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Electronic states of oxygen in gallium phosphide

T. N. Morgan

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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The "classical" model described by Dean and others does not account for a number of the important electronic properties of oxygen in GaP. I summarize here the major experimental results which are unsatisfactorily explained by this model and present a new "weak-bonding" model, which does agree with experiment. This new model, which is based on spin multiplets formed from the four neighboring gallium bond orbitals modified by weak coupling to the central O atom, provides a detailed explanation of the experiments including Jahn-Teller and Zeeman effects and optically detected magnetic resonance.

I. INTRODUCTION

The substitutional oxygen defect in gallium phosphide has been extensively studied both experimentally and theoretically. Two recent reviews by Dean[1,2] (denoted by D1 and D2) describe the history of experimental progress on this system and present what Dean calls the "CD" or classical description. In this description the electronic states associated with the O^+, O^0, and O^- charge states are assumed to be nondegenerate, and the same assumption is made in the conventional defect theories.[3,4] Numerous properties of oxygen in GaP, however, cannot be explained by such a simple model of a deep defect.

(1) There are emission lines and satellites which do not fit easily within the CD,[5] and certain expected transitions are not observed.

(2) Phonon satellites of optical transitions between O^0 and O^+ are very different according to whether the particle captured or released is an electron or a hole—suggesting that two different pairs of deep states are involved.[6]

(3) In careful studies of photoneutralization (PN) of O^+ from the valence band, Samuelson and Monemar[7] found strong evidence for two nearly degenerate O^+ states having very different electronic properties.

(4) The phonon satellites of zero-phonon transitions into the ground states of all three charge states (O^+, O^0, and O^-) provide evidence that a Jahn-Teller effect (JTE) is present.

(5) These satellites also show that the elastic constant for oxygen vibration decreases with increasing number of antibonding electrons in O^+, O^0, and O^- and extrapolates to zero only 0.4 of an electron beyond O^-.

(6) Gal and co-workers found a triplet spin resonance which induced an increase in the circularly polarized 841-meV emission intensity. This resonance, which had a $\langle 110 \rangle$ symmetry axis and exhibited a quartet hyperfine splitting, also appeared as an increase in the donor-acceptor—pair (DAP) emission intensity.[8]

In this paper I review these anomalous properties and show that they can be explained by the energy-level diagrams shown (in two approximations) in Fig. 1 and not by the CD of D1. The energies are a fit to experiment of a molecular-orbital description of a weakly bonded defect on a P site.[9] I refer to this model as the WBD or "weak-bonding description." In Sec. II, I describe in some detail the history and the present state of the WBD, and in Sec. III, I review the anomalous properties and their interpretation within both models. In Table I, I summarize the more obvious of the properties discussed in Secs. II and III, properties which are reported and discussed in Refs. 1, 2, 5, 7, 8, and 10—13.

II. SPIN MULTIPLETS

A. History

The WBD was developed to account for the first five entries in Table I. The complex O^+ energy-level structure needed could not be explained if the bonding orbitals formed between the central oxygen and the galliums were filled in the usual way,[3,4] because this would absorb all of the available O^+ electrons into a nondegenerate ^1S state ($1s^2 2s^2 2p^6$) as shown in Fig. 2(a). It was recognized that the O—Ga bond would be very weak, both for the a_1 (s-like) states, for which the oxygen $2s^2$ levels lie about 20 eV below the bond levels, and for the t_2 (p-like) states, which have little overlap with the small O atom. Hence, it seemed reasonable to ask what would happen in the limit of zero oxygen—gallium bonding. This "vacancy" limit, with the neutral oxygen atom sitting in the middle of the cage of gallium atoms as is shown in Fig. 2(b), was taken as the first step in the process which has led to the present WBD.

Initially, all coupling to the impurity was ignored except through an effective (spherical) potential which simulated the effect of the weak oxygen—gallium bond.[9] The defect, thus, became similar to a phosphorous vacancy with two, three, or four electrons occupying the four unpaired (dangling) gallium bonds, and an additional simplifying assumption was made that no bond would contain more than one electron. This model, which I call the VM or "vacancy model", was analyzed using the dangling Ga

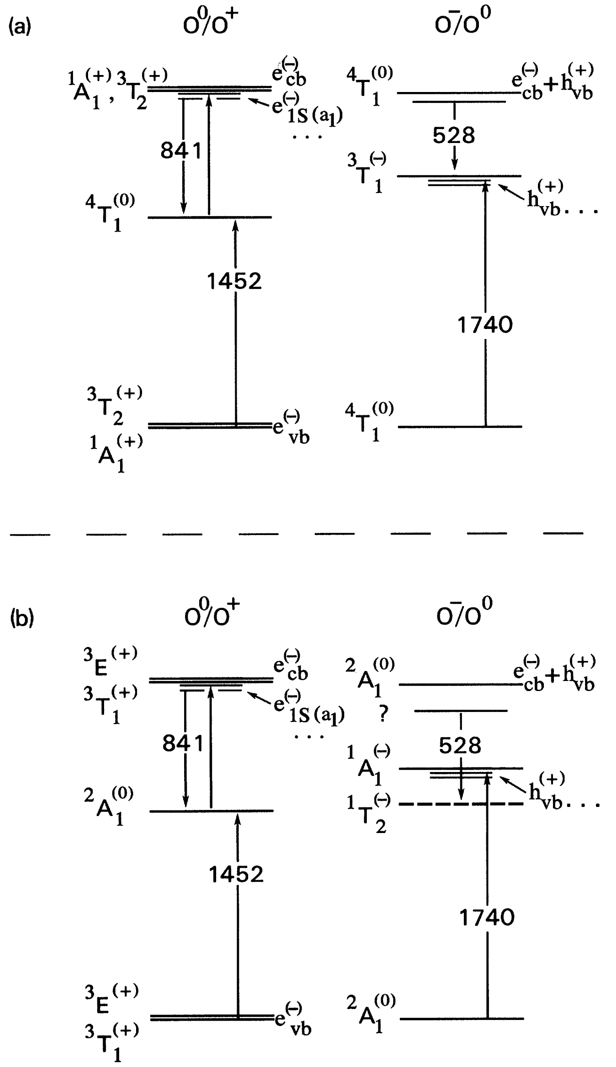

FIG. 1. WBD transitions and energy levels for oxygen in GaP: (a) the "vacancy model" and (b) the complete "coupled model"; first electron transitions are in the left half of each, second electron transitions are in the right half. The states consist of the localized configurations on the left plus, where shown, the EM electrons e^- or holes h^+. Energies are in meV, cb denotes conduction band, and vb denotes valence band. (b) shows the bonding configurations formed by coupling the multiplets in (a) with the ^3P state of neutral oxygen when JT effects are included.

bonds in a molecular-orbital description, and the energies of the resulting spin multiplets were fit to experiment as in Fig. 1(a). The results were in striking agreement with experiment, but there remained several inconsistencies which were not easily understood within the model.

Furthermore, it was recognized that coupling between the vacancylike part of the defect and the central oxygen atom was important and would determine the symmetries and many of the properties of the complete states. In the present work and (in part) in Ref. 14, the Jahn-Teller, orbital, and spin coupling between the vacancy states and the oxygen have been added to modify the states of the simpler problem, as is shown in Fig. 1(b). This is the complete WBD.

Ultimately, quantitative calculations of the coupled multielectron states (including Jahn-Teller distortions and spin-orbit coupling) must be made to complete our understanding of this elusive defect.

In the following discussion I present first the simpler VM, which ignores details of the coupling to the central O atom, and then describe the modifications which must be made when vacancy-oxygen coupling is added. The basis functions used are the weakly bonded a_1 and t_2 orbitals constructed from the one-electron s and p orbitals of the neutral oxygen atom and the a_1 and t_2 orbitals of the gallium dangling bonds. Because of the weak bonding, the bonding orbitals are largely from the oxygen, while the antibonding ones are from gallium.

B. Vacancy model

1. States

In this model the three charge states of the oxygen defect are formed by placing the requisite number of electrons in the four gallium "dangling" bonds surrounding the *neutral* oxygen atom. Thus, these three charge states, normally referred to as O^+, O^0, and O^-, contain, respectively, two, three, or four electrons in the bonds. The spin multiplets which these electrons occupy are described in Ref. 9, and those which lie lowest in energy are listed on the right-hand side of Fig. 2(b). Most of the observed transitions are also indicated in Fig. 1(a). Although the initial and final states are multielectron states, only one electron jumps in any transition, and the selection rules and weak spin couplings guarantee that most transitions resemble those predicted by the CD. (I show below that

TABLE I. Comparison of the CD and WBD of O in GaP.

	Experiment	Observed feature	CD[a]	WBD[a]
(1)	$O^{0/+}$ Binding energy	Same value from DAP and PLE	+	0
(2)	$O^{0/+}$ Isotope shift	Same value for DAP and capture	+	+
(3)	$O^{0/+}$ Phonon satellites	Differ for DAP and PLE	−	+
(4)	$O^{0/+}$ PN	T dependence	−[b]	+
(5)	Capture and PLE	Isotope-dependent satellites	−	+
(6)	0.53- and 1.74-eV lines	Analysis of energies	−[c]	0
(7)	0.84-eV ODMR	Triplet, hyperfine structure	−	+

[a] + denotes support for the model, − denotes a contradiction, and 0 denotes neither strongly.
[b] Becomes 0 only if Dean's alternate model is accepted.
[c] Becomes 0 only if the 42-meV binding energy of O^{-*} is explained.

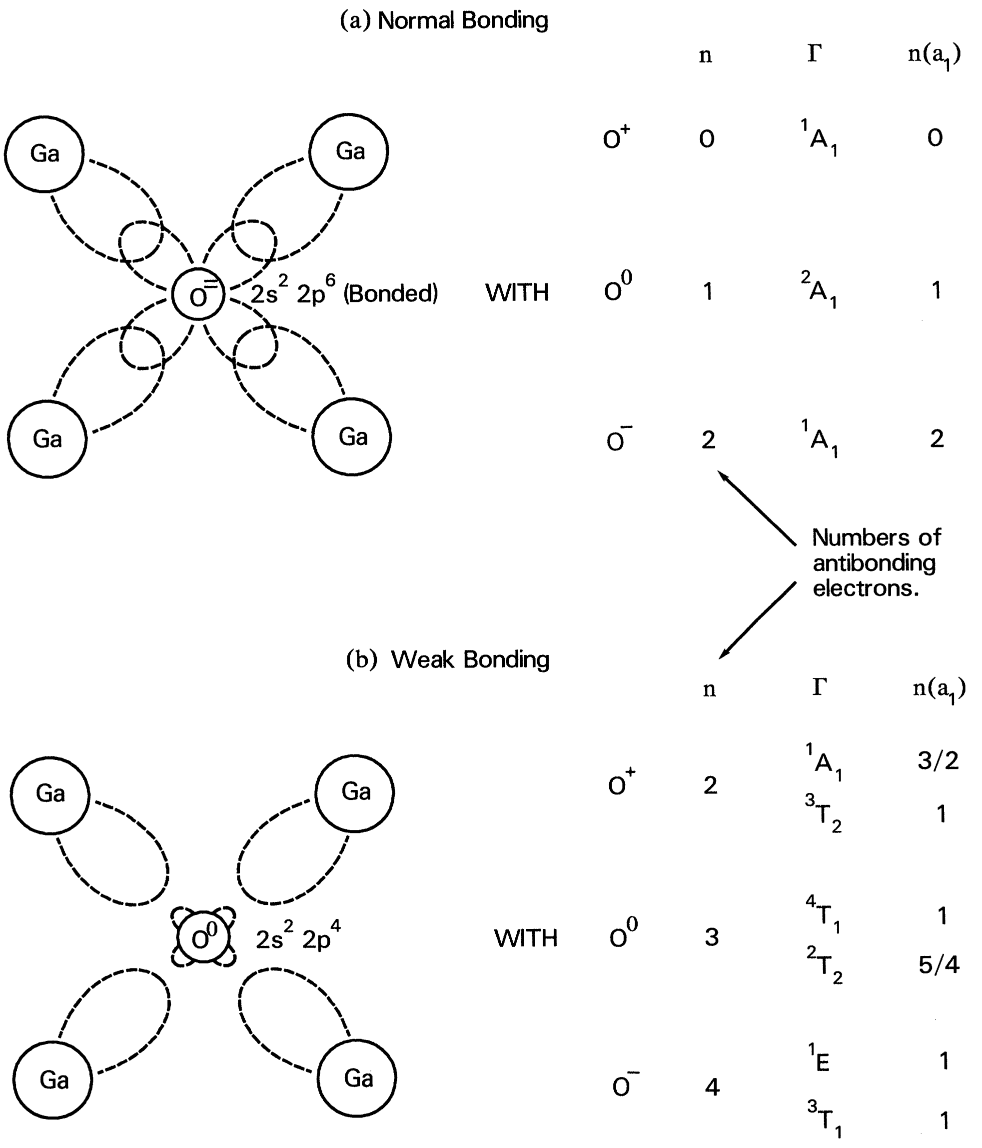

FIG. 2. Schematic comparison of the two bonding schemes for oxygen in GaP: (a) the CD or "normal" bonding; (b) the WBD or weak bonding. On the right-hand side the symmetries of the vacancy multiplets and the number of a_1 electrons are listed for the lowest levels of each charge state (see text).

the coupling to the central oxygen makes this resemblance even closer.) Let us analyze the states and selection rules to determine where the differences lie.

2. Selection rules between O^0 and O^+

There are many states to choose from, but those expected to lie lowest are ${}^1A_1^{(+)}$ and ${}^3T_2^{(+)}$ for O^+ and ${}^4T_1^{(0)}$ for O^0. Furthermore, the two O^+ states are predicted to lie close together because of cancellation between the exchange and Coulomb energies. When it is assumed that these two are the nearly degenerate O^+ states found by Samuelson and Monemar, with ${}^1A_1^{(+)}$ lower in energy, the strange experimental results begin to fall into place. There is an obvious spin selection rule for one-electron transitions between the singlet or triplet and ${}^4T_1^{(0)}$, because in first order a spin-$\frac{1}{2}$ electron can couple only the triplet to a quartet, while a "spin-" $\frac{3}{2}$ hole can couple either. Thus, a part of the difference found between conduction- and valence-band states is accounted for—one of the two possible capture transitions is suppressed,[15] although it might be retained in DAP recombination.

A second important property of the multiplets, the number $n(a_1)$ of a_1 electrons they contain, is also listed in Fig. 2(b). Because electrons in the four dangling bonds in the defect are coupled, they form symmetric a_1 (s-like) and antisymmetric t_2 (p-like) one-electron combinations, with the former expected to lie lower. The states differ not only in symmetry but also in their interactions with the central atom: Only the a_1 electrons overlap the oxygen potential and interact appreciably with it. Hence, this difference in $n(a_1)$ shown in Fig. 2(b) reveals a second important difference between the two possible transitions coupling O^+ and O^0: Those involving ${}^1A_1^{(+)}$ change the number of a_1 electrons in the deep state, while those involving ${}^3T_2^{(+)}$ do not. The change in the number of a_1 electrons is found to lead to an approximate electronic selection rule[16] and to have other observable consequences—see (3) below—again in agreement with experiment.

3. Capture into O^0

Consider capture of an electron from the $1S(a_1)$ effective-mass (EM) state bound to ${}^3T_2^{(+)}$ of O^+ into the O^0 ground state ${}^4T_1^{(0)}$. The overall symmetry of the states does not forbid an optical transition, but it is the one-electron matrix elements which determine the strength of this transition. If we denote the orbital parts of the one-electron wave functions by $|a_1\rangle$ and $|t_2\rangle$ for the bonds and $|\alpha_1\rangle$ for the EM electron, then the multiplet wave functions consist of a sum of terms which we can write symbolically as a spin part multiplied by

$$|a_1t_2t_2\rangle$$

for O^0, and multiplied by

$$|a_1t_2\alpha_1\rangle$$

for an electron bound to ${}^3T_2^{(+)}$ of O^+. As two of the electrons remain unchanged in the transition, the relevant matrix element contains terms such as

$$\text{Matrix element} \propto \langle t_2 | P | \alpha_1 \rangle , \tag{1}$$

where P is the dipole operator and there should be an additional factor insuring conservation of spin.

Symmetry and spin tell us that the matrix element in Eq. (1) need not vanish, because P transforms as T_2, but this takes no account of the conservation of crystal momentum $\vec{k}$ in optical transitions. The p-like dangling-bond wave function $|t_2\rangle$ can be expanded in a basis of band states $|n,\vec{k}\rangle$ and has contributions from both conduction and valence (and other) bands. Its expansion coefficients, however, vanish at the conduction-band edge, which has X_1 symmetry, and, because of the depth of the state, these coefficients increase only slowly with changes in $\vec{k}$. Thus, they remain small throughout the range of $\vec{k}$ spanned by the shallow EM state α_1, and the matrix element in Eq. (1) is very small. This is consistent with the weakness of the zero-phonon line and the long decay time (10 μs) of the emission. Interpretation of the spectra is complicated by the presence of two nearly degenerate initial states, although decay from the ${}^2A_1^{(0)}$ state is also forbidden—in this model by spin.[15]

These transitions are allowed in second order, however, through the EM $2p$ states. The additional coupling is provided by the weak spin-orbit operator and by coupling to the central oxygen. The former relaxes the spin selection rule (and explains why the zero-phonon line shows a normal Zeeman pattern[5,10]), while the latter mixes $\vec{k}$ values in the spin-allowed transitions (and explains the relatively strong JTE satellites).

A similar argument can be applied to the CD, where the forbidden nature of the transition is explained by the $1S(e)$ initial EM state, although it is uncertain that the spin-orbit-coupling strength in the extended $1S(e)$ state is adequate to account for the intensity of the spectrum.

4. Hole capture

Selection rules involving holes are not as easily derived. They are complicated by the p-like character of the cell-periodic part of the wave function, by the importance of spin-orbit coupling in the valence band, and by Jahn-Teller distortion of the defect. It is still true that selection rules based on the total symmetry of the multiplets, although they must be satisfied, give little information about the strengths and k dependences of allowed transitions, but the analysis is not as simple as was suggested in Ref. 9. The transition rates depend on the composition of states near the top of the valence band, which are predominately phosphoruslike, in contrast to those in the gallium dangling bonds. Hence, when a t_2 electron changes (as between ${}^3T_2^{(+)}$ and ${}^4T_1^{(0)}$ plus a hole), the galliumlike t_2 state and the phosphoruslike valence-band state have small matrix elements connecting them, and the transition is weak.

When an a_1 electron changes, however, the analysis is more complicated and is presumed to proceed as follows. An a_1 electron overlaps the O atom on a P site, as t_2 does not. It, therefore, contributes to the phosphoruslike components near the top of the valence band. These would be only the s-like states deep in the band if there were no JTE acting on the defect. The JTE introduces anisotropy into the bond strengths, so that the a_1 electrons develop p character and, hence, a significant matrix element with the top of the valence band.

The above analysis is seen to agree qualitatively with the PN experiments, for which the matrix elements are "allowed" through ${}^1A_1^{(+)}$ but "forbidden" through ${}^3T_2^{(+)}$ at $k=0$ and become strong for the latter only as the hole momentum and energy increase into the valence band.

5. Phonon coupling

The discussion of selection rules just given shows that the WBD predicts two different transitions O^0 and O^+. One of these—through ${}^3T_2^{(+)}$—appears in capture and photoluminescence excitation (PLE), while the other—through ${}^1A_1^{(+)}$—dominates DAP emission. What is, perhaps, more striking is that this model also explains the phonon differences, item (3) of Table I. The dominant capture transitions (between ${}^3T_2^{(+)}$ and ${}^4T_1^{(0)}$) add a t_2 electron to the defect state, as is shown in Fig. 2(b). As this electron does not overlap the oxygen atom appreciably and the charge is delocalized around the four Ga atoms, the equilibrium O-Ga separation is only slightly changed by the capture (or PLE) transition. DAP recombination, on the other hand, changes ${}^4T_1^{(0)}$ into ${}^1A_1^{(+)}$, increases the number of a_1 electrons by one-half [Fig. 2(b)], and thereby changes the overlap with the oxygen. Consequently, only this latter transition changes the equilibrium

O-Ga separation and excites the type-*A* breathing-mode phonons. Modes associated mainly with phosphorus motion are excited whenever the defect changes charge state, but the only significant displacement of the Ga neighbors occurs with changes in $n(a_1)$.

Following the striking success of the WBD for the O^0-to-O^+ transitions, it was desirable to test its application to other transitions and, ultimately, to relax some of the approximations made in its initial form. The first such extension was to O^-.

6. O^- state

When the model was applied to O^-, the same assumption of one electron per bond was made, an assumption supported by the results of Ref. 17. Only three states were found, ${}^5A_2^{(-)}$, ${}^3T_1^{(-)}$, and ${}^1E^{(-)}$, each with one a_1 and three t_2 electrons, and the molecular-orbital calculation predicted that these should appear in increasing energy in the order given. This order agrees with published self-consistent-field (cluster) calculations of the four-electron neutral silicon and diamond vacancies, but disagrees when correlation and configuration interactions are added.[17] In the latter calculation the order is inverted because of correlation effects, with ${}^1E^{(-)}$ the lowest. Hence, the model has been applied[9] to O^- with the positions of the states to be established from the experiments.

One consequence of this analysis supported a conjecture made in 1974 to explain the absence of low-energy photoionization (PI) transitions out of O^-. In the earlier work[16] it was proposed that the electron captured or released in these transitions could be a *p*-like (t_2) electron, so that the optical cross sections for band-edge transitions were reduced by the $\vec{k}$ selection rule discussed above and were difficult to observe. (Indeed, a doubly forbidden transition with a 0.65-eV threshold was found by photoionization, as expected.[16]) In the WBD, capture of the "second electron" would convert the configuration ${}^4T_1^{(0)}$ of $(a_1t_2^2)$ into one of the O^- states belonging to $(a_1t_2^3)$ [see Fig. 2(b)], so that the electron which changes would be in a localized t_2 orbital. Furthermore, the Zeeman measurements on the 1.74-eV absorption—D2 and Ref. 10—show that the O^- state seen has a spin of $\frac{1}{2}$ less than O^0 (see below) and is, therefore, ${}^3T_1^{(-)}$ (although, see the discussion in Sec. II C). Thus, if ${}^1E^{(-)}$ lies lower, as found in Ref. 17, it may provide a nonradiative decay channel and explain the absence of the expected radiative transitions out of ${}^3T_1^{(-)}$. One must remember, however, the uncertainties inherent in finite-cluster calculations and the differences between a silicon vacancy and an oxygen defect in GaP.

C. Coupling to the oxygen atom

The most important extension of the original analysis has been to consider in detail the coupling between the central oxygen and the neighboring gallium atoms. The success of the model depends on preservation or improvement in the original agreement with experiment when coupling is included. This coupling has two different manifestations: (1) a displacement of the central O atom by the action of the JTE to lower the total (vibronic) energy of the coupled system (see Secs. III C and III E), and (2) mixing of the spin multiplets of the Ga bonds with those of the O atom to produce the combined spin multiplet of the entire defect [compare Figs. 1(a) and 1(b)].

1. Double Jahn-Teller effect

Consider first the JTE. The [111] component of the ${}^3T_2^{(+)}$ wave function is composed of one a_1 and one t_2 electron. If $|x\rangle$, $|y\rangle$, and $|z\rangle$ denote the components of $|t_2\rangle$, the wave function is

$$\psi_{111}=|a_1\rangle(|x\rangle+|y\rangle+|z\rangle)/\sqrt{3}\,, \tag{2}$$

which has one electron in the parallel [111] dangling bond but only $\frac{1}{3}$ of an electron in each of the other three. (Note that this concentration of charge in one bond is consistent with the observation of hyperfine coupling to a single Ga atom.) Because these are antibonding electron orbitals, there is a net force on the oxygen atom in the $-[111]$ direction, away from the parallel bond. This force generates a JTE.

An additional JTE is expected from coupling of the ${}^3P$ orbitals of O with the surrounding Ga bonds. This also generates a trigonal displacement, which, because these are bonding orbitals, is in the opposite direction from that described above. Hence, the defect is stable only when the orbital triplets are in different, say [111] and $[1\bar{1}\bar{1}]$, component states. As a consequence, the displacement of the O atom giving the minimum energy is not along a $\langle 111\rangle$ direction, but is a sum of a push along, say, [111] and a pull along $[1\bar{1}\bar{1}]$. This is close to the [011] direction, as the two JTE coupling strengths are approximately equal, and explains the $\langle 110\rangle$ axis found for the resonance in optically detected magnetic resonance (ODMR).[8,18]

Thus, we find that although a single JTE cannot generate a distortion with a $\langle 110\rangle$ symmetry axis, two such effects acting independently can, even if the coupling is not very strong. This leads to the additional conclusion that the bonding discussed below, between the vacancylike states and the oxygen, occurs between relaxed states—including the Jahn-Teller distortion—and is too weak to quench the vibronic interaction. We shall find that this JTE may also alter the symmetry of the stable bonded configuration so that the lowest bonded state is a spin triplet rather than a singlet.

The vibronic eigenstates observed optically need not be statically distorted but will be linear combinations of the twelve $\langle 110\rangle$ axially distorted components. The orbital symmetry of the lowest-energy components can be deduced from an analysis of the coupling matrix in the nine-dimensional space of the two electronic triplets[18] and can be understood as follows. For O^+ the first displacement along, for instance, the $-[111]$ direction lowers the symmetry of the defect from T_d to C_{3v}, splitting the T_2 state into a lower Γ_1 and a higher Γ_3 (doubly degenerate) level. This also splits the oxygen *P* state into a nondegenerate Γ_2 level, raised in energy, and a ground Γ_3 doublet.[19] The coupling of this doublet to the oxygen displacement generates the second JTE, so that the ground vibronic state of oxygen, in the distorted C_{3v} symmetry, becomes Γ_3. By combining these doublets for all four of the $\langle 111 \rangle$ axes of the first distortion, we obtain the three T_d representations $\Gamma_3+\Gamma_4+\Gamma_5$. By analogy with the single JTE (but including an extra sign change from the second electronic state), one can conclude that the Γ_3 (E) state is lowered by "tunneling" to become the ground state. This ground state, although degenerate, is found not to be split by uniaxial stress—in agreement with intuition (because the coupling coefficients have opposite signs) and with the observations of Ref. 5.

Similarly, for ${}^4T_1^{(0)}$ in the [111] component there is $\frac{1}{4}$ of an electron in the parallel bond and $\frac{11}{12}$ in each of the remaining three—the same difference as for O^+, but of the opposite sign. Consequently, the JTE displaces the oxygen in a $\langle 111 \rangle$ direction and lowers the nondegenerate Γ_2 levels of both triplets. As a result, the total symmetry in C_{3v} is $\Gamma_2 \otimes \Gamma_2 = \Gamma_1$. When the four $\langle 111 \rangle$ axes are combined, the two sign reversals, one from each electronic state, invert the usual tunnel splitting, so that the ground state is a singlet.[18]

When we compute the number of electrons in the parallel and nonparallel bonds for ${}^3T_1^{(-)}$, we find that each bond contains exactly one electron, as we assumed at the outset. Thus, the vacancy part of the JTE coupling is small or zero and the JTE in ${}^3T_1^{(-)}$ is due only to vibronic coupling through the ${}^3P$ state of the oxygen.[20]

2. *Spin-dependent bonding*

The above analysis has ignored the complexities of spin except in the permutational symmetry of the electrons, which was considered separately for the vacancy and oxygen parts of the state. The spin-orbit coupling, although present, is apparently too weak to be observed in any experiments other than magnetic resonance. The spin dependence of the bonding between the oxygen and the galliums, which arises from the Pauli principle, however, determines the multiplicity which is observed in the coupled system.

In general, the lowest spin multiplicity coincides with maximum bonding, as in the H_2 molecule. Thus, we should expect the two O^+ states to be ${}^3T_1^{(+)}$ and ${}^1E^{(+)}$, not ${}^3E^{(+)}$ as shown in Fig. 1(b). The appearance of the ODMR experiment of a zero-field splitting in a triplet or quartet (see below) spin state suggests, however, that the stable state formed from the ${}^3P$ of oxygen and the ${}^3T_2^{(+)}$ of the bonds is a spin triplet, ${}^3E^{(+)}$ instead of ${}^1E^{(+)}$. Support for this conclusion is found in the observation by Sturge[21] of a sample-dependent mixing between the two O^+ states in the PN experiment. Such a mixing should not occur if the two states had different multiplicities. The source of this unexpected spin in the bonded O^+ state is presumed to be the double JTE. Here the two coupling coefficients have opposite signs, and this effect favors combinations of electronic states which, in the absence of a JTE, would not give maximum bonding. More work is needed to clarify the nature of this bonding.

In the other multiplets the rule of minimum total spin is apparently followed. In particular, Dean *et al.*[10] find from Zeeman studies that the 1740-meV absorption line is from a spin doublet to a bound exciton formed from a zero-spin electron state and a quartet hole. Thus, the O^0 ground state is ${}^2A_1^{(0)}$, while the lowest O^- state observed is a spin singlet. The strength of this transition and the polarization observed in the Zeeman spectra show that this latter state has the same orbital symmetry as O^0 and is, hence, ${}^1A_1^{(-)}$. This transition is seen only in absorption and it is not known whether other, lower-energy, O^- states exist or not. The fact that the O^- state is not seen in emission, however, strongly suggests that there is at least one lower-energy state through which electrons recombine nonradiatively. This state, if it exists, could be a spin triplet from the ${}^1E^{(-)}$ vacancy state found in Ref. 17 or it could be another singlet (of different symmetry) formed from ${}^3T_1^{(-)}$. This latter suggestion has been incorporated into Fig. 1(b) and the further possibility indicated that the 528-meV transition may go into this lower-energy final state. The symmetry of this state has been shown as ${}^1T_2^{(-)}$, the state which optimizes the bonding between the ${}^3T_1^{(-)}$ and ${}^3P$ components. This assignment, which explains the vibronic satellites observed by Dean[10] in the final states of the 528-meV spectra, requires further experimental verification. Furthermore, it is possible that the 528-meV transition may occur between the ${}^1A_1^{(-)}$ and ${}^1T_2^{(-)}$ states, in which case the latter would fall near midgap about 1.1 eV below the conduction band.

3. *Similarities of triplet and quartet ODMR*

It is of interest to note that the simplest model places the ODMR resonance in a quartet associated with O^{0*}, because the lowest-energy state formed from a spin triplet and a doublet is a quartet. This interpretation differs from that in Ref. 8, which identified the state as a triplet. There is little difference, however, between the ODMR spectra of the two systems. This is because the central $m_s = \pm\frac{1}{2}$ components of a quartet are Kramers doublets and have equal decay rates. Transitions between them, therefore, do not alter the capture rate and are not seen in the emission intensity. Such a spectrum would show only the two resonances connecting $\frac{1}{2}$ to $\frac{3}{2}$ and $-\frac{1}{2}$ to $-\frac{3}{2}$ and would, hence, be nearly indistinguishable from a triplet resonance. One distinguishing feature which might appear in the quartet spectra is resonance associated with a second level crossing—one where the levels differ in spin component m_s by 1, as for a triplet, and another where the difference is 2.[22]

III. ANOMALOUS PROPERTIES OF O IN GaP

Returning to the experiments, we note that the first two items in Table I suggest that the same pair of states is involved in both the DAP and excitation (or capture) transitions. This fact, together with a desire to make the simplest assumptions, has led naturally to the CD. In addition, the assertion in the WBD that there are two O^+ states separated in energy by only 0.4 meV makes this new model seem unlikely unless the supporting evidence is strong.

The remaining five entries in the table, however, require for their explanation the nearly degenerate O^+ states and other states with properties in obvious disagreement with the CD—properties which are found to agree remarkably well with predictions of the WBD. This leaves little choice but to accept the apparently accidental near degeneracy of the O^+ states so that the more definitive consequences of the new model may be identified and tested. Furthermore, there appears to be no alternative explanation for two nearly degenerate O^+ states having different O-Ga separations and very different probabilities for transitions to the O^0 ground state.

In this section I discuss the interpretation, within the CD and WBD models, of the observed properties of O in GaP. In some cases the WBD is used in its vacancy approximation—the vacancy model or VM of Fig. 1(a)—while in others the more complex coupled defect of Fig. 1(b) must be used (see Sec. II).

A. Phonon "signatures"

The unusual phonon properties[6,9] are most clearly seen in a comparison of DAP spectra[12] with photoluminescence excitation (PLE) spectra from O^0.[13] Compare Figs. 13 and 19 of D1. In either transition, O^0 is transformed into O^+ by capture or release of a delocalized effective-mass (EM) particle. The two, however, show very different phonon sidebands. The PLE spectra are dominated by zero-phonon transitions, while in the pair spectra the dominant peaks are satellites involving what I have labeled type-A phonons. The most evident of these phonons, the 19-meV "breathing" mode of the neighboring galliums, is missing in the PLE spectra (as it is in electron capture).[23]

The only difference anticipated between the DAP and PLE transitions is that one involves holes and the other involves electrons. This difference should not alter the coupling of the deep center to the neighboring lattice atoms, for the EM electron or hole in each case is in an extended state many angstroms away from the defect. This anomaly conveys important information.

The modes appearing in the DAP spectra respond to local changes in the electronic configuration near the defect and, hence, provide a "signature" of the transitions taking place close to the defect (within about one lattice spacing).[6] There is always (weak) coupling to the LO phonon modes in an ionic crystal whenever a localized center changes its charge state, and this is observed in both spectra. The type-A modes, however, are excited by a shift in the equilibrium position of the Ga atoms during the transition, and this must, therefore, be occurring only in the pair spectra. Thus, in oxygen two *different* deep level transitions are being observed. As one of these is triggered by shallow bound electrons and the other by shallow bound holes, we conclude that either O^+ or O^0 consists of two nearly degenerate states, which differ in the way they couple to the conduction and valence bands.

B. Photoneutralization (PN) of O^+

Phonon differences in optical spectra are frequently not recognized as important or conclusive. The conclusion, however, that two different states are involved in the O^0/O^+ transitions is supported by more direct evidence given by the data on PN of O^+ from the valence band.[7] These show that the optical cross section for photoneutralization is the sum of two cross sections, σ_A and σ_B, weighted by the two temperature-dependent occupation probabilities P_A and P_B.[24] Thus,

$$\sigma = P_A(T)\sigma_A + P_B(T)\sigma_B \ , \tag{3}$$

where $P_B/P_A \propto \exp(-0.4\ \mathrm{meV}/kT)$. Although both start at the same energy, σ_A is produced by an allowed transition rising rapidly above threshold, while σ_B is forbidden and rises more gradually. This is strong evidence that O^+ consists of two very different thermalized states separated in energy at $T=0$ by 0.4 meV.[21] Although such complex structure cannot be explained within the CD,[10,11] it does fit naturally into the WBD, as is shown in Fig. 1.

C. Isotope-dependent satellites

The fifth item is a consequence of the coupling between the multiplets on the Ga bonds and the central O atom. It has three examples.[14]

(1) The O-dependent satellites of the 0.84-eV line are not consistent with the calculated phonon spectrum of the defect. The latter was found by Feenstra and McGill,[25] Fig. 56 of D1, to contain one or, at most, two local T_2 oxygen modes.[19] Yet *three* isotope-dependent satellites can be identified in the spectra[13] (see Fig. 17 of D1). These three satellites are readily understood if a JTE (Jahn-Teller effect) is present. They can be explained as transitions into excited vibronic states[26] derived from the electronic orbital triplets coupled to a single O-dependent T_2 vibrational mode. Furthermore, the coupling strength and mode energy $\hbar\omega$ can be estimated from the spectra.[14] Chapter 1 of Englman's book[26] makes it clear that in the (normal) JTE an orbital degeneracy is replaced by a vibronic degeneracy and that, in many experiments, static distortions need not be observed. Furthermore, in GaP:O the system is more complicated, as discussed above, because of the presence of a double JTE. The oxygen displacement couples (with approximately equal strength) to two orbitally degenerate states—the ^3P state of the central oxygen and the $^4T_1^{(0)}$ state of the Ga bonds.

(2) The structure in the PLE spectrum labeled $^3P_0$ in Fig. 19 of D1 is probably too strong for $^3P_0$ and can be explained instead in the same manner—as transitions into excited vibronic states of ^3P and $^3T_2^{(+)}$ coupled to the O displacements. This assignment should be tested in O^{18}-enriched samples.

(3) Finally, the anomalous satellites of the 528-meV emission,[27] Fig. 47 of D1, again suggest a $(T_1 \otimes T_2)$ JTE spectrum,[28] and this may also account for their unusual T dependence.[26]

The appearance of a JTE involving oxygen motion in these spectra indicates that the final state in each case contains an orbital triplet. It is significant that a JTE could not appear in any of these transitions for the nondegenerate states of the CD.

The phonon energies given by the JTE analysis, 14.3, 26.5, and 34.6 meV, are found to satisfy the equation

$$(\hbar\omega)^2=500(n_0-n)\ , \tag{4}$$

where $n_0=4.4$ if the number of electrons outside the oxygen is $n=4$, 3, and 2, respectively.[27,28] These values determine the O—Ga elastic constants,

$$K=M\omega^2=1.9(n_0-n)\ \mathrm{eV/\AA^2}\ , \tag{5}$$

which are plotted in Fig. 3. This equation and Fig. 3 show that a little more than four antibonding electrons are needed to reduce the O—Ga bond strength to zero—very nearly what is expected in the WBD where the bonding electrons occupy four p states and two much deeper s states.[14]

An interpretation based on the CD, on the other hand, is much less physically intuitive (see the scale at the top of Fig. 3). There $n_0=2.4$, and it would appear that only 2.4 antibonding electrons suffice to cancel the effect of six p and two s electrons in bonding states, an interpretation which is inconsistent with our usual concept of bonding. Bonding and antibonding levels are formed when two overlapping orbitals mix, with the lower-energy level moving down to stabilize the bond and the higher moving up. If both levels are occupied, the gain from the lowered bonding level is approximately canceled by the loss from the antibonding one. The argument is not rigorous, because we are placing two electrons in states which have been calculated for one, but it does show that the bond formed when both levels are occupied is expected to be much weaker than the pure bonding one.

The message of Eq. (5) may be stated somewhat differently. It is quite possible that the Ga—O bond strengths calculated within the CD would be as weak as those found experimentally. This is because in the calculated charge distributions[3] most of the bonding electrons in excess of the $2s^2 2p^4$ of neutral oxygen actually occur in the gallium bond region where their bonding effectiveness is low. Thus, the labeling of a state as "bonding" or "antibonding" may have little relevance to its function in lowering or raising the energy of the system, and by choosing only "bonding" states we may have gained little in bonding energy at a greater cost in exchange energy. A more useful description (and set of basis functions) would emphasize other aspects of the states, such as the spin-multiplet structure which determines their exchange and correlation energies. This is the approach favored in the WBD.

With the phonon energies discussed above, the WBD can also explain the measured isotope shift of 0.82 meV reported by Dean[10] for the 528-meV line, although it predicts a shift of about 1 meV for the 1.74-eV line, in only fair agreement with both measured values, 0.42 and 0.65 meV, reported in Ref. 10.[29]

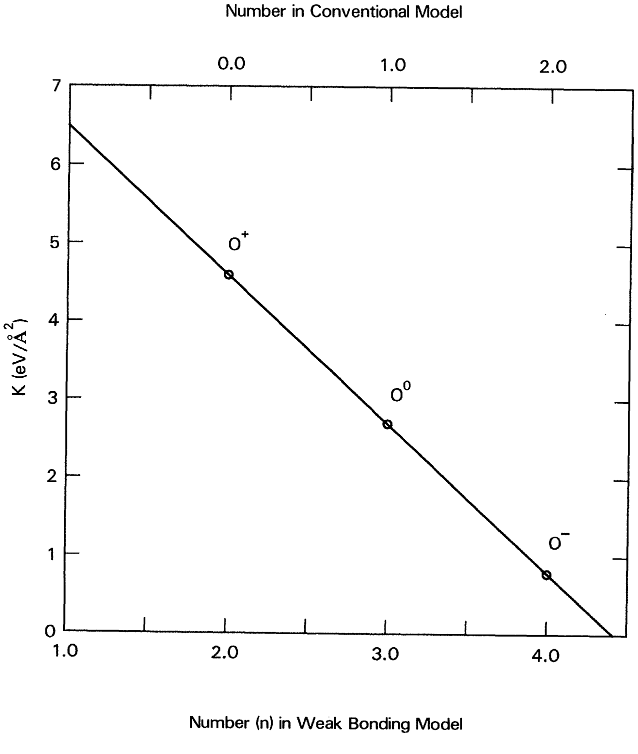

FIG. 3. Effect of n antibonding electrons on the oxygen-gallium elastic constant K for the lowest O^+, O^0, and O^- states. The scale at the bottom applies to the WBD ($n=2,3,4$); that at the top applies to the CD ($n=0,1,2$).

D. O^- energies

For the sixth entry in the table, the 1.74-eV absorption fits the interpretation given by Dean in Ref. 21 and D2—creation of a bound exciton on O^0—and the excited hole states in $(O^0,X)\equiv(O^-,h^+)$ agree quite well with his analysis. The 528-meV emission, on the other hand, is consistent with capture into the same O^- state, as required in the CD, only if the initial state lies 42 meV below the conduction-band edge, and there is a second state 4.5 meV higher. It is difficult to understand within the CD how even one such shallow electron state could be bound in the field of a compact, nondegenerate, *neutral* center.[30] In the WBD, however, there could be excited O^- states of depth near 42 meV associated with either the JTE or higher-energy O^- configurations and, further, as is shown in Fig. 1(b), there could be other choices of initial and final states than those originally assumed.

E. Optically detected magnetic resonance

1. General properties

The optically detected magnetic resonance (ODMR) on the 841-meV capture spectrum, referred to in the seventh entry in the table, has been discussed by Gal *et al.*[8] and interpreted within the CD.[5]

In this experiment an increase in the 841-meV emission intensity is induced by a spin resonance in the electron system showing a g factor near 2. The resonance appears to occur in a triplet system with a zero-field splitting of about 20 μeV which lowers $m=0$ relative to the $m=\pm1$

levels, and the symmetry axis is found to be along $\langle 110 \rangle$. Furthermore, both resonance lines show a quartet hyperfine splitting, and the high-field component is a factor of 10 more intense for left- than for right-circularly-polarized emitted light. The same resonances appear as an increase in the oxygen DAP luminescence but are completely absent in the 528-meV (O^-) emission.[31]

The interpretation proposed in Ref. 5 asserts that the triplet spin resonance could occur in an O^- state and modulate the population of O^0 through Auger capture of a hole. It is based on the assumption that during Auger decay of (O^-,h^+) an electron annihilates a hole, leaving the defect in an excited O^{0*} state. This explanation is completely inconsistent with the tenfold change in intensity of the resonance in right- and left-circularly-polarized emitted light,[8] which places the resonance unambiguously in one of the two states involved in emission and excitation and, most probably, in the initial emitting state.

Even accepting the assertion that the Auger model could work, one would find it difficult to account for the quartet nature of the hyperfine splitting and the $\langle 110 \rangle$ symmetry axis in the resonance. These two features are difficult to explain because the transition occurs in a point defect, an oxygen surrounded by four (spin-$\frac{3}{2}$) gallium nuclei, and any distortion which associates the oxygen with a single gallium, as needed for the hyperfine splitting, should have trigonal symmetry. A static JTE can generate trigonal $\langle 111 \rangle$ or tetragonal $\langle 100 \rangle$ distortions (not those of lower symmetry) and these only if degenerate states are involved.[26] It is significant that the WBD possesses all of the features needed to explain these ODMR results.

2. Interpretation within the WBD

The resonance appears as an increase in the 841-meV emission intensity and in the DAP emission and is markedly dependent on the (circular) polarization of the emitted light. This indicates that it is acting directly on the emission process, as is also consistent with the simultaneous increase in the DAP emission. Thus, a spin flip in the initial $O^{0*} = (O^+,e^-)$ state increases the population of the depleted fast capture channels at the expense of the slow ones, thus bypassing the slower channels and increasing the rate. This simultaneously increases the population of the O^0 state and enhances the DAP emission. A brief summary of the interpretation of the ODMR results within the WBD follows. A more comprehensive discussion appears in Sec. II C.

(1) The resonance occurs in the spin multiplet associated with the gallium bonds in the O^{0*} state (or in the total spin of the defect, including the spin of the $2p^4$ electrons on the neutral oxygen atom). Thus, a spin flip $\delta m_s = \pm 1$ increases the population of the most depleted spin levels, those with the greatest oscillator strength, and increases the light intensity emitted with the corresponding polarization, $\delta m = \pm 1$, as reported in Ref. 8. The spins on (at least) one Ga bond must be involved to account for the strength of the hyperfine coupling.

(2) The orbital part of each of the coupled systems is a triplet, ^3P ($= T_1$) for O and T_2 for the bonds (plus an a_1 EM electron). Hence, each is subject to a trigonal $\langle 111 \rangle$ JTE, and this associates the spin predominantly with one of the Ga atoms, as required by the hyperfine splitting.

(3) The JTE induces a displacement of the O atom which quenches the weak spin-orbit coupling of each system, leaving the g factor near 2, and splits states of differing $|m_s|$ value, as observed in the resonance. This displacement further increases the electron overlap with one of the four Ga nuclei.

(4) The two trigonal JTE distortions are opposite in sign and of approximately equal strength, so that the net displacement is along $\langle 110 \rangle$.

(5) The energy splittings found are of the order of a few microelectron volts, and so are not observable in most other experiments.

F. Stress splittings

The significance of point (5) in Sec. III E is apparent in the interpretation of the Zeeman effect and the transition rates. Many of the effects expected for large-spin systems, in particular spin-orbit splittings and momentum-II C, however, is found to generate vibronic ground states which remain unsplit under stress, so that these experiments agree with both models.

The same is not true of the O^- transitions near 0.53 eV. The CD predicts no splitting of the final state (the O^- ground state) and expects satellites which should duplicate any structure in the zero-phonon line. The WBD as shown in Fig. 1(b), however, predicts degeneracies and splittings associated with an orbital triplet and a normal JTE. (The Jahn-Teller coupling of the O distortion to the vacancy part of the wave function is expected to be absent in O^-.) Furthermore, the splittings of the satellites and the zero-phonon line may differ because of the differing symmetries of the ground and excited vibronic states. There are no published data on these experiments, but stress experiments on the O^- emission lines are in progress.[32] It will be most interesting to see what they reveal.

G. Zeeman splittings

The significance of point (5) in Sec. III E is apparent in the interpretation of the Zeeman effect and the transition rates. Many of the effects expected for large-spin systems, in particular spin-orbit splittings and momentum-dependent transition rates, are not observed in this system (except in the ODMR experiment). This has led to the argument by Dean and others[1,10] that this absence of telltale spin-orbit effects provided strong evidence that the simpler CD model was correct.

The reason for this absence of spin-dependent structure is now understood. It is a consequence of the very extended nature of the defect wave functions, which are restricted to the Ga bonds and couple only weakly to the O atom near the center. Spin-orbit and spin-spin interactions depend on terms which vary with radial distance r as $1/r^3$ or as $\delta(\vec{r})$ and are, hence, very small in these systems. The ODMR spectra give us our only experimental values. The hyperfine coupling is of the order of 5 μeV, and the spin-dependent splitting of the state which shows the resonance is 22 μeV.[8] Such small splittings would be unobservable in most other experiments.

The most pervasive reason for the absence of unusual spin effects, however, is the Pauli principle. The stationary states of the defect are complex multiplets formed by coupling the two-, three-, or four-electron vacancylike states on the gallium bonds to the six-electron ${}^3P$ multiplet of the central oxygen. The effect of this coupling, which is discussed in Sec. II C, is (with one probable exception) to make the most stable (lowest-energy) multiplets those of lowest total spin—thus optimizing the bonding between the two parts. As a result, the overall symmetries of the states (omitting fine structure) are as shown in Fig. 1(b), and most of the Zeeman data are found to be in agreement with both models, a situation not recognized in Ref. 10.

Because the spin-orbit splitting of the vacancylike multiplets is very small, one expects normal (three-line) Zeeman patterns in electron capture only for *spin-forbidden* transitions, i.e., where the weak spin-orbit coupling is responsible for the oscillator strength. The anomalous (unsplit) Zeeman patterns should appear only in *spin-allowed* transitions (where all spin components are conserved). When holes are involved, however (as in bound-exciton transitions), the strong valence-band spin-orbit coupling relaxes these selection rules and makes, effectively, all dipole transitions consistent with conservation of total angular momentum spin allowed.

The zero-phonon 841-meV transition shows a normal pattern[10] and is, thus, spin forbidden. It is presumed to arise from a transition between the ${}^1A_1^{(+)}$ and ${}^4T_1^{(0)}$ components of the vacancy (Ga bond) part of the wave function.[15] This is consistent with the observation that it shows the same O^{18} isotope shift as the DAP lines, which also involve the ${}^1A_1^{(+)}$ state. Capture transitions from ${}^3T_2^{(+)}$ to ${}^4T_1^{(0)}$, which one would predict to be spin allowed, are also forbidden, presumably because of $\vec{k}$ conservation.[9] It appears, however, that, because of the complexities of the double JTE, both O^+ states in the coupled system are spin triplets, and transitions from the upper state are also spin forbidden.[15] In either case, they appear strongly only in their phonon satellites, with assistance from the JTE. Furthermore, the 528-meV O^- capture transition, which shows an unsplit pattern, must be spin allowed and is forbidden only because of $\vec{k}$ conservation, as the WBD predicts. The initial O^{-*} state of this transition, which is, therefore, a triplet in the vacancy model, becomes a spin singlet ($s=0$) in the coupled defect, see below, and produces Zeeman spectra in complete agreement with experiment, contrary to the claims in Ref. 10.

IV. UNANSWERED QUESTIONS

It might appear from my presentation that all problems have been solved. I believe that qualitatively this is almost true, but there are many quantitative questions to be answered before our understanding of this remarkable defect could be called complete. Short of a general first-principles solution, the most basic problem remaining is the resolution of the differences between the one-electron theory used by Jaros[3] and by Baraff *et al.*[4] and the many-electron theory which is so successful in this system. Can the one-electron theory be extended to treat the many-electron states? Is there a strength of bonding for which the molecular-orbital approach will predict the same ground state as the conventional theory? Further work is also needed to understand the strengths of the bonds between the oxygen and the vacancy multiplets and the effect of these many-electron bonds on the Jahn-Teller displacements.

Much more work, both experimental and theoretical, is needed on the O^- system for which fewer data are available. This is especially true for the nonradiative transitions. In addition, further work is needed on the O^+ states to establish whether the near degeneracy is truly accidental or may be, instead, a consequence of a small interaction which splits a single state into two states having the observed properties.

Finally, the model should be tested in other defect systems for which the bond is expected to be fairly weak, to determine where the transition between the weak- and strong-bonding regimes occurs.[33]

V. SUMMARY

I have shown that the WBD provides a detailed qualitative explanation of essentially all the known properties of substitutional oxygen defects in GaP, and that this work has introduced new concepts and revealed failings in old ones in the following areas.

(1) Many-electron effects (exchange and correlation) are important and may even be the dominant factors in determining spin and symmetry properties of deep defect states in semiconductors.

(2) Bond orbitals may provide a more useful and natural basis than do the bands in describing defect electrons in deep states.

(3) Conventional single-particle theory is not appropriate for treating (at least) weakly bonded defect states. The idea that many-electron configurations can be constructed by filling up single-particle states must be used very carefully.

(4) Similarly, in interpreting ESR and other experiments on many-electron "vacancylike" defect states, the idea that a_1 and t_2 one-electron states are filled consecutively must be applied with caution.

(5) Unusual Jahn-Teller effects may appear when two orbitally degenerate and weakly bonded subsystems are vibronically coupled to the same lattice coordinate.

ACKNOWLEDGMENTS

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[1] See the review paper by P. J. Dean, in *Deep Centers in Semiconductors,* edited by S. T. Pantelides (Gordon and Breach, New York, in press). This paper, referred to as D1 in my text, summarizes the controversy surrounding oxygen in GaP, gives early references and reports new results.

[2] P. J. Dean, in *Proceedings of the 16th International Conference on the Physics of Semiconductors, Montpellier, 1982,* edited by M. Averous (North-Holland, Amsterdam, 1983), p. 140, Ref. D2 in the text.

[3] M. Jaros, J. Phys. C 8, 2455 (1975).

[4] G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. Lett. 47, 601 (1981).

[5] M. Gal, B. C. Cavenett, and P. J. Dean, J. Phys. C 14, 1507 (1981).

[6] T. N. Morgan, Phys. Rev. Lett. 40, 190 (1978). This work recognized that different sets of states were involved in the two transitions and proposed that the final state in the capture luminescence might be O^- rather than O^0. The arguments of Ref. 5, however, make it clear that O^0 and O^+ participate in both transitions.

[7] L. Samuelson and B. Monemar, Phys. Rev. B 18, 830 (1978).

[8] M. Gal, B. C. Cavenett, and P. Smith, Phys. Rev. Lett. 43, 1611 (1979).

[9] The basic (vacancy) model is described briefly by T. N. Morgan, Phys. Rev. Lett. 49, 173 (1982). More complete descriptions appear in *Proceedings of the 12th International Conference on Defects in Semiconductors, Amsterdam, 1982,* edited by A. J. Ammerlaan (North-Holland, Amsterdam, 1983), p. 131; *Proceedings of the 16th International Conference on the Physics of Semiconductors, Montpellier, 1982,* Ref. 2, p. 146.

[10] P. J. Dean, M. S. Skolnick, Ch. Uihlein, and D. C. Herbert, J. Phys. C 16, 2017 (1983).

[11] An alternative mechanism based on transitions between shallow excited acceptor states and the oxygen donor has been proposed in Ref. 10 to explain the PN results but has not been shown to account for the complex T dependence observed. One major problem with this mechanism is that it should show a *resonance* near the threshold rather than the broad (>300-meV) spectrum observed. It also appears very unlikely that such a small activation energy from *shallow* states could be generated in any but the purest semiconductors.

[12] B. Monemar and L. Samuelson, J. Lumin. 12-13, 507 (1976).

[13] P. J. Dean and C. H. Henry, Phys. Rev. 176, 928 (1968).

[14] T. N. Morgan, Phys. Rev. B 28, 6107 (1983).

[15] Note that for capture in the coupled model, Fig. 1(b), the initial state is formed when ${}^3T_1^{(+)}$ binds a $1S(a_1)$ EM electron to form a quartet and a doublet. The ${}^4T_1^{(0)}$ is expected, because of the exchange interaction, to lie below the doublet, and the final state is a spin doublet. Hence, in both models the capture transition from the lowest state is spin forbidden. The E state derived from ${}^3T_2^{(+)}$ is probably also a spin triplet. The exchange splitting between the quartet and doublet when the electron is captured, however, may be smaller than kT, making the capture transition appear spin allowed.

[16] H. G. Grimeiss, L. A. Ledebo, C. Ovren, and T. N. Morgan, in *Proceedings of the Twelfth International Conference on the Physics of Semiconductors, Stuttgart, 1974,* edited by M. H. Pilkuhn (Teubner, Stuttgart, 1974), p. 386.

[17] C. A. Coulson and Mary J. Kearsley, Proc. R. Soc. London Ser. A 241, 433 (1957) treated three ($+$, 0, and $-$) charge states of the diamond vacancy. G. T. Surratt and W. A. Goddard III, Phys. Rev. B 18, 2831 (1978); J. C. Malvido and J. L. Whitten, Phys. Rev. B 26, 4458 (1982) have calculated the neutral silicon vacancy. All three papers find for four electrons that ${}^1E^{(-)}$ lies lowest, and the last authors find ${}^3T_1^{(-)}$ 120 meV and ${}^5A_2^{(-)}$ 700 meV higher in silicon.

[18] A more careful analysis of this "double JTE" shows that for equal and opposite coupling the potential surfaces in Q space have rather flat minima perpendicular to the $\langle 100 \rangle$ directions and that the ground state is a doublet with vibronic components derived largely from the twelve $\langle 110 \rangle$ distortions. When both couplings have the same sign, however, the ground state is a singlet composed of the $\langle 111 \rangle$ vibronic components. In either case there is no first-order splitting or energy shift generated by an applied $\langle 111 \rangle$ stress.

[19] Chemist's notation is used for irreducible representations of the tetrahedral T_d group. The symbols a_1 and t_2 are reserved for one-electron states with upper-case symbols (often preceded by multiplicity and followed by charge superscripts) used for two or more electrons. In other groups I use the notation of G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-two Point Groups* (MIT Press, Cambridge, Mass., 1963).

[20] This analysis has assumed that the JTE would be dominated by coupling to the central O atom and has, hence, ignored coupling to the rest of the lattice.

[21] The PN experiment has been repeated by M. D. Sturge, who finds that the difference $(\sigma_A - \sigma_B)$ always exhibits the same dependence on photon energy but has a sample-dependent amplitude—M. D. Sturge (private communication). Such a dependence on sample properties is expected from a mixing of the two nearly degenerate states by local perturbations in the crystals.

[22] G. D. Watkins (private communication).

[23] It has been pointed out by R. M. Feenstra and by M. D. Sturge (private communications) that the satellites of the sharp PLE lines should appear weak because of the linewidths of the phonons. Hence, one cannot conclude that the 19-meV satellite is absent. One can conclude, however, from a careful comparison of the background and the satellites which do appear that the phonon couplings exhibited by the two spectra are not the same.

[24] See Fig. 55 of D1 or Fig. 15 of Ref. 7. In the latter figure the curves labeled $\sigma_{\mathrm{pl},B}$ and $\sigma_{\mathrm{pl},A}$ equal σ_B and $(\sigma_A - \sigma_B)$, respectively, of my Eq. (3).

[25] R. M. Feenstra and T. C. McGill, in *Proceedings of the 16th International Conference on the Physics of Semiconductors, Montpellier, 1982,* Ref. 2, p. 149, and private communication.

[26] See R. Englman, *The Jahn-Teller Effect in Molecules and Crystals* (Wiley, New York, 1972), especially Fig. 3.26 and Sec. 3.3.

[27] It seems probable that the 528-meV emission occurs within the O^- system, as proposed by Dean,[2,10] and not in O^0, as suggested in Ref. 9. This conclusion, which leaves the initial state in the 528-meV capture unexplained in the CD, is strongly supported by the low phonon energies and by Eqs. (4) and (5).

[28] Note that the phonon energies deduced from the spectra would not be significantly altered if the JTE were ignored.

[29] The smaller isotope shifts reported in Ref. 1 for the 1.74-eV absorption may not be reliable. In each case they were made by comparing different samples (private communication from M. Sturge and P. J. Dean). That this may be unsuitable is shown by the 0.7-meV width of the line (Ref. 10) and by some unpublished PLE data of Samuelson and Monemar (private communication) who found that a hysteresis shift of nearly 2 meV could occur in the 1.74-eV line.

[30] M. Jaros and S. Brand, J. Phys. C 15, L743 (1982).

[31] B. Cavenett (private communication).

[32] P. J. Dean (private communication).

[33] A triply degenerate internal structure predicted by the WBD for both the N^0 and N^- states in N-doped GaP has already been found to be in agreement with experiment. T. N. Morgan (unpublished).