparison with the phonon dispersion curves of the gallium phosphide lattice and anticipating the results of the isotopic substitution experiment discussed in Sec. IV A 2. There are some striking similarities between Fig. 1 and the luminescence spectrum of excitons bound to nitrogen isoelectronic substituents in gallium phosphide[17] (see Fig. 1 of Ref. 17). For example, the component O_{TA} has a very similar shape in both spectra. This shape will be shown elsewhere to result from a weighted density of states distribution of transverse acoustical phonons in the gallium phosphide lattice.[18] The cutoff

TABLE I. Energies and possible identification of phonons in the luminescence spectrum of oxygen donors in gallium phosphide.

Component	Phonon energy (meV)	Identification	Component	Phonon energy (meV)	Identification[a]
O_{TA}	13.1	$\hbar\omega_{TA}$	O_D	60.5	$\hbar\omega_{TA}+\hbar\omega_0$
$O_{TA}{}^c$	18.0	$(\hbar\omega_{TA})_{cutoff}$	O_E	71.8	$\hbar\omega_{loc}+\hbar\omega_0$
O_{loc}	24.7	$\hbar\omega_{loc}$	O_F	75.8	$\hbar\omega_{loc}'+\hbar\omega_0$
O_{loc}'	28.4	$\hbar\omega_{loc}'$	O_G	92.4	$\hbar\omega_{TO}{}^\Gamma+\hbar\omega_0$
O_A	43.0	$\hbar\omega_A$	O_H	93.6	$\hbar\omega_B+\hbar\omega_0$
$O_{TO}{}^\Gamma$	44.8	$\sim\hbar\omega_{TO}{}^\Gamma$	O_I	96.3	$\hbar\omega_C+\hbar\omega_0$
O_B	46.1	$\hbar\omega_B$	O_J	123.5	$\hbar\omega_{loc}'+2\hbar\omega_0$
O_C	48.7	$\hbar\omega_C$	O_K	140.1	$\hbar\omega_{TO}{}^\Gamma+2\hbar\omega_0$
$O_{LO}{}^\Gamma$	49.8	$\hbar\omega_{LO}{}^\Gamma$			

[a] The multiphonon replicas are all consistent with the emission of one or more ~47.5 meV phonons $\hbar\omega_0$ in addition to the phonons listed in cloumn 3.

[17] D. G. Thomas and J. J. Hopfield, Phys. Rev. 150, 680 (1966).

[18] J. L. Yarnell, J. L. Warren, R. G. Wenzel, and P. J. Dean, in Proceedings of the International Conference on the Inelastic Scattering of Neutrons, Copenhagen 1968 (unpublished).

of this component at $O_{TA}{}^c$ marks the maximum energy of TA lattice vibrations which occurs along the $\langle 110 \rangle$-type axes of the reduced zone. The TO^Γ and LO^Γ zone center phonons are prominent in both spectra, also the phonon of energy near 48.5 meV (O_C in Fig. 1). The 46.1 meV phonon O_B is not present in the nitrogen exciton spectrum, and the oxygen spectrum deviates considerably from the nitrogen exciton spectrum near the maximum in the longitudinal acoustical density of states distribution at ~ 30 meV because of the local modes O_{loc} and O_{loc}'. These similarities between the phonon structure in the oxygen and nitrogen spectra occur because electrons are bound by short-range forces to each of these impurity atoms.[19] The most significant difference between the spectra is the relatively large strength of the phonon cooperation in Fig. 1, due to the compact wave function of the electron tightly bound to the oxygen donor ($E_D \sim 0.89$ eV) compared with the electron bound to a nitrogen atom ($E_e \sim 0.01$ eV) in gallium phosphide and probably also to the fact that the no-phonon transition O_0 is largely forbidden (see Sec. IV A 3).

Table I also shows that the prominent features of the single-phonon sideband in Fig. 1 are replicated at lower energy by the emission of additional ~ 47.5-meV phonons (phonon components $O_D \rightarrow O_K$ in Fig. 1).

2. Spectral Shifts due to Isotopic Substitution $O^{16} \rightarrow O^{18}$

The excited state for the no-phonon transition O_0 lies at $\sim (E_D)_{\text{eff mass}}$, or ~ 50 meV,[20] below the conduction band (inset to Fig. 1). This is consistent with expectation for electron-capture luminescence by the deep oxygen donor according to Sec. I. The association of this spectrum with oxygen is also supported by the

[19] R. A. Faulkner, Phys. Rev. 175, 991 (1968).

[20] We assume that $(E_D)_0$ is 0.893 ± 0.002 eV as obtained from Ref. 1.
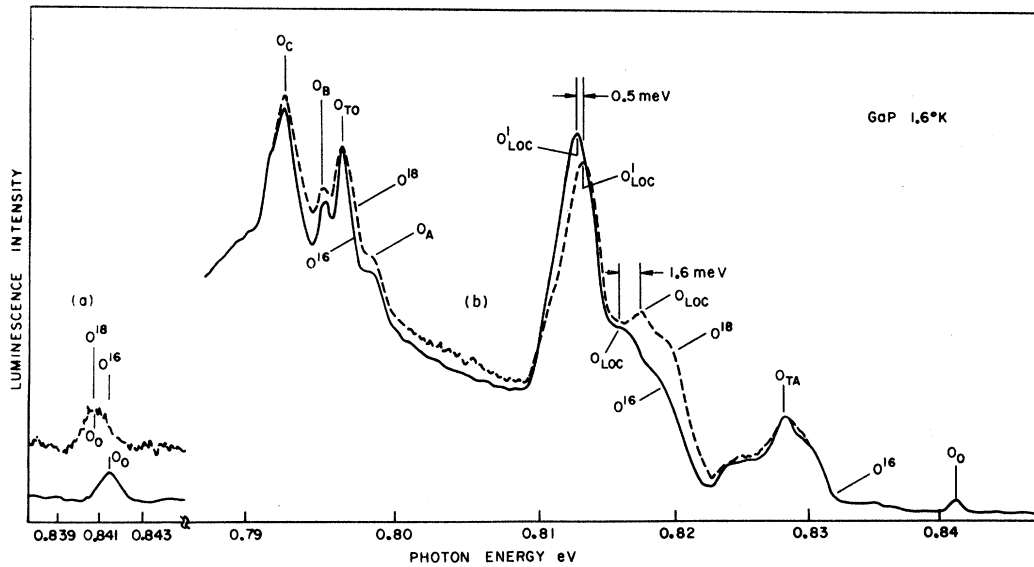
FIG. 2. Comparison between infrared photoluminescence spectra obtained from gallium phosphide doped with O^{16} and with O^{18}. (a) shows the shift to lower energy of the no-phonon line O_0 due to the isotopic substitution $O^{16} \rightarrow O^{18}$. In (b) the spectrum from O^{18}-doped gallium phosphide has been shifted relative to the indicated energy scale so as to superpose the no-phonon lines O_0. Comparison of the two spectra then reveals the changes in the energies of phonons associated with the vibronic structure caused by the isotopic substitution.

increase in strength of the infrared luminescence shown in Fig. 1 observed from crystals grown from gallium solution containing increasing amounts of Ga_2O_3.

Convincing proof that oxygen is indeed involved in these transitions has been obtained from a comparison of the infrared spectra of crystals deliberately doped with O^{18} with those from crystals containing only the natural isotope O^{16}. Figure 2(a) shows that the no-phonon line is displaced to *lower* energy by 0.67±0.05 meV when O^{16} is replaced by O^{18}. Each no-phonon line in the infrared DA pair spectra involving the deep oxygen donor shifts 0.71±0.02 meV to *higher* energy under the same conditions.[1] These two results are mutually consistent. According to the arguments of Morgan *et al.*, the isotope shift of the no-phonon lines arise if the vibrational frequencies associated with the oxygen donor change due to the electronic transition.[21] If we assume one set of frequencies ω_i when the electron is tightly bound in the $1s(A_1)$ state of the donor and another set $\omega_i + \Delta\omega_i$ when the electron is either removed from the oxygen atom (as in the final state of a DA pair recombination) or is in a loosely bound excited state such as $1s(E)$, then it can easily be shown that isotope shifts of the pair transitions and the oxygen EC transitions will be equal and opposite. If, when O^{16} is replaced by O^{18}, the mass associated with the ith mode changes by δM_i and if ω_i and $\omega_i + \Delta\omega_i$ are both proportional to $(M_i)^{-1/2}$, then the isotope shift of the no-phonon line in the EC spectrum will be

$$\Delta E = -\tfrac{1}{4}\hbar \sum_i \Delta\omega_i \frac{\delta M_i}{M^i}. \qquad (1)$$

[21] T. N. Morgan, B. Welber, and R. N. Bhargava, Phys. Rev. **166**, 751 (1968).

The isotope shift of the oxygen DA pair no-phonon lines will be $-\Delta E$.

Isotopically induced changes in the energies of some of the prominent phonon replicas were also observed when O^{16} was replaced by O^{18}. In Fig. 2(b) the spectrum from the O^{18}-doped crystal has been shifted by $\sim$0.7 meV to higher energy to make its no-phonon line coincident with that in the spectrum from the O^{16}-doped crystal. This procedure brings the O_{TA} phonon replica and the group of optical phonon replicas just above 0.79 eV into coincidence in the two spectra. The replicas between 0.81 and 0.82 eV clearly shift to higher transition energy (lower phonon energy) when O^{18} replaces O^{16} as expected if they involve vibrations in which much of the kinetic energy is due to motion of the oxygen atom. These phonon replicas are therefore labeled in Figs. 1 and 2 as involving localized modes. According to the expression

$$\Delta\omega_{loc} = -\tfrac{1}{2}\omega_{loc}\frac{\Delta M}{M}, \qquad (2)$$

where M is the mass of the oxygen atom, ΔM is the mass change in the isotopic substitution and ω_{loc} is the local mode frequency, the calculated energy shifts $\hbar\Delta\omega_{loc}$ for the 28.4 and 25.2 meV O_{loc}' and O_{loc} local mode replicas indicated in Fig. 2(b) are, respectively, -1.8 and -1.6 meV. The corresponding measured shifts are ~ -0.5 and ~ -1.6 meV. We therefore conclude that replica O_{loc} in the oxygen luminescence spectrum involves motion of the oxygen atom alone, unlike the more prominent phonon replica O_{loc}'.

No significant changes in the energies of individual phonon replicas were observed in the red luminescence

spectra due to electron-hole recombinations at nearest-neighbor DA pairs involving the oxygen donor,[22] or in the infrared luminescence spectra due to recombinations at remote pairs,[1] although shifts in the no-phonon lines were clearly observed in both of these spectra when O^{16} was replaced by O^{18}. Small shifts $\lesssim 1$ meV were not detectable in the broad components of the infrared pair spectra, however.

3. Effect of Uniaxial Stress on the Oxygen Capture Luminescence Spectrum

We have seen in Sec. I that the ground state of the luminescence transition at the oxygen donor should be a singlet $1s(A_1)$. From energy considerations alone, the excited state, which lies at about $(E_D)_{EM}$ below E_c (Fig. 1 inset), might be the upper component [doublet $1s(\Gamma)$] of the ground state split by the large valley-orbit interaction, or it might be the singlet $2s(A_1)$ level. It is unlikely to be a p state, since one would not expect such a state to lie below the s-like levels mentioned above, particularly for a very deep donor (Sec. I). It is clear that the observed luminescence must come from the lowest-lying excited state, which must lie below the adjacent excited state by an energy which is $\gg kT$ at 4.2° K. In addition, the absence of the transition O_0 in the absorption spectrum (Sec. IV B) strongly suggests that this transition is forbidden, i.e., that the excited state is s like.

The effect of uniaxial stress on the electronic transition can be used to determine whether the excited state is $1s(E)$ or $2s(A_1)$. The doublet $1s(E)$ level is split by a uniaxial stress oriented other than along $\langle 111 \rangle$-type axes of the crystal so as to lift the degeneracy of the three $\langle 100 \rangle$ conduction band valleys, whereas the singlet $1s(A_1)$ and $2s(A_1)$ levels are merely displaced without splitting under this perturbation.[23] In the present experiments, signal-to-noise limitations precluded unixial stress measurements other than at temperatures too low for the observation of luminescence from both components of the split excited state because of thermal depopulation of the upper state. Measurements could not be made on the sharp but very weak no-phonon components O_0, so the relatively broad but strong 28.4 (O_{loc}') and 48.7 meV (O_C) replicas were studied. Figure 3 shows that quantitatively similar results were obtained from both of these transitions. The transition energies decrease for both stress directions, but much more rapidly for $\langle 100 \rangle$ stress.

We suggest that the shift for $\langle 111 \rangle$ stress arises from the hydrostatic component of this stress deformation. The hydrostatic stress coefficient of the oxygen EC transition should be nearly equal to that of the ionization energy of the deep oxygen donor, since the shallow
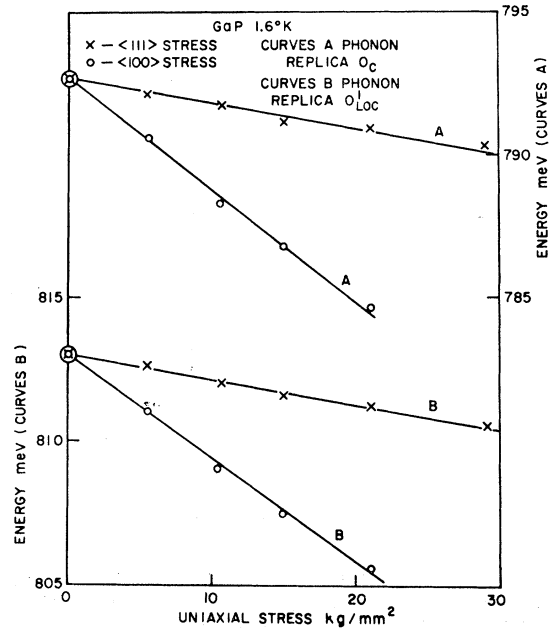
[22] C. H. Henry, P. J. Dean, D. G. Thomas, and J. J. Hopfield, in Localized Excitations in Solids, edited by R. F. Wallis (Plenum Press, Inc., New York, 1968), p. 267.
[23] D. K. Wilson and G. Feher, Phys. Rev. 124, 1068 (1961).

FIG. 3. The energy shifts in the prominent components O_c and O_{loc}' of the infrared photoluminescence spectra due to the radiative capture of electrons by deep oxygen donors in gallium phosphide induced by uniaxial stress aligned along $\langle 111 \rangle$ and $\langle 100 \rangle$ crystallographic axes.

excited state of the donor is composed from Bloch functions chosen close to the conduction band minima. Analogy with the behavior of deep donors in silicon[24] suggests that this coefficient may be approximately equal to the (negative) pressure coefficient of the $\Gamma_{15} \rightarrow X_1$ indirect energy gap. The coefficient dE/dX obtained from Fig. 3 is -0.9×10^{-6} eV cm^2 kg^{-1}, which implies that the hydrostatic stress coefficient of the indirect energy gap is $\sim -2.7 \times 10^{-6}$ eV cm^2 kg^{-1}. Direct measurements of this pressure coefficient[25] yield a somewhat lower value of $\sim -1.1 \times 10^{-6}$ eV cm^2 kg^{-1}, but significantly larger value of $-(4.5 \pm 1.5) \times 10^{-6}$ eV cm^2 kg^{-1} has been obtained from the uniaxial stress splitting of the thresholds in the intrinsic indirect absorption edge of gallium phosphide.[26] The reasonable agreement between these independently measured stress coefficients and the value obtained from the present measurements provides support for the suggested interpretation of the shift shown in Fig. 3 for $\langle 111 \rangle$ stress.

The large difference between the shift rates for $\langle 100 \rangle$ and $\langle 111 \rangle$ stress shown in Fig. 3 is believed due to a splitting under $\langle 100 \rangle$ stress of the excited state of the luminescence transition, which is thereby identified as $1s(E)$. Neglecting the effect of the hydrostatic component of the applied $\langle 100 \rangle$ uniaxial stress, the $1s(E)$ state should split approximately symmetrically relative to the unstressed state if the splitting is sufficiently

[24] M. I. Nathan and W. Paul, Phys. Rev. 128, 38 (1962).
[25] R. Zallen and W. Paul, Phys. Rev. 134, A1628 (1964).
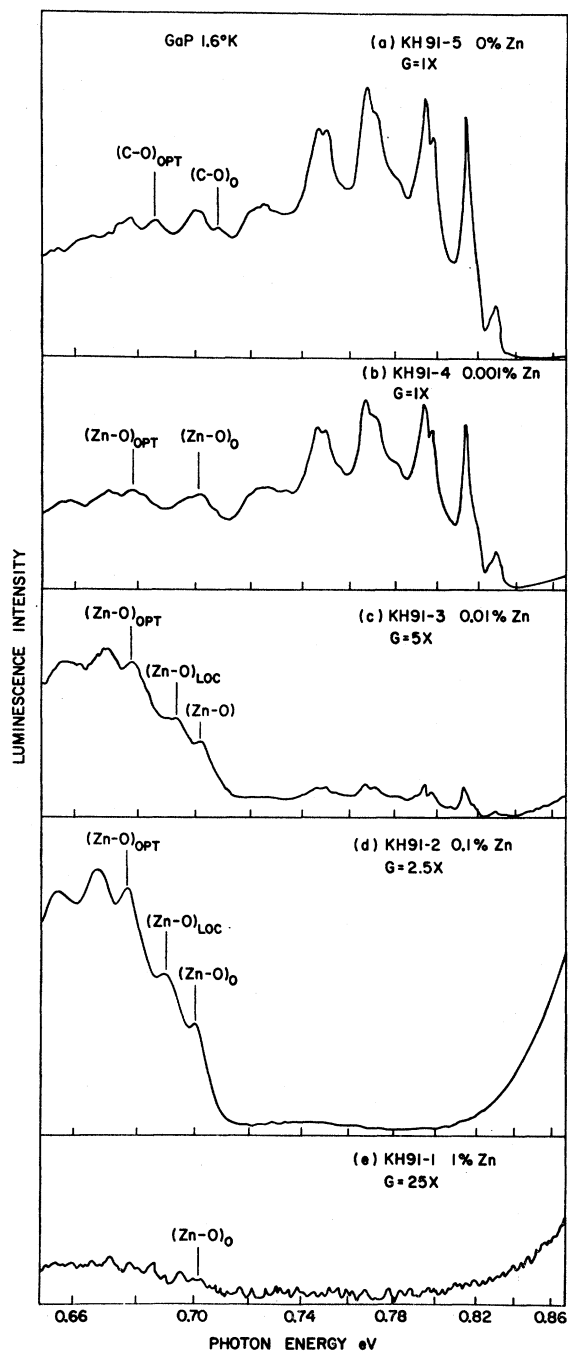[26] I. Balslev, J. Phys. Soc. Japan Suppl. 21, 101 (1966).

FIG. 4. Unsaturated infrared photoluminescence spectra from gallium phosphide grown from gallium solution containing 0.02 mole% Ga_2O_3 and the indicated at.% of zinc. Spectrum (a) is mainly due to the radiative capture of electrons by deep oxygen donors (see Fig. 1), but contains weak contributions below 0.71 eV due to electron-hole recombinations at oxygen-carbon DA pairs recorded in second order of the grating. Spectrum (b) is similar, except that the weak pair transitions are predominantly due to zinc acceptors and the low energy tail of the red luminescence characteristic of Zn,O-doped gallium phosphide appears (in second order) above 0.84 eV. Spectra (c) → (e) show that the EC luminescence becomes negligible compared with the infrared Zn-O pair and the red luminescence with increase in the concentration of zinc acceptors. All these luminescence processes

small that the mixing of the $1s(A_1)$ subcomponent of the excited state and the $1s(A_1)$ donor ground state is negligible.[23] This condition is easily justified for the oxygen donor in gallium phosphide because the stress-induced shifts are negligible compared with the $1s(A_1)$ → $1s(E)$ energy separation. According to Fig. 3, the stress coefficient for the splitting of the $1s(E)$ level[27] is $(5.7\pm0.7)\times10^{-6}$ eV cm² kg⁻¹. This coefficient should be $\frac{2}{3}$ of that for the splitting between the conduction band valleys for small ⟨100⟩ stress.[23] Thus the stress coefficient for the splitting of the ⟨100⟩ conduction band valleys is predicted to be ~$(8.5\pm1.0)\times10^{-6}$ eV cm² kg⁻¹, in good agreement with the ⟨100⟩ stress coefficient derived by Balslev[26] from piezo-optical measurements on the intrinsic absorption edge of gallium phosphide, $(8.6\pm0.8)\times10^{-6}$ eV cm² kg⁻¹. The compliance constants used by Balslev are significantly larger than those recently derived from accurate ultrasonic pulse velocity measurements on gallium phosphide.[28] Thus the magnitude of the deformation potential constant Ξ_u corresponding to a splitting coefficient of ~$(8.5\pm1.0)\times10^{-6}$ eV cm² kg⁻¹ is increased from 6.2 ± 0.6 to 6.8 ± 0.8 eV.

4. Quenching of Oxygen EC Luminescence by Shallow Neutral Donors and Acceptors

In p-type gallium phosphide crystals, all shallow (sulphur) and deep (oxygen) donors will be compensated at equilibrium. Some of the free electrons generated in the conduction band under interband photo-excitation will be captured by the deep unassociated oxygen donors, thereby producing the EC luminescence described in Sec. IV A 1. Holes will also be captured nonradiatively by shallow acceptors. Crystals grown from sealed silica capsules as described in Sec. II invariably contain significant but somewhat uncontrolled concentrations of the shallow acceptor carbon.[29] The electrons and holes bound to distant but interacting pairs of these neutralized donors and acceptors can recombine radiatively producing the near infrared DA pair luminescence associated with the deep oxygen donor.[1] Nonradiative recombination processes involving interactions between more than two neutral centers should be insignificant at neutral acceptor concentrations well below 10^{18} cm⁻³.[30] It was therefore

[27] The coefficient for the 28.4-meV replica was 5.4×10^{-6} eV cm² kg⁻¹ and for the 48.7-meV replica 6.1×10^{-6} eV cm² kg⁻¹.

[28] R. Weil and W. O. Groves, Bull. Am. Phys. Soc. 11, 764 (1966).

[29] The total concentration of carbon acceptors is typically ~10^{17} cm⁻³ in this type of material. Appreciable fluctuations in this concentration may occur, however, apparently due to inadvertent trapping of carbon-containingd ebris in the sealed silica tubes (see Ref. 16).

[30] J. C. Tsang, P. J. Dean, and P. T. Landsberg, Phys. Rev. 173, 814 (1968).

become inefficient at the highest zinc concentration (spectrum e). The relative gain of the recording system is denoted by G. According to Ref. 32 the concentrations of neutral zinc acceptors for spectra (b) → (e) should be, respectively, 1.5, 5, 15, and 50×10^{17} cm⁻³.

anticipated that, under low excitation intensities such that the infrared DA luminescence is unsaturated, the intensity of the oxygen EC luminescence should be proportional to that of the infrared DA luminescence.

This expectation was not realized. Figure 4 shows that the EC luminescence was stronger than the oxygen-carbon DA luminescence recorded in second order [Spectrum (a)] from a crystal deliberately doped only with Ga_2O_3.[31] The intensity of the DA luminescence increased considerably relative to the EC luminescence intensity from crystals containing increasing concentrations of shallow zinc acceptors [spectra (b) → (d)]. The ionized oxygen donors must have been capturing photogenerated electrons to account for the appearance of the DA pair luminescence involving the oxygen donor in these p-type crystals. It is difficult to explain the differential quenching of the EC luminescence unless nonradiative EC processes are induced at the oxygen donors in the presence of neutral zinc acceptors. The most obvious nonradiative EC process involves an Auger transition in which the energy released in the EC transition is taken up by the ejection of a hole from a nearby neutral acceptor into the valence band. The probability of this Auger transition should increase rapidly with the acceptor concentration, as required by the spectra in Fig. 4, because of the increased wave-function overlap between the donor and acceptor sites. In this connection it is interesting to note that the oxygen EC luminescence was also strongly quenched in crystals containing only $\sim 4 \times 10^{17}$ cm^{-3} neutral tellurium donors. Finally at the highest zinc concentration, 1% zinc added to the gallium solution which corresponds to $\sim 5 \times 10^{18}$ cm^{-3} zinc acceptors,[32] the intensity of all the luminescence bands was severely reduced. This latter decrease is probably due to impurity band Auger radiationless recombinations[30] involving a zinc acceptor impurity band. The reduction appeared to be least severe for the red luminescence due to recombinations at nearest-neighbor Zn-O pairs,[33] as would be expected since the radiative lifetime of this allowed higher-frequency exciton transition is considerably shorter than for the infrared DA and EC transitions. The low energy tail of the red Zn-O luminescence appears in second order at the high energy limit of spectra (b) → (e) in Fig. 4. No such effect is seen in spectrum (a), since carbon and oxygen cannot aggregate to form nearest-neighbor DA pairs in gallium phosphide.

Figure 5 shows that the infrared DA luminescence saturates with increase in the excitation intensity much more rapidly than the oxygen EC luminescence. This

effect also cannot be understood unless other processes exist for the removal of electrons from the ground state of the deep oxygen donor, so providing for further radiative EC transitions, in addition to the radiative capture of these electrons by holes bound to distant shallow acceptors. A definitive identification of such alternative processes has not yet been made. It is very plausible to assume that excitons can bind to neutral oxygen donors[34] and that this complex has an even larger Auger coefficient, because of the greater localization of the wave functions of the two electrons, than the corresponding complex involving shallow sulphur donors.[35] Such an Auger process could account for the data in Fig. 5, since many of the electrons released from the neutral oxygen donors at high excitation intensities by the Auger transition would be recaptured at these donors, and the EC luminescence would thereby be enhanced.

B. Absorption of Oxygen Donors

1. Absorption (Luminescence Excitation) Spectrum

The absorption spectra of shallow donors due to impurity substituents in semiconductors such as silicon have been extensively investigated.[36] The spectra consist of a set of very sharp lines, corresponding to transitions from the $1s(A_1)$ ground state to $2p$-like excited states, converging to a continuum corresponding to photoionization of the donor. These transitions can be readily observed in transmission, since the peak absorption coefficients in the sharp lines reach ~ 100 cm^{-1} and the continuum absorption reaches ~ 10 cm^{-1} just above threshold for only $\sim 6 \times 10^{15}$ cm^{-3} shallow donors.

It is relatively difficult to measure directly the photo-excitation spectrum for the deep oxygen donor in gallium phosphide for two reasons. First, the inter-bound-state transitions from the deep $1s(A_1)$ ground state will each exhibit strong phonon cooperation, qualitatively similar to the luminescence spectrum in Fig. 1. The sharp no-phonon lines will therefore contain very little of the total oscillator strength of these transitions, unlike the shallow donor spectra in silicon. Second, Lucovsky has shown[37] that the calculated peak absorption coefficient of the continuum due to photoionization occurs at ~ 3.2 E_D. This means that the

[31] The spectra in Fig. 4 are uncorrected for the spectral response of the PbS detector. For a typical PbS detector, this correction would involve an increase of the relative intensity of the pair band by only $\sim 15\%$.

[32] F. A. Trumbore, H. G. White, M. Kowalchik, R. A. Logan, and C. L. Luke, Electrochemical Society Fall Meeting, Washington 1964, Abstract No. 146 (unpublished).

[33] T. N. Morgan, B. Welber, and R. N. Bhargava, Phys. Rev. 166, 751 (1968); C. H. Henry, P. J. Dean, and J. D. Cuthbert, ibid. 166, 754 (1968).

[34] This complex has been observed for the shallow phosphorus site donors sulphur, selenium, and tellurium [P. J. Dean, Phys. Rev. 157, 655 (1967)] and is theoretically stable for very deep donors. See J. J. Hopfield, in Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964 (Dunod Cie., Paris, 1965), p. 725.

[35] D. F. Nelson, J. D. Cuthbert, P. J. Dean, and D. G. Thomas, Phys. Rev. Letters 17, 1262 (1966).

[36] G. Picus, E. Burstein, and B. Henvis, J. Phys. Chem. Solids 1, 75 (1956); H. J. Hrostowski and R. H. Kaiser, ibid. 4, 184 (1958); 4, 315 (1958); S. Zwerdling, K. J. Button, and B. Lax, Phys. Rev. 118, 975 (1960); J. W. Bichard and J. C. Giles, Can. J. Phys. 40, 1480 (1962); R. L. Aggarwal and A. K. Ramdas, Phys. Rev. 137, A602 (1965), 140, A1246 (1965).

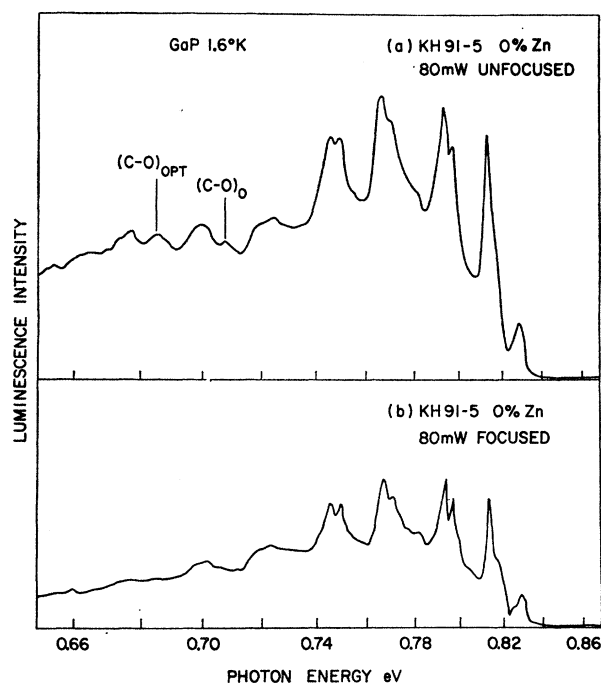[37] G. Lucovsky, Solid State Commun. 3, 299 (1965).

Fig. 5. Infrared photoluminescence spectra from gallium phosphide grown from gallium solution containing 0.02 mole% Ga_2O_3 under two widely different excitation intensities. The oxygen-carbon DA pair luminescence saturates much faster than the EC luminescence at the deep oxygen donor with increasing excitation intensity, and is therefore not observable in spectrum (b).

TABLE II. Energies and possible identifications of structure in the absorption spectrum of oxygen donors in gallium phosphide.

Component	Energy (eV)	Identification[a]	Component	Energy (eV)	Identification[a]
A_0^1	0.8634	$1s(A_1) \rightarrow 2p_0(A_1)$	A_C^4	0.936$_0$	$A_0^4 + \hbar\omega_C$
A_0^2	0.8772	$1s(A_1) \rightarrow 2p_0(E)$	A_{BB}^1	0.9565	$A_0^1 + 2\hbar\omega_B$
A_0^3	0.8810	?	A_{BB}^2	0.970$_0$	$A_0^2 + 2\hbar\omega_B$
A_0^4	0.8870	$1s(A_1) \rightarrow 2p_\pm$	A_{BB}^3	0.979$_2$	$A_0^3 + 2\hbar\omega_B$
A_0^5	0.8903	?	A_{BBB}^1	1.002$_5$	$A_0^1 + 3\hbar\omega_B$
E_0^I	0.897	$1s(A_1) \rightarrow$ cond. band			
A_B^1	0.9098	$A_0^1 + \hbar\omega_B$			
A_C^1	0.912$_2$	$A_0^1 + \hbar\omega_C$			
A_B^2	0.923$_7$	$A_0^2 + \hbar\omega_B$			
A_B^4	0.9334	$A_0^4 + \hbar\omega_B$			

[a] The identification of the no-phonon electronic transitions is tentative (see text). The energies of phonons $\hbar\omega_B$ and $\hbar\omega_C$ involved in the Stokes phonon replicas are, respectively, ~46.4 and 48.8 meV. These phonons have been labeled consistently with phonons of similar energy observed in the luminescence spectrum of oxygen donors (Table I).

photoionization spectrum of the oxygen donor in gallium phosphide will be very broad. The magnitude of the absorption coefficient for this process is inversely related to this spectral breadth, and will therefore also be relatively difficult to measure.

For these reasons, the present study was limited to the detection of the weak but sharp interbound-state donor excitations close to E_D, using the luminescence excitation technique outlined in Sec. III. The spectra in Fig. 6(a) contain a number of sharp lines, some of which are evidently phonon replicas of lower-energy features (Table II). The energy of the most prominent phonon replica in the absorption spectrum (~46.3±0.2 meV) is close to that of a relatively insignificant phonon replica in the EC luminescence spectrum (Table I). A close correspondence between the structure in the phonon sidebands of the absorption and emission spectra would be fortuitous. Different electronic transitions occur in these two spectra. In addition the isotope shift of the no-phonon transition implies a strongly non-linear electron-phonon interaction between a given pair of electronic states, as has been observed in the electronic spectra of Cd-O nearest-neighbor pairs.[22,23] It is notable that no significant absorption can be seen in Fig. 6(a) at the no-phonon energy of the luminescence spectrum. This is consistent with the predictions in Secs. I and IV A 3 that the low-temperature lumines-

cence will be due to an electronic transition between s-like donor states. Optically allowed transitions $1s \rightarrow np$ should predominate in the absorption spectrum.

The absorption in Fig. 6(a) evidently commences abruptly at line $A_0^1(h\nu = 863.4$ meV), 22 meV above the luminescence transition energy. Most of the excitation spectral rise above this energy can be attributed to an increase in the oxygen absorption coefficient, mainly due to unresolved phonon-assisted interbound-state transitions. Line A_0^1 was just detectable in an expanded ordinate scale transmission spectrum obtained with a crystal ~6-mm thick doped with 0.04% Ga_2O_3, and the peak absorption coefficient of this line was only ~0.02 cm^{-1} (line ~0.8-meV wide due to instrumental limitations).

The association of the structure shown in Fig. 6(a) with transitions at the oxygen donor was *suggested* by the fact that the transitions were only observable in *n-type* crystals grown from gallium solution containing appreciable concentrations of Ga_2O_3. The experimental arrangement used in these luminescence excitation spectral measurements (Sec. III) allowed only luminescence within the limits shown in Fig. 1 to fall upon the detector. No luminescence band other than that due to oxygen shown in Fig. 1 has been detected in this energy region from the gallium phosphide crystals used in these experiments. The isotope shift of the no-phonon line was once again used, as in Sec. IV A 2, to *prove* the association of these transitions with oxygen. Unfortunately, it was difficult to grow a relatively large crystal required for the luminescence excitation measurements from gallium solution in a silica capsule containing a high isotopic ratio O^{18}/O^{16} because of a reaction with the silica.[38] However, the shapes of the emission and absorption no-phonon lines O_0 and A_0^1 shown in Fig. 6(b) are both consistent with the assumption of a weaker (~30%) secondary line ~0.7 meV *below* that observed in

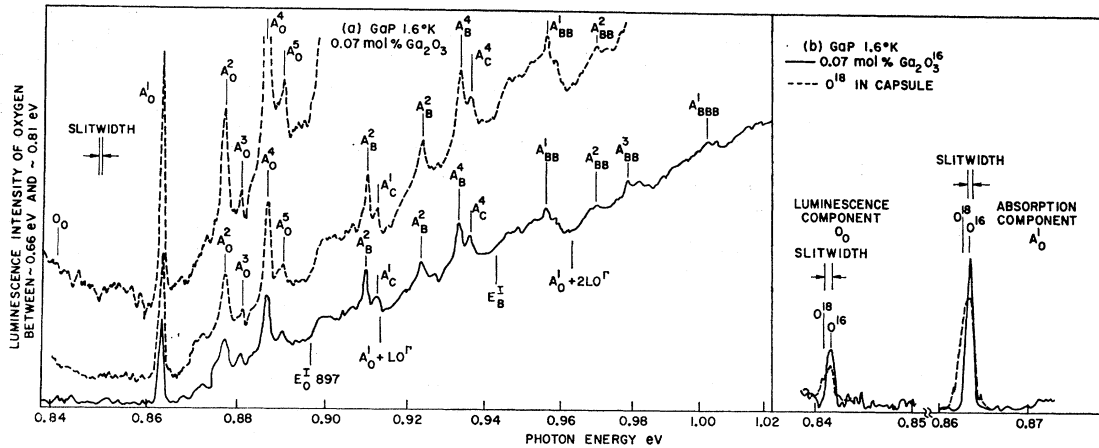[38] D. A. Hutchison, J. Chem. Phys. **22**, 758 (1954).

FIG. 6(a). Threshold absorption of neutral oxygen donors in gallium phosphide measured from excitation spectra of the interbound-state luminescence shown in Fig. 1. The luminescence occurs from a slightly deeper excited state than those responsible for the structure shown in this spectrum. The no-phonon line O_0 of the luminescence spectrum is not discernable in the luminescence excitation (absorption) spectrum. The slowly increasing response particularly evident below the predicted position of O_0 in the high-gain spectra is due to the transmission tail of the interference filter used to separate the exciting and emitted light. The notation used for the structure in these spectra indicates whether the lines are believed due to no-phonon or phonon-assisted electronic transitions (Table II). (b) A comparison of no-phonon lines in the absorption and emission spectra attributed to the oxygen donor in gallium phosphide made between crystals containing only the isotope O^{16}, and crystals in which a small proportion ($\sim25\%$) of the oxygen is O^{18}. A low-energy shoulder is present in each type of spectrum from the crystal containing the isotope O^{18}. These shoulders are consistent with the notion that the absorption and emission no-phonon lines are both shifted ~0.7 meV to lower energy for electronic transitions occurring on the O^{18} donors. This effect is shown much more clearly for the emission no-phonon line in Fig. 2(a), where the O^{18}-doped crystal contained only $\sim15\%$ of O^{16}.

crystals containing only the natural isotope O^{16}, consistent with the result for the luminescence transition shown in Fig. 2(a). It was not possible with this crystal to observe any effect of the isotopic substitution on the phonon replicas in the absorption spectrum. The predominantly O^{18}-doped crystal used for Fig. 2(a) could not be used to study the isotope shift in the luminescence excitation spectrum because this crystal was also lightly doped with zinc and was p type.

2. Classification of Oxygen Absorption Lines

No uniquely determined classification scheme can be offered for these lines at present. The displacements below $(E_D)_0$ of the prominent no-phonon lines shown in Fig. 6(a) do not agree closely with the ionization energies of the p-like excited states of low orbital quantum number calculated on the effective-mass theory of donor states in gallium phosphide. Significant increases of the ionization energies above the predictions of the effective-mass theory are certainly plausible even for the p-like excited states in a pathologically deep donor such as oxygen in gallium phosphide. If line $A_0{}^1$ is due to the lowest strongly allowed optical transition $1s(A_1) \to 2p_0$, then it must involve a component split off from the $2p_0$ effective-mass state by[20] ~16 meV because of the central cell effect of the oxygen atom [i.e., $2p_0(A_1)$]. The component $A_0{}^2$ may then involve transitions to the $2p_0(E)$ excited state, which is ~2 meV below the best estimate of the effective-mass position of the $2p_0$ level calculated by Faulkner.[2] Line $A_0{}^4$ in Fig. 6(a) may represent the $1s(A_1) \to 2p_\pm$ transition, although it is ~2 meV *higher* than predicted

from the effective-mass theory if $(E_D)_0$ is 893 meV. However, identification of the relatively sharp thresholds marked by the arrows $E_0{}^I$ and $E_B{}^I$ with the onset of no-phonon and ~46.3-meV phonon-assisted photoionization transitions of the deep oxygen donor suggests that $(E_D)_0$ may be 897 ± 1 meV, i.e., $\sim4\pm3$ meV higher than derived from the infrared DA pair spectra involving the oxygen donor.[1] The latter estimate could not be altered beyond the quoted error limits unless the value of the ionization energy of shallow sulphur donors was increased above the recently revised values reported in Refs. 1 and 16. Faulkner has recently shown[39] that the structure in the "two-electron" spectra from which $(E_D)_s$ is derived must be due to $s \to s$ rather than $s \to p$ donor excitations as has been assumed hitherto.[40,41] The earlier estimates are therefore invalid, but it is believed that $(E_D)_s$ is not significantly larger than the value, 102 ± 1 meV, which is consistent with Ref. 1.

The relatively large value of the ratio

$$[I_{1s(A_1)\to 2p_0(A_1)}]/[I_{1s(A_1)\to 2p_\pm}]$$

in Fig. 6(a) according to the above identifications[42] is consistent with a large central cell splitting of the $2p_0$ level and the absence of a significant central cell splitting for the $2p_\pm$ level. Both of these effects are caused by the

[39] R. A. Faulkner (personal communication).

[40] P. J. Dean, J. D. Cuthbert, D. G. Thomas, and R. T. Lynch, Phys. Rev. Letters 18, 122 (1967).

[41] A. Kasami, J. Phys. Soc. Japan 24, 551 (1968).

[42] The intensity ratio $I_{A_0{}^1}/I_{A_0{}^4}$ is >1 in Fig. 6(a). The intensity ratio $[I_{1s(A_1)\to 2p_0(A_1)}]/[I_{1s(A_1)\to 2p_\pm}]$ is generally ~0.35 in the absorption spectra both of effective-mass-like donors (antimony) and relatively deep donors such as bismuth (Ref. 9) and even neutral sulphur (Ref. 11) in silicon.

relatively large proportion of the $2p_0$ excited-state wave function within the central cell volume defined by the very compact $1s(A_1)$ ground state, arising from the absence in the $2p_0$ wave function of azimuthal nodes present in the wave function of the $2p_\pm$ state.[43] Faulkner has shown that the intensity ratio

$$[I_{1s(A_1)\to 2p_1(A_1)}]/[I_{1s(A_1)\to 2p_\pm}]$$

increases from ~ 0.32 for an effective–mass-like donor in silicon (or in gallium phosphide) to ~ 0.85 for the deep oxygen donor, according to a simplified model in which the ground-state wave function of the oxygen donor is assumed to be hydrogenic with range $[(E_D)_{EM}/(E_D)_0]^{1/2}$ times the range for an effective-mass ground state of energy $(E_D)_{EM}$. According to this theory, the maximum value of the intensity ratio

$$[I_{1s(A_1)\to 2p_0(A_1)}]/[I_{1s(A_1)\to 2p_\pm}]$$

is 1.29.

V. SUMMARY

The infrared luminescence due to the capture of electrons by deep ionized oxygen donors in gallium phosphide is efficient in lightly doped crystals at low temperatures.[44] The no-phonon transition is largely forbidden since the transition energy and the behavior under uniaxial stress suggest that the transition probably occurs between the $1s(E)$ and $1s(A_1)$ states split by the valley-orbit interaction due to the strong potential of the oxygen atom. This transition is not observed in the excitation spectrum of the donor luminescence. The excitation spectrum contains sharp lines at slightly *higher* transition energies, possibly mainly due to allowed $1s \to 2p$ transitions together with their phonon replicas.

The spectral effects of substitution of the natural isotope O^{16} by O^{18} have been exploited to identify these optical spectra with oxygen. The no-phonon lines in the luminescence and absorption spectra shift ~ 0.7 meV to *lower* energy, consistent with a similar shift to *higher* energy previously reported in the no-phonon lines of the infrared pair spectra involving the deep oxygen donor. This shift is accompanied by a reduction in the energies of certain local mode phonons which make a prominent contribution to the strong vibronic sideband in the luminescence spectrum. This effect was not detected in the DA pair spectra.[1,22] The EC luminescence is inherently efficient at the deep oxygen. The electronic transition represents a large number (17) of optical lattice phonons so that the transition rate due to the competing multiphonon EC process is negligible, unlike the situation for the shallow donors in gallium phosphide and silicon.

The EC luminescence becomes inefficient compared with the infrared DA pair luminescence in crystals containing $\gg 10^{17}$ cm^{-3} neutral acceptors or donors. This is attributed to a competing two-center Auger process in which the energy released when an electron is captured by an oxygen donor is given to a hole (or electron) which is ejected from a nearby acceptor (or donor) into the valence (or conduction) band. An Auger process is also hypothesized to account for the more rapid saturation of the DA pair transitions compared with the oxygen EC transition with increasing excitation intensity in lightly doped crystals. Here it is suggested that electrons may be ejected from the ground state of the deep oxygen donor as a result of the Auger recombination of indirect exciton—neutral oxygen donor complexes, the observed luminescence occurring when the ejected electrons are recaptured by the oxygen donors.

---

[43] The authors are grateful to R. A. Faulkner for this suggestion.

[44] The temperature dependence of the oxygen EC luminescence has not yet been investigated in detail, but it has been established that appreciable thermal quenching occurs between 4 and 80° K. It seems likely that this is due to a reduction in the capture cross section of the oxygen donor arising from thermal ionization of the shallow excited states which determine this cross section (Ref. 14).