PHYSICAL REVIEW B VOLUME 25, NUMBER 2 15 JANUARY 1982

Enfeebled oxygen bonding and metastability in GaP:O

G. A. Baraff, E. O. Kane, and M. Schlüter
Bell Laboratories Murray Hill, New Jersey 07974
(Received 23 September 1981)

Using the self-consistent Green's-function method, the self-consistent supercell technique, and a modified valence force model, we study the bonding of oxygen to the surrounding gallium atoms in the point defect GaP:O. Norm-conserving Hamann-Schlüter-Chiang nonlocal pseudopotentials are used in the self-consistent calculations. Total ground-state energies are obtained for the neutral state of this defect. We calculate a Ga$-$O bond which is surprisingly weak compared to that inferred from data on the GaO molecule and the Al_2O_3 crystal where, as in GaP:O, the oxygen atom is surrounded by four cations. A simple tight-binding model of the electronic structure accounts for the charge distribution found in the Green's-function calculation and makes plausible both the weakness of the bond and its marked softening with electron capture. The calculations imply that capture of a second electron to give O^- may weaken the Ga$-$O bond so much that, as suggested originally by Kukimoto and Henry, a completely different bonding configuration is more stable. The model does suggest that the original symmetric bonding configuration, although not necessarily the lowest-energy one, is, nonetheless stable against small displacements, i.e., metastable. We cite experimental evidence which supports its existence.

I. INTRODUCTION

The point defect GaP:O, in which an oxygen atom replaces a phosphorus atom in the GaP crystal, has been studied intensively for more than a dozen years and a wealth of experimental information has been acquired.[1] Interpretation of that information has led to controversy. In the past, calculations have been used to bolster one or another of the controversial interpretations. However, many of the calculations achieved agreement with experiment by making assumptions, e.g., about the band structure of the host crystal, about the wave function of the defect, or about the atomic positions, which could not be fully supported. Consequently, they were not as definitive as it was hoped they would be.

During the past three years, two new calculational tools have become available which have not yet been applied to the study of this defect: first, the highly sophisticated self-consistent Green's function techniques for calculating the electronic states, charge densities, and eigenvalues associated with an isolated point defect,[2,3] second, a new generation of first-principles, nonlocal pseudopotentials.[4] The utility of these pseudopotentials in calculating ground-state total energies with sufficient precision to account for structural and vibrational properties of solids has recently been demonstrated.[5]

In this paper, we apply these tools to the study of the defect GaP:O. The second section of this paper gives some of the experimental background about this defect and in general terms, some of our findings. The third section of the paper presents a molecular orbital model for interpreting the results. The fourth section describes the Green's function, supercell, and modified valence force calculations, which convince us that the Ga$-$O bond is unexpectedly feeble. The fifth section discusses in detail the theoretical arguments which lead us to believe that O^- has a metastable ground state. Its properties, aside from an energy shifted upwards by about 0.4 eV due to the electron repulsion, and aside from a finite lifetime against decay to the highly relaxed stable O^- ground state, are much like those of O^0, e.g., weak coupling to the lattice. We cite evidence which supports its existence. A short summary concludes the paper.

II. EXPERIMENTAL BACKGROUND AND OVERVIEW

Information about the detailed atomic positions at the defect is incomplete. Donor-acceptor pair (DAP) spectra have established that the oxygen is accurately substitutional on the phosphorus site and that the surrounding crystal retains the full tetrahedral symmetry.[6] The four adjacent gallium atoms are usually assumed to move radially towards the oxygen, preserving the full T_d symmetry, as in Fig. 1, because the oxygen is so much smaller than the phosphorus it replaces. The defect is known to exist in three different charge states, O^+, O^0, and O^-, and it is assumed that the charge state of the defect can influence the Ga-O equilibrium separation. Jaros has already calculated energy levels for this system, assuming that the Ga$-$O bond length for O^- is 0.55 a.u. *shorter* than for O^0.[7]

Although the DAP spectrum arises in an $O^0 \rightarrow O^+$ transition, it provides direct information only about the geometry of O^+: There is a Coulomb interaction $-e^2/\epsilon R$ between the oxygen donor in the state O^+ and the charged acceptor at a distance R. This interaction energy is absent in the state O^0 where both donor and acceptor are neutral. Consequently, the DAP spectrum does not give direct information about the geometry of O^0.

There are several pieces of indirect evidence which suggest that the oxygen in O^0 remains accurately in the same tetrahedral configuration as O^+: First, the lattice relaxation energy involved in going between O^0 and O^+ influences several observed emission and absorption energies. In each of these, the relaxation energy appears to be small, $\sim$0.085 eV.[6,8,9] This argues against a strong change in configuration. Second, Toyotomi and Morigaki observe electron spin resonance in the state O^0 and report only one g value.[10] This implies that the anisotropy of the g tensor is small. Although they suggest that the observed linewidth might be evidence of stress anisotropy, they do not call attention to site anisotropy. Third, Dean and Henry[8] note the absence of an expected no-phonon line in the photoluminescence excitation of O^0.[8] They interpret this absence as being caused by a selection rule. Other examples of the same selection rule appear in that spectrum. The selection rule breaks down if the oxygen moves off center. The data suggests that it has not broken down by much.

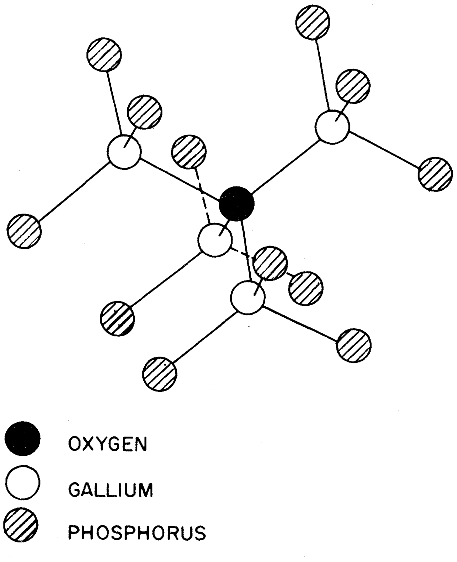

FIG. 1. Position of the atoms in the vicinity of the defect GaP:O before any lattice relaxation occurs.

There is an indirect theoretical argument which strengthens the proposition that O^0 has the full tetrahedral symmetry: All calculations (the present one included) of the state in which the electron resides assign it A_1 symmetry.[7,11,12] Therefore, no *linear* Jahn-Teller effect from small site distortions is present to lower the symmetry. Although an off-diagonal, or pseudo-Jahn-Teller effect may be operative, it is likely to give rise either to *no* site distortion or to *large* site distortion. The failure to find a large anisotropy of the g tensor and the failure to find a large breakdown of the selection rules can then be regarded as evidence of no site distortion. We assume, therefore, in our calculations of O^0 that the oxygen remains symmetrically bonded to each of the four adjacent gallium atoms.

The energy of the localized mode, their isotope shifts, and the isotope shift of the no-phonon line, all reported in the electron capture luminescence studies of Dean and Henry,[8] are important data for the present study. Dean and Henry identified two localized modes in which oxygen was involved. One of them, at 24.7 meV, was observed to shift by -1.6 meV when the isotope ^{18}O was substituted for ^{16}O. This shift was recognized as being 100% of what is expected if only the oxygen is moving while the other atoms are all at rest. In that case, the mode must be threefold degenerate, one mode for each of the three orthogonal directions along which the oxygen can vibrate. Its frequency, ignoring any bond bending forces, will be approximately

$$\omega_{\rm loc}=[\tfrac{4}{3}(K/M)]^{1/2}\,, \tag{2.1}$$

where K is the Ga$-$O bond stretching constant and M is the mass of the oxygen. A reasonable estimate of K, based on data from the GaO molecule and the Al_2O_3 crystal (see the Appendix), suggests that this mode should be at about 70 to 100 meV, not at 25 meV. There are only two explanations possible for the discrepancy: Either one or two of the bonds has already been broken and the oxygen is vibrating in a way that only weakly stretches the remaining bonds, or else the four Ga—O bonds in this situation are much weaker than estimated. The calculations to be presented here, although still quite rough in many respects, reinforce the second of these explanations.

Somewhat after the Dean-Henry work, Kukimoto, Henry *et al.*[13] discovered that the GaP:O center can capture a second electron. They suggested that the capture, producing O^-, was accompanied by a large lattice displacement, indicating that a substantial change in the O^--host bonds takes place. There is no direct information on what that new bonding configuration might be, and indeed, the large lattice relaxation itself has, in the past, been regarded as controversial.[14] Our calculations, although carried out only for the symmetric configuration, do reinforce the Kukimoto-Henry suggestion. They suggest that the symmetric configuration for O^- is *locally* stable—, i.e., that the GaO bond is not destroyed altogether but merely made so weak that there is only a small potential barrier over which the oxygen must pass to leave the symmetric bonding configuration on its way to the new bonding configuration which Kukimoto and Henry had proposed. We shall explore this idea further in Sec. V.

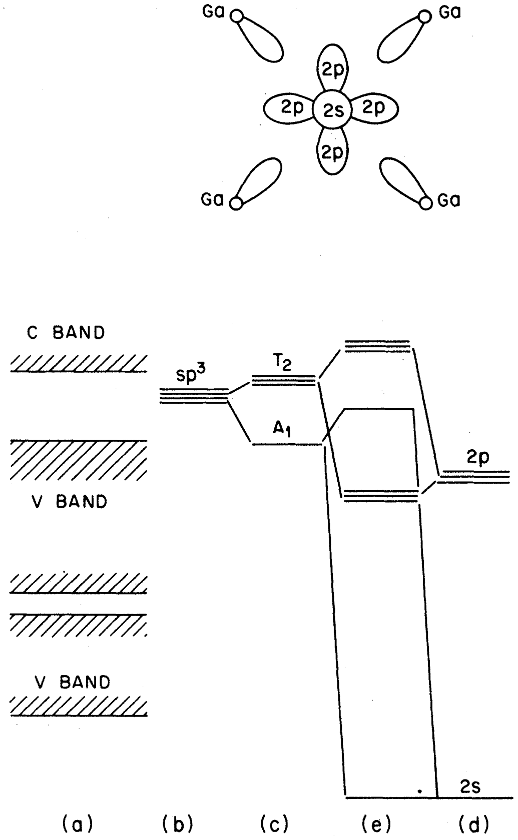

FIG. 2. Tight-binding model for the defect GaP:O (a) Density of states for perfect GaP crystal; (b) the four sp^3 broken bond orbitals; (c) A_1 and T_2 molecular orbitals, (d) at extreme right, the oxygen orbitals; (e) the molecular orbitals for GaP:O. Upper panel—a two-dimensional schematic representation of the orbitals from which the tight-binding model is built.

III. A DEFECT MOLECULE MODEL

Before describing the results, it is useful to have a simple orbital model to interpret them. Consider GaP:O as a phosphorus vacancy into which an oxygen atom will later be placed. (This idea also appears in Refs. 12 and 15.) The defect molecule for the phosphorus vacancy is built from the four dangling orbital on the four adjacent Ga atoms. In the tetrahedral environment, these four orbitals combine into an A_1 molecular orbital, which is the totally symmetric (*s*-like) combination, and a threefold-degenerate T_2 set of orbitals, the *p*-like combination of these four gallium dangling bonds. The A_1 state will be somewhat below the top of the valence band and the T_2 state will be about 2 eV higher, in the optical gap as shown in Fig. 2. The oxygen atom contributes three degenerate *p* orbitals whose energy is in the upper valence band of the GaP crystal, and an *s* orbital whose energy is about 15 eV lower than the *p* levels. This puts the *s* orbital about 8 eV below the bottom of the lowest GaP valence band, making it a "hyperdeep state" in the sense used by Hjalmarson *et al.*[15]

The oxygen *s* orbital interacts only with A_1 combination of gallium dangling bonds. The p_x oxygen orbital interacts only with the *x*-like partner of the T_2 combination of gallium dangling bonds. Bonding combinations are lowered in energy; antibonding combinations are raised. Interaction between the *s* level and the A_1 orbital is weak because of the large energy difference. The bonding A_1 state is therefore almost solely oxygen *s*, while the antibonding A_1 state, now pushed up slightly into the gap, is almost solely the four gallium dangling bonds. In this state, a nodal surface separates the oxygen from its four-nearest neighbors. Interaction between a p orbital and its corresponding T_2 partner is somewhat stronger because of the smaller energy difference. Thus, the bonding combination has a wave function ψ, made up perhaps of $\sqrt{2/3}$ oxygen p and $\sqrt{1/3}$ gallium dangling bonds, while the antibonding combination, now pushed up slightly into the conduction bands, has these weights reversed. (The weights given here are estimates based on integrating the charge centered on the oxygen as calculated in the next section, and reinterpreting that number in terms of a tight-binding set of orbitals. They are not precisely defined quantities and they will depend on the Ga—O bond length.)

For the defect O^+, these molecular orbitals must accommodate eight electrons, three from the four gallium atoms and five from the oxygen. The first empty orbital available to a ninth electron (O^0) or a tenth one (O^-) is thus the A_1 gap state, where the electron sits on the symmetric combination of gallium dangling bonds, and only minimally on the oxygen.

For all three charge states, the bonds holding the oxygen in the centered location consist of bonding T_2 states, all of which are occupied. It is evident from the geometry (which is depicted schematically as being two dimensional in the top panel Fig. 2), that spatial overlap between an oxygen p and the gallium dangling orbitals is going to be small. This suggests that the bonds between the oxygen and the gallium are likely to be weak. The small overlap occurs because the p orbitals of oxygen are directed along the six [100] directions, while the dangling orbitals for gallium are along the four [111] directions. Their overlap is significantly less than if they were directed towards each other as in a normal covalent bond. If the oxygen 2s were not so low, the oxygen could form sp^3 bonds which would overlap well with the gallium. The weakness of the bond thus comes about because so much of the gallium configuration is used to satisfy its bonding requirements to the rest of the crystal while the oxygen 2s is so low that the oxygen p states cannot take advantage of their environment. Admittedly, the normal oxygen bond is not covalent but is ionic, so this conclusion of weak covalent bonding is, by itself, premature. It is however, a hint of what will emerge from the detailed calculations which follow.

The ninth and tenth electrons, going into an *anti*bonding state, should weaken the bond. Thus, one would expect the Ga—O separation to be greater, for O^0, than for O^+, and for O^-, to be greater still.

IV. DESCRIPTION OF THE CALCULATIONS

A. Green's-function calculation

Calculations of the self-consistent charge density, eigenvalues, and eigenstates of the defect GaP:O were carried out using the self-consistent Green's-function technique in the manner described for the silicon vacancy.[16] The only essential new feature of the calculation here arises because a nonlocal pseudopotential is needed for the oxygen ion. In this calculation, all three ionic potentials (i.e., Ga, P, and O) are derived from all-electron, local-density-functional atomic calculations using the Hamann-Schlüter-Chiang (HSC) prescription.[4] In spectroscopic calculations, nonlocality is not so much needed for Ga and P as for oxygen, so for each of these two, a local potential, obtained by suitably averaging over the l-dependent potentials was used. The oxygen pseudopotential is given in Fig. 3. These calculations used the Wigner exchange-correlation form, a Gaussian-orbital basis, ten orbitals (s, p, d, and r^2) per decay constant, and two decay constants per atom. The decay constants were 0.2 and 0.5 a.u. for Ga and 0.2 and 0.8 a.u. for P. The tight Gaussian, 0.8 a.u., is

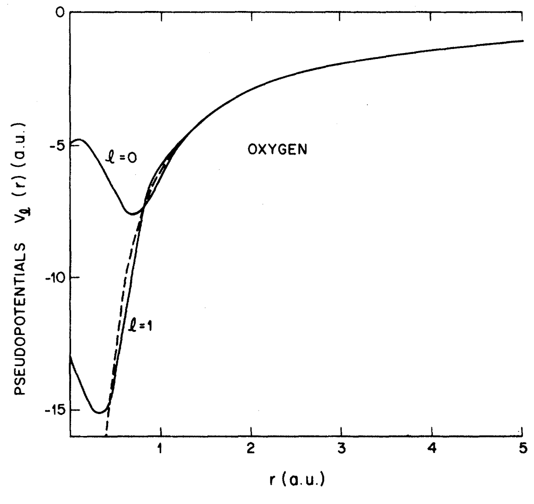

FIG. 3. Nonlocal Hamann-Schlüter-Chiang (HSC) pseudopotential for oxygen.

somewhat tighter than is optimum for the phosphorus in the band structure. It is a compromise that gives an adequate description of the oxygen atom which replaces the phosphorus in the defect calculation.

These calculations were carried out for oxygen in the undistorted tetrahedral position for charge states O^+, O^0, and O^-. Calculations, described elsewhere,[17] were also carried out for various amounts of breathing distortion, in which the four nearest neighbor Ga atoms were moved radially and equally towards the central oxygen. The results of interest from the Green's-function calculations for the undistorted crystal are as follows:

1. There is only one deep bound state in the gap. That state has A_1 symmetry. Its eigenvalue depends on whether it is populated by 0, 1, or 2 electrons. The difference between adjacent eigenvalues is 0.45 eV before lattice relaxation. Therefore, we conclude on the basis of Slaters transition-state argument that the electron repulsion U, the *extra* energy cost to add an electron to this state if it already contains one electron and does not relax, is 0.45 eV.

The charge density for this state is shown as a contour plot in Fig. 4, and is plotted radially along the [111] direction in Fig. 5. Both figures make it clear that this is the antibonding state whose charge is predominantly associated with the gallium dangling bonds. The charge centered on the oxygen and lying within the nodal sphere is about 1% of the charge in the state.

2. The total charge in the bonding region is reduced by the oxygen. Figure 6 depicts the total valence charge density for the perfect GaP crystal, for the neutral GaP:O defect, and the difference between these two. The charge densitites, plotted along the [111] direction, are shown in Fig. 7. (None of these plots contain the contribution of the hyperdeep A_1 state, which is essentially the oxygen s orbital and extends out to less than 2 a.u.) Both figures show that the oxygen has attracted charge from the covalent bonding position to itself.

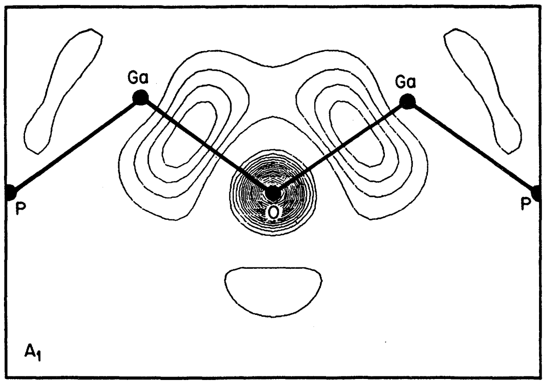

FIG. 4. Charge-density contour plot, in a (110) plane, of the A_1 gap state of GaP:O. Notice that the charge resides on the gallium dangling bonds. The small accumulation of charge on the oxygen holds about 1% of the total charge in the state.

The integrated electronic charge in the neighborhood of the oxygen out to a radius of 2.5 a.u. (counting also the two electrons in the hyperdeep state) is about $-6.5e$, so the integrated total charge within this region, including the $+6e$ core, is $-0.5e$, a negative charge. The charge in the A_1 gallium dangling-bond state, which is singly or doubly occupied for O^0 or O^-, lies beyond this radius. It will be repelled by the negative oxygen in the center. This will push the gallium atoms *away* from the central oxygen as electrons are added to the defect, quite the opposite of what Jaros's calculations had assumed,[7] but in accord with what the antibonding (i.e., bond weakening) character of the A_1 state would imply. Other aspects of the Green's-function calculation, discussed in Ref. 17, provide detailed support for the simple molecular orbital molecule picture as described in Sec. III.

B. Supercell calculations

Self-consistent band-structure calculations of the total energy for crystalline silicon, diamond, and GaP have been carried out elsewhere using Hamann-Schlüter-Chiang norm-conserving nonlocal pseudopotentials in a basis of twenty Gaussian orbitals (s, p, d, and r^2, each with two decay constants) per atom.[18] The Gaussian decay constants

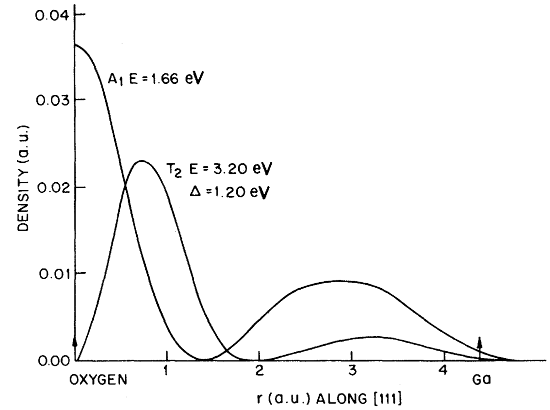

FIG. 5. Charge density for state shown in Fig. 4 plotted along the [111] direction.

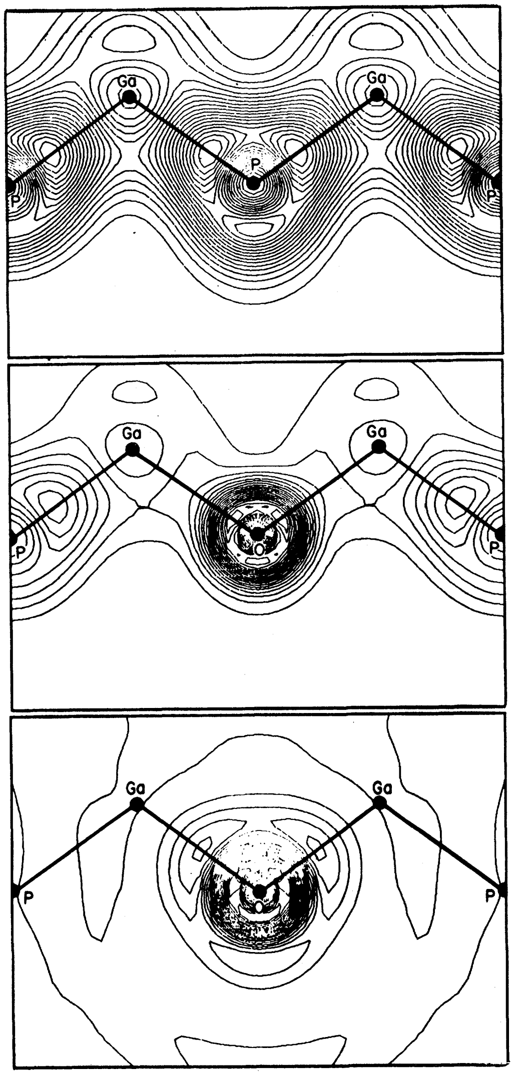

FIG. 6. Charge densities in the (110) plane for the perfect GaP crystal, (top panel), the GaP:O defect (middle panel) and the difference between the two (lower panel). The charge density in the hyperdeep state is not included in this figure.

were varied to minimize the total energy at the known lattice constant and then the total energy was recalculated, using these fixed orbitals, for several lattice constants. The calculated lattice constant and compressibility were in good agreement (i.e., $\lesssim 4\%$) with experiment. We now use the same potentials, orbital basis, and r-space technique to calculate the total energy per unit cell of a periodic array of GaP:O point defects. In the limit of large separation between defects, that energy would approach the energy of a single isolated GaP:O point defect. Total energy calculations, in contrast to the spectroscopic eigenvalue calculations of Sec. IV A, require use of the nonlocal potentials. For gallium and phosphorus, the potentials are depicted in Figs. 8 and 9. The supercell technique, as are all techniques for studying the total energy of an infinite periodic system, can be used only for a unit cell which is electrically neutral. Consequently, in our study of GaP:O, we can calculate only for O^0. The purpose of this total energy calculation is to determine the elastic restoring forces governing the motion of the oxygen with respect to the fixed crystal. We can do this (see below) without lowering the symmetry of the defect point group, by studying a breathing distortion of the gallium atoms about the oxygen.

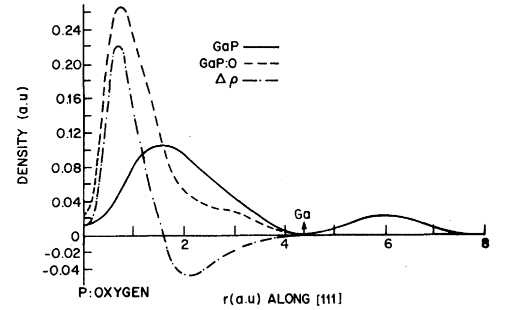

FIG. 7. Charge densities of Fig. 6, plotted numerically along the [111] direction.

Experience has shown that the bound-state eigenvalues, require very large supercells for convergence,[19–21] presumably because of overlap of the wave function from one unit cell to the next. The total energy, on the other hand, can be expressed in terms of the local density, the kinetic

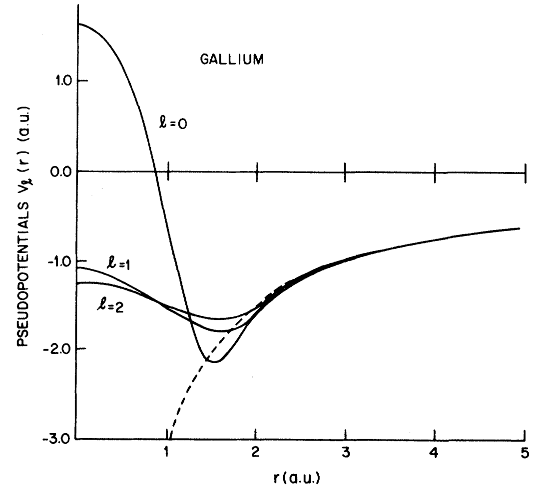

FIG. 8. Nonlocal Hamann-Schlüter-Chiang pseudopotential for gallium.

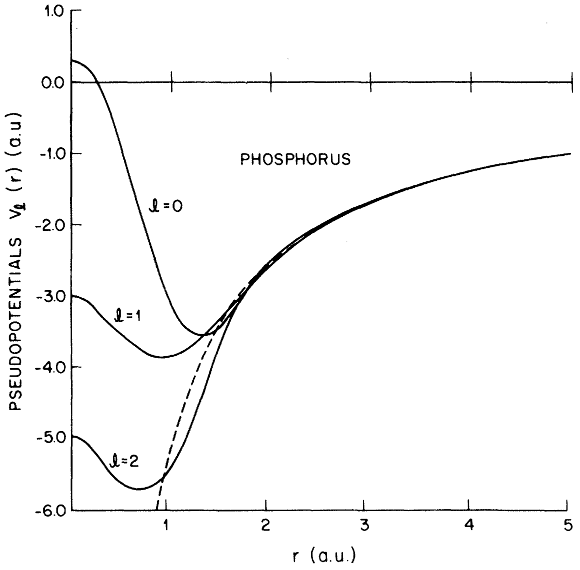

FIG. 9 Nonlocal HSC pseudopotential for phosphorus.

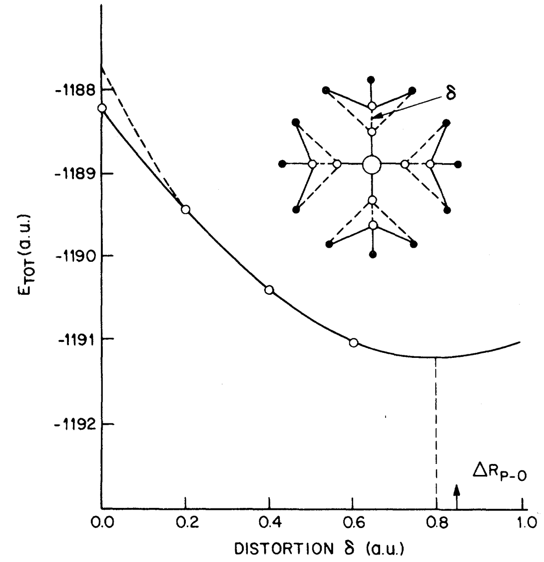

FIG. 10. Total energy per unit cell for the breathing distortion as calculated using a supercell in which adjacent oxygen atoms are separated by four bonds, as a function of the gallium motion towards the oxygen.

energy density and the ionic positions without using any eigenvalues at all. Therefore, it is likely to converge once the supercell is large enough to enclose the charge disturbance around the point defect. It has been demonstrated repeatedly that the bound-state eigenfunctions extend much farther from a defect than does the charge disturbance.[2,3,22] For this reason, one would expect that the total energy would converge to the point-defect limit using a much smaller supercell than would be needed for studying the bound-state eigenvalues.

A weakness in the calculation presented here is that we have not recalculated for larger size supercells. We are therefore unable to place limits on how well the calculation corresponds to the isolated defect limit. However, if we ask only the very rough question—is the Ga—O bond a strong one (i.e., comparable to that inferred by analogy with Al_2O_3) or a weak one (e.g., considerably weaker than the bonds in the host GaP crystal), the answer provided by this minimal sized supercell calculation is—a weak one. We believe that a better converged calculation would show it to be weaker still.

The supercell chosen describes a periodic array of oxygen atoms substitutional on phosphorus sites in the GaP crystal, forming by themselves a simple cubic lattice. Each oxygen is separated from its nearest oxygen neighbor by a chain of four bonds along which the sequence of atoms is O-Ga-P-Ga-O. The simple cubic supercell has 4 times the volume of the primitive unit cell of GaP. It consiste of a face-centered cubic sublattice of phosphorus sites and, displaced by $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, a face-centered sublattice of gallium sites. In the phosphorus sublattice, the sites at the cube corners are occupied by oxygen atoms, the face-centered sites in this sublattice are occupied by phosphorus. If the oxygen atoms were changed back to phosphorus, the supercell would describe, in an inefficient way, a pefect Ga-P crystal.

Such a supercell is large enough to contain the charge distrubance about the substutional oxygen atom in the unrelaxed GaP:O crystal. That disturbance is virtually identical to the Green's-function result shown by Fig. 6. However, we now consider breathing-mode distortions about the defect. In their presence, the isolation of one defect from the next is not as good as in their absence.

The breathing distortion around the oxygen is simulated by moving each gallium atom radially inwards towards its nearest-neighbor oxygen by the same given amount. The phosphorus atoms and the oxygens remain fixed. Total energy, in electron volts per unit cell, was calculated for the four displacements shown in Fig. 10, using *r*-space calculational technique of Ref. 18. The solid curve shown is a parabolic fit to the three largest displacements considered. A fifth calculation at or beyond the minimum was not carried out because the supercell gap states start to cross into the supercell valence band if the relaxations are made larger, rendering self-consistent calculations ambiguous.

By itself, the curve of Fig. 10 implies an equilibrium gallium distortion of 0.8 a.u. towards the oxygen. This is almost exactly the difference in radius between the oxygen atom and the phosphorus it replaces. The spring constant $[\Delta E=\frac{1}{2}k_s \times(\Delta x)^2]$, obtained by fitting the parabola in Fig. 10, gives $k_2=10$ eV/(a.u.)^2=35.7 eV/Å^2. However, the spring constant and equilibrium distortion quoted here are misleading. They will not apply to the isolated defect until sizable corrections, described in the next section, are introduced.

C. Valence force calculations

We are in interested in calculating the restoring force acting on oxygen bonded symmetrically to its four nearest-neighbor gallium atoms in the GaP crystal. Consider instead a five-atom cluster, made up of a central oxygen surrounded by four tetrahedrally placed gallium atoms, each of which interacts only with the central oxygen. If the spring constant between the oxygen and a single gallium atom is K, then the change in energy caused by moving each of the four gallium atoms towards the oxygen by an amount ΔX will be

$$\Delta E_b=4[\tfrac{1}{2}K(\Delta X)^2] . \tag{4.1}$$

On the other hand, if the four gallium atoms are held fixed and the oxygen moves directly towards one of the four by an amount ΔX and away from the other three at an angle $\theta=\cos^{-1}(-\frac{1}{3})$, then the change in energy will be

$$\Delta E_T=\tfrac{1}{2}K(\Delta X)^2+3[\tfrac{1}{2}K(\Delta X\cos\theta)^2] \tag{4.2a}$$

$$=\tfrac{1}{3}\Delta E_b . \tag{4.2b}$$

The symmetry of the situation is such that (4.2) describes the energy change for *any* direction of oxygen displacement. Displacement of the oxygen in any of the three orthogonal directions gives rise to a local mode having the frequency described by Eq. (2.1). It is by this argument that the change in energy caused by a breathing distortion, such as we calculated using the supercell, can be related to the local-mode frequency. This argument neglects the change in energy caused by bond bending, which will contribute to (4.2) but not to (4.1). That energy change is small however, because the bond bending forces in GaP are so much smaller than the bond stretching ones.

The energy change ΔE_b, calculated using the supercell as we described it in the last subsection, has a contribution from the compression of the Ga—O bonds, which we are interested in, and a contribution from the stretching and bending of the Ga—P back bonds, which we want to estimate and discard. In order to do so, let us consider a related problem, namely, a particular breathing distortion about a phosphorus vacancy in an infinite GaP crystal. The four nearest-neighbor gallium atoms are displaced radially inwards towards the vacancy by a distance ΔX. Instead of allowing the rest of the crystal to relax inwards following the motion of the gallium atoms, imagine it to be held rigidly fixed. The change in energy caused by the motion ΔX is primarily contributed by the stretching and bending of the Ga—P back bonds cited above. Therefore, subtracting this particular breathing distortion energy from the energy we calculated via the supercell technique will give an approximation to the energy change caused solely by the compression of the Ga—O bonds.

The energy change for this particular breathing distortion about the phosphorus vacancy in a GaP crystal has been calculated *exactly* within a two-parameter Keating force-constant model, similar in detail to that we used for calculating the spring constant around the silicon vacancy.[16] The parameters were chosen, as they were in our silicon work, by fitting the compressibility of the GaP crystal (this determines the bond stretch parameter α since β, the bond bending parameter is so much smaller) and retaining the β/α ratio we determined for the silicon vacancy. The motivation for this latter choice is that Martin's work determining Keating-model parameters shows that β/α for GaP is almost exactly the same as for silicon,[23] while our own work for silicon showed that, for describing these highly localized distortions, a β chosen to fit the lowest phonon branch over the whole zone is a more appropriate choice than is one, such as Martin's which fits only at the zone center.[16] We took $\alpha=50.3$ and $\beta=4.59\times10^3$ dyn/cm. The energy change, calculated for a displacement ΔX, is

$$\Delta E_v=\tfrac{1}{2}k_v(\Delta X)^2 \tag{4.3}$$

with $k_v=18$ eV/Å^2=5 eV/(a.u.)^2.

V. DISCUSSION OF RESULTS AND THE METASTABLE O$^-$

By subtracting the energy change of the back-bond stretching from that of the supercell calculation, we obtain the energy change due to the Ga—O bond compression alone. Thus, in Eq.

(4.1), we have $4K=k_s-k_v=35.7-18=17.7$ eV/Å^2. This gives a Ga—O bond stretching constant of $K=4.4$ eV/Å^2, which is about half as strong as the covalent gallium-phosphorus bond constant, estimated from the compressibility of the GaP crystal, and about $\frac{3}{4}$ of the 6.1 eV/Å^2 Ga-O force constant which Jain and Prabhakaran had estimated.[24] The localized mode frequency (2.1) resulting from this bond is $\hbar\omega_{\text{loc}}=39$ meV. This is still more energetic than the observed 24.7 meV but it is far below the 70 to 100 meV we had anticipated based on data from the GaO molecule. It lends support to the idea that the oxygen is bound by four rather weak bonds rather than by two or three stronger ones which it does not stretch.

If this view is accepted, it becomes possible to work back from the experimental data in the Dean-Henry paper[8] and to deduce Ga-O force constants for the states O^+, O^0, and O^-. Let us outline the argument we shall now make: We accept the idea that the Ga—O bond will be weak, but we make no use of the approximate value we have just calculated. Instead, we set up a model, based on its calculated weakness, from which the bond stretch constant can be extracted from an observed localized mode. The value, so extracted, is, in fact *very* weak, and so justifies, *a posteriori*, the use of the model. The rest is simply an extrapolation, using ideas which emerge from the calculated forms of the states involved, to situations where observations have not yet been made.

We start by considering the vibrational properties of an oxygen atom on a phosphorus site and bound, via the four gallium atoms at the nearest-neighbor tetrahedral positions, to the rest of the crystal. Our total energy calculations have just shown that the Ga—O bond is considerably weaker than the Ga—P bonds. We can idealize this situation immediately by treating the rest of the crystal, compared with the flexibility and lightness of the oxygen, as being infinitely massive and rigid.

Recall that if the oxygen moves directly toward one of the Ga atoms by ΔX and away from the other three at an angle $\theta=\cos^{-1}(-\frac{1}{3})$, the change in energy due to bond stretching is

$$\Delta E=\tfrac{1}{2}K(\Delta X)^2+3\tfrac{1}{2}K(\Delta X\cos\theta)^2\ ,$$

where K is the Ga—O bond stretching constant. Ignoring the bond bending contribution to the energy change as a small correction, we get the vibrational frequency of Eq. (2.1), namely,

$$\omega_{\text{loc}}=(4K/3M)^{1/2}\ , \tag{5.1}$$

where M is the mass of the oxygen atom. The symmetry of the situation is such that the direction of the displacement does not matter. Thus, there are three independent modes, one for each orthogonal direction of displacement, having this frequency. If the usual ^{16}O isotope is replaced by ^{18}O whose mass is greater by ΔM, the corresponding change in frequency is

$$\Delta\omega=-\tfrac{1}{2}\omega_{\text{loc}}(\Delta M/M)\ . \tag{5.2}$$

Dean and Henry,[8] observing electron capture into the ground state of O^0, noted two modes, one at energy 24.7 meV and one at 28.4 meV, whose energies shifted by -1.6 and -0.5 meV, respectively, under this isotopic substitution. These shifts are 100% and 28%, respectively, of what is to be expected from Eq. (5.2). On that basis, the 28.4-meV mode must have some gallium and/or phosphorus motion, and must therefore involve more bonds than just the Ga—O bond, while the 24.7-meV mode must have only oxygen motion and must therefore be described by Eq. (5.1). Using Eq. (5.1), we obtain $K^0=1.77$ eV/Å^2, which is about $\frac{1}{5}$th of the Ga—P bond stretching constant as estimated from compressibility. Our reluctance to commit ourselves to accepting the tetrahedral configuration for O^0 in an earlier study[17] was based on the above finding: We were skeptical that a bond involving oxygen could be so weak until we actually obtained the 4.4-eV/Å^2 result in our rough calculation.

Now let us consider the isotope shift of the no-phonon line: Dean and Henry observed luminescence at 0.841 eV, and ascribed it to an electronic transition from an excited effective-mass-like state of O^0 (with an electronic density like that of O^+ near the oxygen) to the ground state of O^0. The energy of this no-phonon line was observed to shift by -0.72 meV (Refs. 8 and 25) on substituting ^{18}O for ^{16}O. If when ^{16}O is replaced by ^{18}O, the mass M_1 associated with the ith mode changes by δM_i and if ω_i, the frequency in the mode in the final state of the electronic transition, and $\omega_i+\Delta\omega_i$, the frequency of the initial state of the electronic transition, are both proportional to $(M_i)^{-1/2}$, then the isotope shift of the no-phonon line in that electronic transition will be[8]

$$\Delta E=-\tfrac{1}{4}\hbar\sum_i\Delta\omega_i\frac{\Delta M_i}{M_i}\ . \tag{5.3}$$

Although the sum extends over all modes showing oxygen participation, we now argue that only the threefold degenerate mode at 24.7 meV makes an appreciable contribution to the sum. There are two reasons for this: Firstly, $\delta M_i/M_i$ for the other mode is only 28% of what it is for the 24.7-meV mode. Secondly, our Green's-function calculations of the charge distribution for the bound (ground) state of O^0 shows, as is evident in Figs. 4 and 5, that the charge is astride the Ga—O bonds and barely present near other bonds. Hence, the strength of the other bonds will not depend on the charge state of the defect. This means that $\Delta\omega_i$ for the 28.4-meV mode will also be comparably small since that mode also involves other bonds in addition to the Ga—O bond. We can thus solve Eq. (5.3) for the energy shift of the 24.7-meV mode, the only unknown there, and (recalling the threefold degeneracy) we obtain $\hbar\Delta\omega=7.7$ meV. This gives $24.7+7.7=32.4$ meV as the energy of the comparable mode in O^+, and from Eq. (1), the corresponding spring constant is $K^+=3.04$ eV/Å^2.

It is interesting to note that the frequency ratio $\omega^0/\omega^+=24.7/32.4=0.76$, which is very close to the ratio 0.78 Henry and Lang[26] needed to account for hole and electron capture rates σ_{nl} and σ_{pl} in their configuration coordinate diagram. This suggests that the appropriate configuration coordinate strongly involved stretching of the Ga—O bond.

Capture of the first electron into O^0 has weakened K by $3.04-1.77=1.27$ eV/Å^2. The initial phase of the capture of the second electron into O^- involves, before the defect has had time to relax, a capture into the same state as the first. At small distortions, it should therefore produce the same change in spring constant as was produced by capture of the first electron. On this basis, we expect $K^-=1.77-1.27=0.50$ eV/Å^2. This is exceedingly weak, about $\frac{1}{6}$ of K^+ and about $\frac{1}{18}$ of the Ga—P bond stretch constant. It is then very likely that some rebonded configuration, such as that ascribed to O^- in the DHK model, is more stable. Nonetheless, K^- is positive and, using Eq. (5.1), it produces a localized mode with 100% oxygen participation at 13.1 meV. Use of Eq. (5.3) now predicts an isotope shift of 1.0 meV for the no-phonon line in the O^0 to O^- electronic transition.

Let us temporarily ignore the rebonded configuration of O^- and summarize what we have without it. There are three stable charge states having O in a tetrahedral position. There is one deep bound state in the gap whose charge density is given in Figs. 4 and 5. Populating it with 0, 1, and 2 electrons gives O^+, O^0, or O^-. Our self-consistent Green's-function calculation of the three eigenvalues indicates that the level for the capture into O^- lies 0.45 eV above the level for capture into O^0 before lattice relaxation. The observed relaxation of 0.085 eV for the first electron lowers this to 0.37 eV, so that the binding energy for O^- is $0.893-0.37=0.52$ eV. Aside from certain obvious differences in detail, the transitions into O^- should be like the transitions into O^0. In particular, the lattice relaxation should in both cases be nearly equal, namely, about 0.085 eV, which is very small. If we now include the rebonded O^- configuration, then the O weakly bonded centered O^- is likely to be only mestastable, since the energy normally associated with forming two new bonds is likely to be large, while the energy to keep the O^- centered is, as we have just seen, very small. We suggest that two experiments can be interpreted very simply if we postulate the existence of a centered metastable O^- level at ~0.52 meV below the conduction band.

The first is unpublished work of Bachrach,[27] who found a sharp O-related absorption line at 1.738 eV, which he interpreted as creation of a bound exciton at an O^0 center. Subtracting 1.738 eV from the band gap, 2.34 eV, and correcting for the hole binding energy using an effective-mass estimate of 0.05 eV, he determined an O^- level at 0.55 eV. This absorption line appeared only for a Fermi-level range between -0.89 eV and -0.55 eV relative to the conduction band, indicating the need for the presence of O^0 and the absence of O^- in the initial state of the absorption process.

We agree with this interpretation and would alternatively describe the bound exciton as the O^- metastable configuration, two electrons in the A_1 state, accompanied by a loosely bound (effective-mass-like) hole. Dean,[28] commenting on the preprint in which the metastable state was first proposed,[29] suggested that such a centered metastable state of O^- would probably decay by Auger emission, i.e., nonradiatively. Some evidence supporting this is provided by Fig. 11, taken from Sameulson's thesis,[30] which shows a *dip* in the luminescence intensity when the photons incident on GaP:O had an energy of 1.738 eV. The incident phonons at this energy apparently create this bound, nonradiative, exciton at the expense of other, radiative, excitations.

The second experiment is a series of O-related emission lines reported in Ref. 25, whose highest energy component lies at 0.528 eV. Our interpretation is that this line results from capture of an electron from the conduction band or a high-lying excited state into the metastable ground state. The difference between 0.55 and 0.528 eV would then be attributed either to the binding energy of the excited state or to a hole binding energy greater than the 0.05 eV estimated by Bachrach. The two sharp lines at 0.520 and 0.517 eV are probably local-mode phonon replicas of the weak no-phonon line at 0.528 eV. We note that in the O^0 emission, there are also two local-mode replicas of the weak no-phonon line. In the O^- situation, we have predicted a local mode due to oxygen alone at 13.1 meV. This is close to the 11-meV difference between the 0.517-eV line and the weak 0.528-eV line. We do not have a complete explanation of either the 28.4-meV O^0 or 8-meV O^- lines, but we feel that they are probably related to modes in the unperturbed phonon spectrum to which are weakly coupled the closely adjacent oxygen vibrations (24.7 or 11 meV) in the two cases.

The question of the metastable lifetime is a difficult one. If the only motion to go from the metastable to the rebonded configuration were that of oxygen, one would expect the lifetime to be rather short. If substantial rearrangement of the surrounding gallium atoms is also required, it could be much longer. We feel that we have made a strong case that the metastable transition has been observed. This argues for a substantial gallium distortion, such as would be expected for a rebonded configuration as suggested by Henry and Kukimoto.

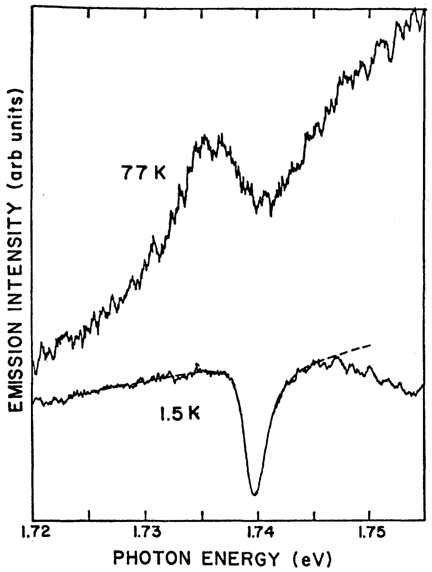

FIG. 11. Emission intensity vs photon energy for GaP:O taken with permission from thesis of Lars I. Samuelson, Ref. 30.

As we have stressed, because the O^- bond is so very weak, it is quite likely that the oxygen can reach a lower energy situation by moving off center to establish a more favorable bonding configuration. One asymmetric possibilty, certainly not the only one, is like that proposed for the Si-*A* center, where the oxygen bonds to two of its four nearest neighbors. There are then six equivalent configurations available, each with oxygen bonded to a different pair of gallium atoms. The possibility of a stable asymmetric configuration for O^- suggests the use of uniaxial stress experiments where oxygen can be made to sit preferentially at one or another of the equivalent asymmetric positions, and ultrasonic absorption experiments, in which oxygen is induced to move from one to another equivalent asymmetric position as a probe of the geomtery.

Situations of still lower symmetry are not ruled out. For example, the *A*-center geometry proposed here need not be fully symmetric with respect to mutual interchange of either the two gallium atoms to which the oxygen bonds, nor of the two remaining gallium atoms. Recent calculations of the pairing reconstruction on the (100) silicon surface[31,32] have shown that, in spite of the equivalence of the two surface atoms forming the new pair bond, a tilted bond, where one of two otherwise equivalent atoms is up and the other is down, has lower energy. The same asymmetry, rendering different two *a priori* equivalent atoms, could occur in the *A*-center geometry proposed here, so that the oxygen is not bonded equally to the two gallium atoms.

TABLE I. The state O^- is predicted to have a metastable configuration similar to the tetrahedral centered configuration observd for O^+ and inferred for O^0. The localized phonon mode at $\hbar\omega_{\rm loc}=24.7$ meV observed in O^0 will have counterparts in O^+ and O^0 with the properties below. $X_{\max}$ is the classical maximum distortion for the zero point vibrational phonon energy, $\frac{1}{2}KX^2=\frac{1}{2}\hbar\omega_{\rm loc}$.

State	$\hbar\omega_{\rm loc}$ (meV)	Ga—O bond K (eV/Å^2)	$X_{\max}$ (Å)
O^+	32.4	3.04	0.09
O^0	24.7	1.77	0.10
O^-	13.1	0.50	0.14

VI. SUMMARY

In this paper, we have studied the electronic structure of GaP:O using a combination of self-consistent Green's-function calculations, self-consistent supercell calculations, and a modified Keating model. The self-consistent calculations were carried out using Hamann-Schlüter-Chiang norm-conserving pseudopotentials which, for Ga and P, have elsewhere been shown to give the correct lattice constant and compressibility for the infinite crystal. A tight-binding molecular orbital model was proposed which accounted for the spatial form of the states, which suggested that the Ga$-$O bond is weak and which suggested that the bond will be further weakened as more electrons are added to the defect. The quantitative calculation of the Ga$-$O bond predicted that it was *very* weak. One can understand that, in spite of the observed softness of the oxygen local phonon, all four bonds to the oxygen are intact. This lead to a specific model which made it possible to extract from experimental data on $O^0 \rightarrow O^+$ transitions alone the values given in Table I for the Ga-O bond. This strongly reinforces the idea that rebonding—perhaps to a silicon$-A$-center configuration—occurs. We suggested that O^-, in the symmetric configuration at low temperatures, is metastable and we discussed some of the characteristics by which such a configuration could be identified. We also cited two experiments which are simply explained by postulating the existence of the metastable O^- whose properties we have calculated and discussed.

ACKNOWLEDGMENTS

It is a pleasure to thank C. H. Henry, D. V. Lang, M. D. Sturge, and T. A. Kennedy for many discussions, G. B. Bachelet for assistance in deriving the pseudopotentials, P. J. Dean for having sent us copies of his recent unpublished work, R. Z. Bachrach for allowing us to cite his unpublished results, and to Professor B. Monemar for permission to use Fig. 11.

APPENDIX: ESTIMATES OF THE GaO BOND STRENGTH FROM THE MOLECULAR VIBRATIONS AND ELASTIC CONSTANTS

We attempt a crude prediction of the GaO bond-stretching constant and local-mode frequency by looking at the vibration frequency of the Ga ^{16}O molecule which is given in Herzberg[33] as 95 meV. Using $\omega_{\mathrm{MOL}} = \sqrt{k/M_{\mathrm{red}}}$ we obtain $k_{\mathrm{MOL}} = 28.0$ eV/Å^2. For an oxygen local mode in the crystal with the same spring constant in which the Ga atoms did not move we would have $\omega_{\mathrm{loc}} = \sqrt{4/3}\,\omega_{\mathrm{MOL}}\,\sqrt{M_{\mathrm{red}}/M_0} = 99$ meV.

The bonding configuration of the molecule is undoubtedly quite different from that of the crystal. In the crystal Ga_2-O_3 oxygen is tetrahedrally surrounded by gallium. No elastic constant data is available for this material but for the analogous compound Al_2O_3 the elastic constants[34] are $C_{11} = 49.5$, $C_{12} = 16.0$, $C_{13} = 11.5 \times 10^{11}$ dyn/cm^2. Making an isotropic distortion of $\Delta l/l$, the elastic energy per unit volume is

$$V = \tfrac{3}{2}(\Delta l/l)^2(C_{11} + C_{12} + C_{13}) \; .$$

The above values of C_{ij} yield $V = 25.4$ eV/bond for $\Delta l/l = 1$. At an average Al$-$O spacing of 1.92 Å, the spring constant in the crystal is 13.9 eV/Å^2 as compared to the molecular value of 26.3 eV derived from the Al-O vibration frequency, given as 104.7 meV in Herzberg. If the Ga_2O_3 bond strength were reduced by the same amount the crystalline bond strength would be 14.8 eV/Å^2, leading to a local mode frequency of 72 meV. Although O is surrounded by four Ga atoms in Ga_2O_3, each gallium is surrounded by six oxygen atoms. Hence, the bond is probably more ionic than covalent. Nevertheless, it is surprising that the Ga$-$O bond in GaP:O is so much weaker than these estimates.

---

[1] P. J. Dean, The Story of O in GaP and Related Semiconductors (in press).

[2] G. A. Baraff and M. Schlüter, Phys. Rev. B 19, 4656 (1979).

[3] J. Bernholc, N. O. Lipari, and S. T. Pantelides, Phys. Rev. B 21, 3545 (1980).

[4] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979).

[5] M. T. Yin and Marvin L. Cohen, Phys. Rev. Lett. 45, 1004 (1980).

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

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

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

[9] B. Monemar and L. Samuelson, J. Lumin. 12/13, 507 (1976); Phys. Rev. B 18, 809 (1978); L. Samuelson and B. Monemar, Phys. Rev. B 18, 830 (1978).

[10] S. Toyotomi and K. Morigaki, J. Phys. Soc. Jpn. 29, 800 (1970).

[11] S. T. Pantelides, Solid State Commun. 14, 1255 (1973).

[12] N. P. Illin, V. F. Masterov, B. E. Samurokov, and K. F. Shtelmakh, Fiz. Tekh. Poluprovod. 10, 1581 (1976) [Sov. Phys.—Semicond. 10, 940 (1976).

[13] H. Kukimoto, C. H. Henry, and F. R. Merritt, Phys. Rev. B 7, 2486 (1973); C. H. Henry, H. Kukimoto, G. L. Miller, and F. R. Merritt, *ibid.* 7, 2499 (1973).

[14] H. G. Grimmeiss, L. A. Lebedo, C. Ovren, and T. N. Morgan, in *Proceedings of the International Conference on the Physics of Semiconductors, Stuttgart, 1974,* edited by M. H. Pilkukn (Teubner, Stuttgart, 1974), p. 386; T. N. Morgan, J. Elect. Mat. 4, 1029 (1975); T. N. Morgan in *Proceedings of the International Conference on the Physics of Semiconductors, Edinburgh, 1978,* edited by B. L. H. Wilson (Institute of Physics, Bristol, 1978), p. 311.

[15] H. R. Hjalmarson, P. Vogl, D. J. Wolford, and J. Dow, Phys. Rev. Lett. 44, 810 (1980).

[16] G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B 21, 3563 (1980).

[17] G. A. Baraff and M. Schlüter, in *Proceedings of the XI International Conference on Defects and Radiation Effects in Semiconductors, Oiso, Japan, 1980,* edited by R. R. Hasiguti (Institute of Physics, Bristol, 1981), p. 287.

[18] G. B. Bachelet, H. S. Greenside, G. A. Baraff, and M. Schlüter Phys. Rev. B 24, 4745, (1981).

[19] A. Zunger, J. Chem. Phys. 62, 1861 (1975); 63, 1713 (1975).

[20] S. G. Louie, M. Schluter, J. R. Chelikowsky, and Marvin L. Cohen, Phys. Rev. 13, 1654 (1976).

[21] U. Lindefelt, J. Phys. C 11, 3651 (1979).

[22] J. A. Appelbaum and D. R. Hamann, Rev. Mod. Phys. 48, 479 (1976).

[23] R. M. Martin, Phys. Rev. B 1, 4005 (1970).

[24] K. P. Jain and A. K. Prabhakaran, Phys. Rev. B 8, 1503 (1973).

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

[26] C. H. Henry and D. V. Lang, Phys. Rev. B 15, 989 (1977).

[27] R. Z. Bachrach (private communication).

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

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

[30] Lars I. Samuelson, thesis, Department of Solid State Physics, University of Lund, Sweden, 1977 (unpublished).

[31] D. J. Chadi, Phys. Rev. Lett. 43, 43 (1979).

[32] M. T. Yin (private communication).

[33] G. Herzberg, *Molecular Spectra I., Spectra of Diatomic Molecules,* 2nd ed., (Van Nostrand, Princeton (1950).

[34] R. Bechmann, R. F. S. Hearmon, and S. Kurtz, *Elastic, Piezoelectric, Piezooptic, Electrooptic Constants, and Nonlinear Dielectric Susceptibilities of Crystals,* Group III, Vol. II, of *Landolt-Börnstein,* edited by K. H. Hellwege and A. Hellwege (Springer, Berlin, 1969), p. 8.