Electronic States of Oxygen in Gallium Phosphide, an Example of Weak Bonding

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(Received 29 April 1982)

Existing theoretical models are unable to account for a number of important optical properties of oxygen in GaP. In this paper an energy-level structure is proposed which explains in detail the optical spectra in terms of spin- and k-conserving one-electron transitions. This scheme is based on spin multiplets formed from the neighboring gallium orbitals, which interact only weakly with a *neutral* O atom. Its striking success exposes limitations of more conventional single-particle theories.

PACS numbers: 71.55.Fr, 78.50.Ge

Substitutional oxygen in GaP exhibits numerous anomalous properties, which have remained unexplained for several years.[1-7] (1) It binds two electrons in an O^- state having unusual optical properties.[2,3] (2) Optical transitions between neutral oxygen and effective mass (EM) hole states[4] have very different phonon satellites from those between neutral oxygen and its excited EM electron states,[5] although the energies and isotope shifts[1,5,6] suggest that the same bound state is involved in each transition. (3) In careful studies of photoneutralization of O^+ from the valence band, Samuelson and Monemar found evidence for two nearly degenerate O^+ states having very different electronic properties.[7]

These inconsistencies were noted previously[8] where it was proposed that the final state in the capture luminescence might be O^- rather than O^0. In more recent work Gal, Cavenett, and Dean[6] have argued convincingly that the state involved is, indeed, O^0, and it shows the shallow excited states expected for a neutral donor in GaP.[9]

These properties indicate clearly that a more complex model than that normally devised for a deep substitutional defect is needed. The most likely source of this complexity is in the Ga bonds surrounding the O atom, bonds which differ from those in most other defects because of the depth of the oxygen atomic levels[10] and the resulting weakness in GaP of the Ga-O bond.[11] In this Letter I show that the properties described above can be explained by the energy-level diagrams in Fig. 1. These energies are a fit to experiment of a molecular orbital (MO) analysis of a weakly bonded defect on a P site.[12]

In the present model, the Ga-O bonds are formed from the O atomic orbitals and the four Ga sp^3 bond orbitals which extend into the P vacancy occupied by O. The covalent nature and the orientation of these bond orbitals are fixed by orthogonality to the Ga-P "back" bonds surrounding the defect, although their lengths are not. According to Baraff, Kane, and Schlüter,[13] the Ga dangling bond orbitals lie above the middle of the gap with the $3p$ orbitals of P slightly lower. The atomic $2p$ level in O^0 lies about 7 eV below $3p$ in P with $2s$ another 15 eV lower. The $2p$ level in O^-, however, lies close to the vacuum level,[14] far above the conduction-band edge, and is, therefore, not stable. Further, overlap of the Ga and O orbitals is small because of the small radii of the O orbitals and relaxation of the Ga ions away from the oxygen.[15] Hence, the electrons on the oxygen remain in a nearly atom-

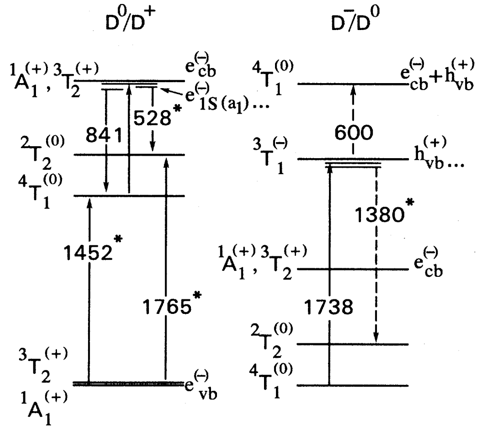

FIG. 1. Energy levels and observed oxygen transitions in GaP: "first"-electron transitions on the left, "second"-electron transitions on the right. The fine structure is approximate. The states consist of the deep MO configurations shown to the left of the levels plus (where shown) the EM electrons $e^{(-)}$ or holes $h^{(+)}$ on the right; charges are shown in parentheses. Energies are in millielectronvolts, cb is the conduction-band edge, vb is the valence-band edge, and the asterisks mark transitions which excite type-A phonons. The dashed lines indicate transitions that are unconfirmed.

ic O^0 configuration, the defect electrons go into the surrounding Ga orbitals (as in the P vacancy), and the bound impurity states are very different from those assumed by the usual "bond-orbital" models.[10,13]

The bond-orbital model puts six electrons in the O $2p$ shell and only zero, one, or two in the Ga bonds, while the lowest-energy MO configurations put four p electrons on O and two, three, or four electrons in the dangling bonds. Although both methods find nearly the same radial distribution of charge, with O approximately neutral, the former is unable to take maximum advantage of the Coulomb and exchange energies associated with the Ga orbitals. An additional problem, the difficulty of computing multiplet structure with local-density theory[16] is circumvented here by use of molecular orbitals.

The MO model of this Letter includes only the central atom and the four weakly coupled (dangling) Ga bonds. For deep states, $E_b > 0.5$ eV, more distant orbitals will not make major contributions, and shallow, extended states can be treated in the EM approximation. The neutral, positive, and negative charge states of the oxygen "donor" are denoted by D^0, D^+, and D^-, respectively, with the symbols O^0, O^+, and O^- reserved for the O atom and ions.

In the D^+ center there are eight valence electrons. Six of these go into the low-lying oxygen $2s$ and $2p$ shells to form O^0 and two remain in the bonds. An electron added to this configuration to form the neutral D^0 defect goes into the Ga dangling bonds and appears as a bound "one-electron" state within the forbidden gap. A "second" electron in the negative D^- center is presumed also to go into the bonds, as the O^- ion is not stable. Thus, the O^0 atom is present in all three charge states and is not altered in the transitions between them. I analyze the consequences of this model in view of the constraints imposed by experiment on the theory and its parameters.

For the D^+ center, the two electrons in the dangling bonds occupy combinations of the a_1 and t_2 orbitals formed from the four bonds.[17] Because of the Coulomb repulsion between two electrons on the same bond, however, states in which the electrons reside on different bonds are stable and form the singlets shown in Table I.[18] The relative energies of these are determined by their Coulomb and exchange energies and by a term which I write $n_\epsilon \epsilon$. Here ϵ is the matrix element of the total potential (crystal plus impurity) between two different (orthogonalized) bond orbitals and is found to be negative, $\epsilon \approx -1$ eV. The coefficients n_ϵ are related, through Eq. (1) below, to the number of a_1 electrons in the state; see Table I.

TABLE I. Allowed states for the positive, neutral, and negative oxygen defect in GaP. n_ϵ, the coefficient of the two-center potential energy integral ϵ, depends on the number, $n(a_1)$, of a_1 electrons. See Eq. (1).

	(+)			(0)		$(-)^a$	
$^m\Gamma$	n_ϵ	$n(a_1)$	$^m\Gamma$	n_ϵ	$n(a_1)$	$^m\Gamma$	n_ϵ
$^1A_1$	4	3/2	$^4T_1$	1	1	$^5A_2$	0
$^3T_2$	2	1	$^2T_2$	2	5/4	$^3T_1$	0
$^1T_2$	0	1/2	^2E	0	3/4	^1E	0
$^3T_1$	−2	0	$^2T_1$	−2	1/4		
^1E	−2	0	$^4A_2$	−3	0		

[a] $n(a_1) = 1$.

It is significant in explaining the phonon spectra that the charge distribution at the oxygen site, which depends on the number of a_1 electrons present, is greatest for the $^1A_1^{(+)}$ state and, therefore, that the Ga atoms are displaced (outward) for this state, relative to the others, by interaction with the oxygen. I label the breathing-mode phonons which this displacement excites type "A" ($\hbar\omega = 19$ meV, etc., in O^+) and the remaining symmetric phonons, type "B."[8] Hence, the type-A phonons arise, mainly, from transitions involving the $^1A_1^{(+)}$ state and, as I show below, this must be the ground state. Theory predicts that the next lowest state is $^3T_2^{(+)}$, which, to explain the temperature dependence of the photonuetralization results,[7] must lie only 0.4 meV higher at 0 K.

For the D^0 center, the next electron goes into the bonds to make them neutral, and all three electrons are again assumed to avoid each other. Such a configuration forms the doublets and quartets shown in the table. Of these the $^4T_1^{(0)}$ is found to lie lowest (because of the exchange energies), with $^2T_2^{(0)}$ only ≈ 310 meV higher. The experimental data are consistent with this choice for the following reasons. Spin conservation predicts that an EM electron captured by the singlet state of D^+ cannot relax radiatively into the quartet ground state of D^0, and only the $^3T_2^{(+)}$ to $^4T_1^{(0)}$ transition will occur. Further, the $^3T_2^{(+)}$ and $^4T_1^{(0)}$ states have the same number of a_1 electrons (one), so that transitions between them do not excite type-A phonons. Thus, the type-A phonons should be absent in the 0.841-eV electron capture transition, as is observed, but they do appear in the 0.528-eV transitions, which end in the doublet excited state. (Transitions exciting type-A phonons are marked by asterisks in Fig. 1.)

Note that, as these states avoid the central atom, spin-orbit coupling is small and spin a good quantum number.[19] When the captured particle is a $j=\frac{3}{2}$ hole, however, as in pair spectra, both the singlet-quartet and the triplet-quartet transitions become allowed as a consequence of the strong spin-orbit coupling in the valence band. To understand why the former transition is favored in the D-A pair spectra and in (low temperature) photoneutralization we must consider k conservation[3] between the bound electrons and the band hole.

States of s-like symmetry (a_1) have nonvanishing Fourier components at $k=0$, while p-like states do not. Thus, k conservation predicts that transitions between states which differ in the number of a_1 electrons can couple to band-edge holes (or electrons); transitions which change only t_2 (p-like) electrons (for simple bands) cannot. Thus, band-edge or shallow bound holes can couple ${}^4T_1{}^{(0)}$ only to ${}^1A_1{}^{(+)}$, as in the D-A pair spectra, and not to ${}^3T_2{}^{(+)}$. As noted above, this excites the type-A phonons. The "forbidden" triplet-to-quartet transition becomes allowed as k and the hole energy increase, and, further, the triplet D^+ state, at 0.4 meV above the singlet, becomes populated as temperature increases. Thus, as found in Ref. 7, a new photoneutralization spectrum, the triplet-to-quartet one, appears with increasing temperature, and this resembles a spectrum with a higher energy threshold than that of the "allowed" singlet-to-quartet spectrum.

For the D^- center the bond energy is expected still to lie below O^-,[14] so that the four electrons in the Ga bonds form the three states shown in the table with no two electrons on the same bond. The MO model finds ${}^5A_2{}^{(-)}$ to lie lowest, although corrections apparently alter this order.[18] As shown in the table the electron removed in the D^- to D^0 (ground-state) transition has t_2 symmetry, in agreement with the suggestion in Ref. 3 that the "second-electron" state is "p-like." Although it is possible that this state could be metastable and relax to a distorted configuration,[2,11] this may not be necessary to explain the optical spectra. Both the weakness of the photoionizing absorption and the absence of the expected 1.74-eV emission in hole capture are explained for D^- by k conservation and by transitions into excited D^0 (or D^+) states; see Fig. 1. Unfortunately, the only well-resolved D^- transition is the 1.738-eV absorption, and this may not be into the ground state.[18] Preliminary Zeeman studies of this line,[20] which do not fit a quartet-to-quintet-plus-hole transition, are consistent with the model shown in the figure where the final D^- state is the triplet ${}^3T_1{}^{(-)}$.

The states described above also explain many other transitions, some of which are shown in Fig. 1.[6,21] I shall mention only the dashed transition which is estimated to lie near 1380 meV, where it would be obscured by the D-A pair band. If observed, this transition would locate the D^- ground state and confirm its stability. Finally, preliminary analyses of Zeeman data appear consistent with the one-electron transitions described above. There are no obvious Jahn-Teller effects, and coupling to the central ${}^3P$ oxygen atom seems not to alter the essential properties and ordering of the spin multiplets.

The Coulomb and exchange energies are responsible for bringing the ${}^3T_2{}^{(+)}$ and ${}^1A_1{}^{(+)}$ states, which contain both a_1 and the higher-energy t_2 electrons, below the state composed of two a_1 electrons. The composition $C=n(a_1)a_1+n(t_2)t_2$ of any of these n-electron states can be calculated from the relation

$$C=(n/4)(a_1+3t_2)+(n_\epsilon/4)(a_1-t_2). \tag{1}$$

Arguments similar to those presented above can be applied to other defects such as N or F on P sites and the P vacancy in GaP and similar defect states in other hosts.

In summary I have shown that (1) the O defect in GaP resembles a P vacancy weakly perturbed by a *neutral* O atom; (2) the Ga bond orbitals provide a physically appropriate MO basis for describing the electrons external to the O atom; (3) exchange and Coulomb energies of the spin multiplets must be accurately treated; (4) the predictions of the model agree in striking detail with experiment and resolve many long-standing problems; (5) the basic assumptions of the bond-orbital approach to defect problems must be critically examined.

It is a pleasure to acknowledge the contributions of the many experimental physicists who found the pieces of the puzzle which motivated this work. Further, I wish particularly to thank Bo Monemar, Lars Samuelson, Paul Dean, Chuck Henry, Dave Lang, Michael Sturge, Socrates Pantelides, Nunzio Lipari, Frank Stern, and Ken Stevens for valuable discussions. This work was supported in part by the U. S. Office of Naval

Research under Grant No. N00014-80-C-0376.

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