PHYSICAL REVIEW B VOLUME 1, NUMBER 2 15 JANUARY 1970

Self-Consistent Orthogonalized-Plane-Wave Band Calculation on GaAs

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(Received 14 April 1969; revised manuscript received 7 July 1969)

The self-consistent orthogonalized-plane-wave (SCOPW) method is used to calculate the electronic structure of GaAs. It was found that the results obtained using Slater's approximation for the exchange operator match experiment more closely than those obtained using the other approximations. The comparison of the SCOPW results with photoemission, hydrostatic pressure, and reflection data is presented. Three minima in the conduction band are found; the lowest minimum occurs at the Γ point; the second lowest minimum, which occurs at the L point, was 0.38 eV above the Γ-point minimum; and the highest minimum, occurring along Δ at (π/a) (0.82, 0, 0), was 0.82 eV above the Γ-point minimum. This last minimum is about $\frac{1}{2}$ eV higher than is predicted by the customary experimental interpretation. Using the same SCOPW programs, GaP energy bands were calculated and the estimates of the band gaps of $GaAs_{1-x}P_x$ are also given.

I. INTRODUCTION

During the last ten years GaAs has been the object of a great amount of theoretical and experimental study. One of the main reasons for this extra study is that the lowest minimum in the conduction band is at the Γ point ($k=0$, see Fig. 1). Other minima are located away from this point at an energy which is approximately 0.4 eV higher. This is the origin of the Gunn effect[1] which makes GaAs interesting for transport investigations.[2,3] In Refs. 2 and 3, it was assumed that only one other minimum (neglecting equivalent minima) beside the lowest one takes part in the Gunn effect. In both papers it was assumed that this second minimum was located at the X point in the Brillouin zone. This conclusion was based primarily on pressure studies of Si which has an off-axis transition as the minimum band gap. For Si the maximum valence band energy occurs at $k=0$ and the conduction band minimum occurs along the Γ-X symmetry line. The assumption that the second minimum is at the X point for GaAs was also based on the assumption that in GaP the lowest minimum of the conduction band occurs at the X point. When going across the alloy range from GaP to GaAs only one change is found; namely, that the off-axis minimum changes to the Γ-point minimum of the conduction band.

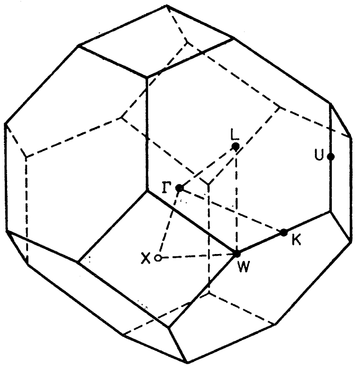

FIG. 1. Zinc-blende Brillouin zone with high symmetry points labeled.

Two recent investigations[4,5] of the electronic band structure of GaAs have produced two inequivalent minima within 0.1 eV of each other in the conduction band away from the Γ point; namely, a minimum at X and one at L, both being $\sim$0.4 eV above the Γ-point minimum. Cohen and Bergstresser[4] used the pseudopotential method in which they adjust the Fourier coefficients of their potential to fit their interpreted experimental results. Herman and Spicer[5] started from a more fundamental point of view, in that they first formed their potential from the superposition of overlapping atomic potentials in the orthogonalized plane-wave method (labeled NSCOPW). They found a minimum at the X point when using Slater's approximation for the exchange[6] which appears about 1 eV too high in energy to fit their interpreted experimental results. When they used Kohn-Sham's exchange approximation,[7] the X_{1c} eigenvalue moved down relative to the Γ_{1c} and the L_{1c}. At this point they adjusted their calculated results by changing the Fourier coefficients of the NSCOPW potential to fit the energies to the 0.4-eV energy difference of the Γ- and X-point conduction-band minima and to fit the fundamental band gap at Γ to experiment. Thus, one has the problem of two inequivalent minima of the conduction band at approximately the same energy above the Γ point. This also points out the need for an investigation of which exchange approximation to use for these crystals.

The purpose of this paper is to present the energy bands of GaAs as calculated using a self-consistent orthogonalized-plane-wave method (SCOPW). In Sec. II a description of the calculational model is given. There is also in the same section a discussion of energy values obtained using various exchange approximations

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and Koopman's corrections. From this discussion the "best" exchange approximation is selected. In Sec. III a detailed comparison with experiment and other theoretical results is made with the results of the "best" exchange approximation used in the SCOPW method. In this work no adjustments are made once the exchange operator is determined. The conclusions are given in Sec. IV.

II. SELF-CONSISTENT OPW MODEL

The orthogonalized plane-wave method of Herring[8] is used to calculate the electron energies. The deep core states are assumed to see a spherically symmetrized potential. The valence states, the $4s$ and $4p$ states of As and the $4s$ and $4p$ states of Ga, and the conduction states are described by a Fourier expansion in plane waves in which each plane wave is orthogonalized to all of the core states. Relativity is neglected. A discussion of this nonrelativistic approximation is given at the end of this section.

The starting potential of the self-consistent calculation was obtained from Herman's[9] overlapping atomic potential model. The core states are the free atomic states obtained from the programs of Herman and Skillman.[10] The energies of these states are shifted by the sum of the free atomic potentials of neighboring atoms at the atom in question (the sum is called the "core shift"). The potential used in the calculation of the valence states is a linear superposition of the free atomic potentials.

In the self-consistent calculation, core states and valence states are calculated in turn with the crystalline potential being constantly updated. This is continued until self-consistency is obtained. The integrals over the Brillouin zone are approximated by weighted averages over the high symmetry points Γ, X, L, and W. About ten iterations are necessary to obtain self-consistent results.

The imaginary part of the dielectric constant, ϵ_2, derived from the theoretical energy bands can be compared with the ϵ_2 obtained from reflection data. In order to calculate the theoretical ϵ_2, a pseudopotential fit is made to the relevant energy levels at the Γ, X, L, and W points. The pseudopotential technique is then used to calculate energy differences and transition matrix elements throughout the Brillouin zone.[11,12]

To determine the "best" exchange, one must start with the many-body Hamiltonian. The nonrelativistic Hamiltonian for the electronic system of a crystal (in atomic units) is

$$H=-\sum_i \nabla_i^2-\sum_{i,\alpha}\frac{2}{|\mathbf{r}_i-\mathbf{R}_\alpha|}+\sum_{i<j}\frac{2}{r_{ij}}. \qquad (2.1)$$

The first term is the kinetic energy operator of the electrons; the second is the electron-nuclear interaction; and the last term is the electron-electron interaction term. If one assumes that the wave function of the system is a Slater determinant of one-electron orbitals, the total energy $\langle\psi|H|\psi\rangle$ becomes (neglecting nuclear-nuclear interactions)

$$E_{\text{total}}=\sum_i \langle i|H_1|i\rangle+\tfrac{1}{2}\sum_{i,j}\left\{\langle ij|\frac{2}{r_{12}}|ij\rangle-\langle ij|\frac{2}{r_{12}}|ji\rangle\right\}, \qquad (2.2)$$

where H_1 includes the kinetic energy operator and electron-nuclear interaction. Minimizing the total energy with respect to the orbitals and requiring that the orbitals be orthogonal to each other, one obtains the Hartree-Fock equations for the orbitals

$$H_1\varphi_i(x_1)+\left\{\sum_j\int d\tau_2\varphi_j^*(x_2)\varphi_j(x_2)\frac{2}{r_{12}}\right\}\varphi_i(x_1) -\left\{\sum_j\int d\tau_2\varphi_j^*(x_2)\varphi_i(x_2)\frac{2}{r_{12}}\right\}\varphi_j(x_1) =\epsilon_{i,\text{HF}}\varphi_i(x_1). \qquad (2.3)$$

Assuming that the orbitals would not change if the ith electron is removed, the binding energy is defined as $E_{\text{total}}{}^{N}-E_{\text{total}}{}^{N-1}$:

$$B_{i,\text{HF}}{}^{\text{HF}}=\langle i|H_1|i\rangle+\sum_j\left\{\langle ij|\frac{2}{r_{12}}|ij\rangle-\langle ij|\frac{2}{r_{12}}|ji\rangle\right\}, \qquad (2.4)$$

where N denotes the number of electrons in the system. One should note that the binding energy of Eq. (2.4) is identical to the eigenvalue of Eq. (2.3) (Koopman's theorem[13]). The assumption that the orbitals do not change is not justified for atomic systems.[13–15] However, if one removes an electron which is spread out in the crystal, there should be little difference in the potential that the remaining electrons see. Thus the rigid orbital assumption should be much better for crystals and is made in this discussion.

In crystals, the Hartree-Fock equations are very difficult to solve for the electronic states because the exchange term results in a different potential for each of the interacting electrons. Simplified one-electron exchange operators have been given by Slater,[6] Kohn and

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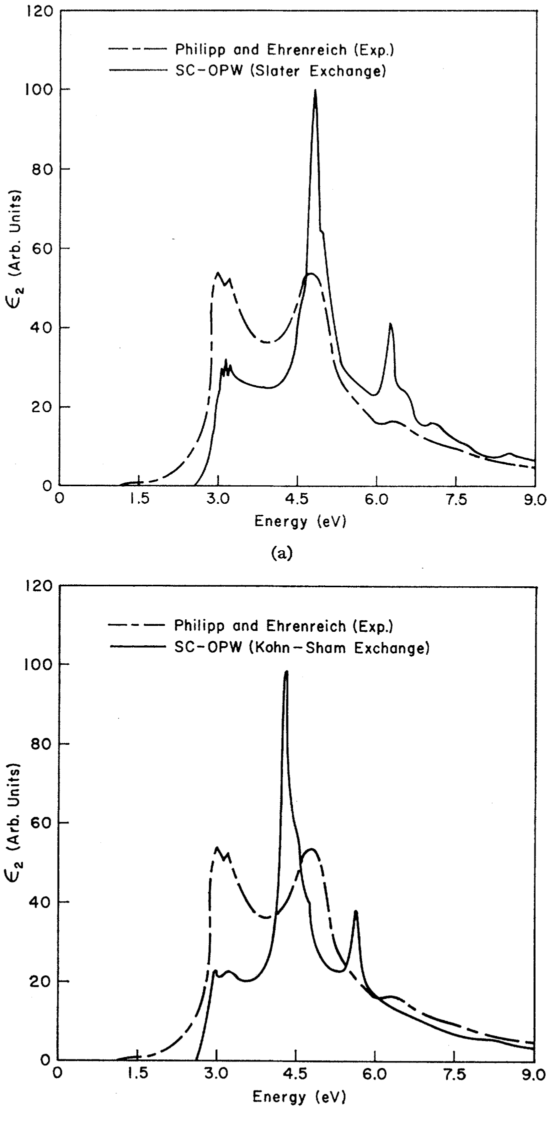

FIG. 2. Comparison of theoretical and experimental ϵ_2 curves for GaAs. The solid line gives the SCOPW ϵ_2 curve for (a) Slater's exchange and for (b) the Kohn-Sham exchange. The dashed line in each case shows the experimental results of Philipp and Ehrenreich.

Sham,[7] and Liberman.[16] It is very important to note in which part of the above derivation one makes the approximation for the exchange term. For example, if one makes Slater's exchange approximation in Eqs. (2.3) and (2.4), one finds the binding energy and eigenvalue are equivalent. However, if one substitutes Slater's approximation into Eq. (2.2) and then varies the total energy with respect to an orbital, one gets Kohn-Sham's approximation[7] for the exchange term in Eq. (2.3). Using the orbitals obtained from the Kohn-Sham exchange approximation, but with Slater's approximation for the exchange term used in Eq. (2.4), one has a nonzero difference between binding energy and eigenvalue. This difference is defined as the Koopman correction K,

$$K_{i,A}{}^{C} = B_{i,A}{}^{C} - \epsilon_{i,A}\,, \tag{2.5}$$

where A denotes the approximation with which the orbitals were derived, and C denotes the approximation used to calculate the binding energy. It is obvious that one can have a large number of different Koopman corrections. For example, if one substitutes the Slater approximation into the total energy of the N and $N-1$ particle systems, one can then define the difference of the two total energies as the binding energy. The Koopman correction between these binding energies and the Kohn-Sham eigenvalues is proportional to $N^{-2/3}$, which can be neglected for large systems. At this point, one has a large number of possible paths in making exchange approximations. The one which is more fundamental is not clear cut. If one compares results of the different paths with experiment for a large number of crystals (we have looked at Si, GaP, GaAs, AlAs,[17] AlP,[18] CdS,[19] CdSe, ZnS, and ZnSe[20]), the Slater exchange approximation in Eqs. (2.3) and (2.4) $[K_{i,s}{}^{s}=0]$ produces the only results which match experiment closely. This is true for all the crystals listed with no exceptions. (We have also looked at Ge and found that no results for any path fit experiment at all closely.) Thus, Slater's exchange approximation is selected as the "best" approximation. A more detailed discussion of the exchange problem, other approximations and different path results are given in Ref. 15.

The SCOPW ϵ_2 curves resulting from the use of Slater's exchange and from the Kohn-Sham exchange are compared with the experimental curve of Philipp and Ehrenreich in Figs. 2(a) and 2(b). One should compare peak positions and not peak shapes. Crude pseudopotential wave functions are used to calculate transition matrix elements. And what is probably more important, electron-hole and electron-phonon interactions have been neglected in the theoretical treatment. The success of Slater's exchange is striking, while the Kohn-Sham result is typically bad. We have seen exactly the same success of Slater and failure of Kohn and Sham with the other tetrahedrally bonded semiconductors that we have worked with. Slater's exchange is clearly much more successful at giving correct band-energy differences at individual points of the Brillouin zone. Consequently, we use the Slater SCOPW results in the rest of this paper.

Before leaving the discussion of the exchange problems, there is one more observation which is generally true for all the crystals studied. The differences of eigenvalues at the Γ point using the SCOPW method with Slater exchange are close to the differences of

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[18] D. J. Stukel and R. N. Euwema, Phys. Rev. (to be published).

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TABLE I. Eigenvalues of atomic Ge obtained both relativistically and nonrelativistically using Slater exchange approximation. The values are given in Ry.

	Nonrelativistic	Relativistic	ΔE_{Rel}
$1s_{1/2}$	−801.76	−813.32	−11.56
$2s_{1/2}$	−100.43	−102.99	−2.56
$2p_{1/2}$	−89.98	−92.20	−2.22
$2p_{3/2}$		−89.79	+0.19
$3s_{1/2}$	−12.69	−13.10	−0.41
$3p_{1/2}$	−9.124	−9.432	−0.308
$3p_{3/2}$		−9.096	+0.028
$3d_{3/2}$	−2.818	−2.767	+0.051
$3d_{5/2}$		−2.724	+0.094
$4s_{1/2}$	−1.001	−1.023	−0.022
$4p_{1/2}$	−0.399	−0.404	−0.005

eigenvalues obtained from an overlapping free atomic potential using the Kohn-Sham exchange operator. However, away from the Γ point, namely, at the X point, the differences between the eigenvalues of the two methods are not the same. And, as pointed out earlier, the SCOPW results using Kohn-Sham exchange do not fit experiment. So if one uses overlapping atomic potentials, one has to proceed with extreme caution.

This model does not include relativistic effects. In order to estimate the change in energy one expects for these compounds, both the nonrelativistic and relativistic calculations were made for atomic Ge using the Slater exchange (see Table I). The values for the top $4s$ and $4p$ energy shifts should approximate the crystalline shifts. If the conduction band is made up of $4s$-like functions and the valence band of $4p$-like functions, a shift of −0.23 eV is the atomic estimate for the change in band gap of Ge. Herman[21] found, comparing relativistic and nonrelativistic NSCOPW energies with a free atomic potential model, that their maximum gap changed −0.7 eV, a factor of three larger than what one expects from the atomic results. This is a dangerous procedure as he is looking at small differences between the results of two bad (nonself-consistent) models. However, even if one assumes that their results are reasonable, there is no method of calculation studied which give results which are nearly as close to experiment as those of the SCOPW method using Slater exchange. One could conclude that Slater's approximation magically accounts for relativity in the nonrelativistic SCOPW model or that −0.7 eV is much too large since Slater's nonrelativistic values match experiment.

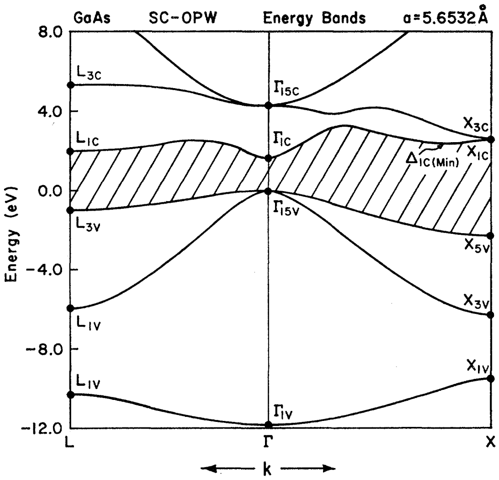

FIG. 3. Band structure of GaAs calculated by the SCOPW method. The dots above symmetry points Γ, X, L as well as values at W were used in the self-consistent iterations. After self-consistency is obtained, the final potential was used to generate the eigenvalues along Δ and Λ symmetry lines. The results are shown as solid lines.

TABLE II. Energies for GaAs with the energy of the top of the valence band (Γ_{15v}) set equal to zero. In the first column the self-consistent OPW values are given. In the second column are Herman's adjusted OPW values, and in the third column are photoemission results of Spicer and Eden.

	Self-consistent OPW (eV)	Adjusted[a] OPW (eV)	Photoemission[b] Expt (eV)
Γ_{12c}	10.78	10.6	10.2 to 10.9
Γ_{1c}	9.11	9.0	9.0 to 9.1
Γ_{15c}	*4.34*	4.6	*4.6* to *5.0*
Γ_{1c}	1.61	1.54	1.35 to 1.5
Γ_{15v}	0 00	0.00	0.00
Γ_{1v}	−11.81	−12.4	
X_{3c}	2.62	2.5	*2.40* to *2.45*
X_{1c}	*2.57*	*1.90*	1.70 to 1.85
X_{5v}	−2.23	−2.3	−2.3 to −2.6
X_{3v}	−6.29	−5.5	
X_{1v}	−9.48	−10.7	
Min. along Δ at 0.82 of way to X	*2.43*		
L_{3c}	5.36	5.3	5.0 to 5.3
L_{1c}	*1.99*	*2.00*	*1.80* to *1.95*
L_{3v}	−0.95	−0.9	−0.9 to −1.1
L_{1v}	−5.96	−5.6	−5.9 to −6.7
L_{1v}	−10.22	−11.1	

[a] See Ref. 5.

[b] W. E. Spicer and R. C. Eden, in *Proceedings of the Ninth International Conference on the Physics of Semiconductors*, edited by S. M. Ryukin (Nauka Publishing House, Leningrad, 1968).

One further omission of the model at present involves the effects of correlation. An estimate of the energy shifts due to correlation are given in Ref. 15, where it is shown that they are also small.

III. RESULTS AND COMPARISON

The results of the SCOPW calculations are presented in the first column of Table II and the graph of the energy band structure is given in Fig. 3. For comparison, in column two the adjusted OPW calculations of Ref. 5 are given, and in column three the photoemission data are recorded. The largest differences between Herman's adjusted OPW interpretation of the photoemission results with the SCOPW interpretation are italicized. Most of these differences are related to the location of the X_{1c} or Δ_{1c} minimum in the conduction band. From the SCOPW calculation, the photoemission result labeled X_{3c} would correspond to the Δ_{1c} minimum. The

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[21] F. Herman (private communication).

TABLE III. Energy peaks of the imaginary part of the dielectric constant obtained from experiments of Philipp and Ehrenreich are listed in column one. In column two are given the reflectivity structure energies obtained by Thompson, Wooley, and Rubenstein, and in column three are given the calculated energy peaks of the imaginary part of the dielectric constant. All values are in eV.

	ϵ_2(Expt)[a]	Reflectivity (Expt)[b]	ϵ_2(Calc)
E_1	3.0	2.90	3.1
$E_1+\Delta$	3.2	3.13	
E_0'		4.45	4.34
E_2	4.7–4.8	5.04	4.8
E_1'	6.5	6.63	6.3
$E_1'+\Delta$		6.89	

[a] See Ref. 23.
[b] See Ref. 24.

experimental data labeled X_{1c} would be labeled L_{1c} in the SCOPW results. The model of this paper does not identify the weak structure found experimentally (see Figs. 3 and 4 of James *et al.*[22]) which corresponds to L_{1c} in the adjusted OPW model. Also from the SCOPW calculations the value of 4.34 eV of the Γ_{15c} is at least 0.26 eV too low to match the photoemission value of 4.6–5.0 eV.

However, turning to the data of Philipp and Ehrenreich[23] who obtained the imaginary part of the dielectric constant, ϵ_2, [see Fig. 2(a)] one finds close agreement between the SCOPW results and these experimental results. The peak energies, together with the experimental reflection results of Thomas, Wooley, and Rubenstein,[24] are listed in Table III. The only structure which does not match closely is the peak position of the E_1' which appears 0.2 eV lower in energy than the measured value. Also note that the experimental E_0' peak, which is thought to originate from the $\Gamma_{15c}-\Gamma_{15v}$ transition, agrees better with the SCOPW value than the SCOPW value does with the photoemission data. At this point, let us compare the adjusted OPW results of Ref. 5 to ϵ_2 to see if they match this experiment as well as they match their interpreted photoemission results. In order to do this, the adjusted energies were matched with a pseudopotential scheme and the resulting ϵ_2 curve was calculated. The results are given in Fig. 4. One sees that the E_1 peak is 0.2 to 0.3 eV too small and the E_1' energy is off by about half an electron volt. This result was expected because the E_1 peak energy in all of the crystals studied lies between the energy difference of $X_{1c}-X_{15v}$ and $X_{3c}-X_{15v}$. Thus, to bring the adjusted OPW results into closer agreement with experiment one must now adjust the adjusted bands so that the X_{5v} is lowered by 0.3 eV relative to the other results. This move would also still match the photoemission data to within experimental error.

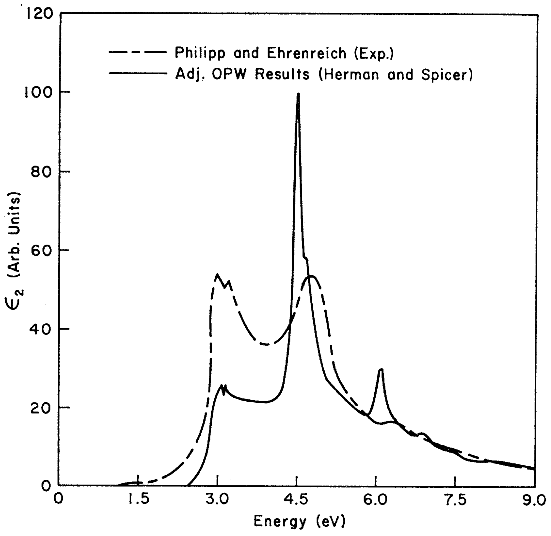

FIG. 4. ϵ_2 curve resulting from Herman's adjusted band structure is compared with the experimental ϵ_2 curve of Philipp and Ehrenreich.

The above discussion points out a possible defect of the SCOPW model using Slater's local exchange approximation. While the energy differences are certainly correct as long as one is looking at energy differences at the same k value in the Brillouin zone, the "off-axis" energy differences could be incorrect. In order to see if this is due to an intrinsic defect in the SCOPW model one can look at a calculation of a band structure for a crystal in which a conduction minimum in the X direction is well established. Such a crystal is Si which has an off axis band gap with the maximum of the valence band at Γ, and the minimum in the conduction band at Δ. Experimentally the energy difference is 1.13 eV,[25] while the calculated SCOPW value is 1.10 eV. This is very good agreement. In addition the calculated value is on the low energy side by 0.03 eV.

Other arguments presented[2] which would indicate that the X_{1c} (or Δ_{1c}) is lower than the calculated SCOPW value by about 0.5 eV are based on relations of energy bands of GaAs to those of GaP, and on interpretations of pressure data. It was thought that the minimum energy gap in GaP occurs between the top of the valence band at Γ to a minimum at X or along the Γ-X line. Looking at the band gap of the mixed crystal $GaAs_{1-x}P_x$ one finds only one change in slope as X changes from 0 to 1, somewhere around 0.5. Hence, the same SCOPW energy band programs were used to calculate GaP, and it was found that the lowest energy in the bottom conduction band is at the L point. If the curving of the energy lines of the mixed crystal is ignored (the largest deviation from linearity is only 0.06 eV[26]), and straight lines are drawn between the Γ_{1c}

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[26] J. A. Van Vechten and T. K. Bergstresser (unpublished).

TABLE IV. Shifts in band energy when the lattice constant is changed from 5.64 Å to 5.6532 Å ($\Delta E = E_{5.64} - E_{5.6532}$) are in column one. The change in energy with respect to pressure are given in column two. To obtain these values it is assumed that the band gap has $\Delta E/\Delta p = 1.1 \times 10^{-2}$ eV/kbar.

	ΔE (eV)	$\Delta E/\Delta P$ (10^{-2} eV/kbar)
Γ_{15c}	0.10	0.8
Γ_{1c}	0.23	1.8
Γ_{15v}	0.09	0.7
X_{3c}	0.09	0.7
X_{1c}	0.08	0.6
X_{3v}	0.06	0.5
L_{3c}	0.09	0.7
L_{1c}	0.12	0.9
L_{3v}	0.08	0.6

position of GaAs and GaP and between the L_{1c} and X_{1c} energies of the two compounds, the resulting band gap for the mixed crystal will be that shown in Fig. 5. The only change in slope (at $X = 0.75$) is similar to the change found experimentally.[27]

By varying the lattice constant from 5.6532 Å to 5.64 Å the effect of hydrostatic pressure was calculated. In order to insure that jiggling associated with self-consistent iteration (if one stops too soon) does not mask the energy shifts, the iterations were continued until there was less than 0.002 eV change from iteration to iteration. The results are given in Table IV. The first observation is that in column one all of the energy changes are positive with the minimum of the conduction band, Γ_{1c}, changing by approximately twice as much as each of the other energy changes. The values of the pressure coefficients given in the second column were obtained by assuming the band gap ($\Gamma_{1c} - \Gamma_{15v}$) pressure coefficient was 1.1×10^{-2} eV/kbar. The most important point is that the closure rate of the L_{1c} and Γ_{1c} conduction minima is -0.9×10^{-2} eV/kbar and the value of the Δ_{1c} and Γ_{1c} is -1.2×10^{-2} eV/kbar. The experimental value for the two lowest minima were found to be 0.96×10^{-2} eV/kbar to 0.97×10^{-2} eV/kbar by both Balslev[28] and Hutson, Jayaraman and Coriell.[29] The value given in Ref. 29 was obtained when they assumed the lattice constant was a linear function of pressure (as was assumed in this calculation). Also in Ref. 28, only two minima were found away from the zone center. One was at 0.43 eV above the minimum in the conduction band at Γ, and the other was at 0.78 eV above the primary minimum. These two values are in good agreement with the respective values of 0.38 and 0.82 eV found in this calculation.

TABLE V. Effective masses of the three minima in the conduction band are given for lattice constants of 5.6532 Å and 5.64 Å as well as estimates from experiments for the two lowest minima. The values are given in a.u.

	Calc ($a = 5.6532$ Å)	Expt[a]	Calc ($a = 5.64$ Å)
M_Γ^*	0.11	0.07 to 0.08	0.14
M_L^* (along Λ)	1.78	1.2 to 1.4	1.78
M 0.82 of X (along Δ)	0.97		1.00

[a] See Refs. 2 or 3.

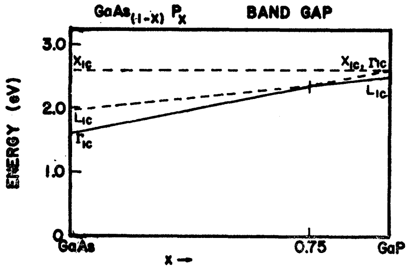

FIG. 5. Energy of the band gap (solid line) of GaAs$_{(1-x)}$P$_x$ as a function of concentration of As and P where x goes from 0 to 1. The lines were obtained by calculating the energy difference of Γ_{1c}–Γ_{15v}, L_{1c}–Γ_{15v}, and X_{1c}–Γ_{15v} for both GaAs and GaP and drawing straight lines from one compound to the other. Since the curving of the bands in going from GaAs to GaP is not calculated, the value of x at which the crystal goes from a direct to an indirect gap is not precise.

Since the symmetry lines Γ-X and Γ-L of the SCOPW model have been calculated, one can obtain the effective masses along these lines. The values obtained are given in Table V. The calculated values appear higher than the experimental estimates. However, the ratio of the Γ-point effective mass to the L-point effective mass is about the same as the estimated ratio used in transport calculations.[2,3] One point should be noted: the M_L^* was only calculated along Λ and anisotropic effects were not considered. The effective mass at Γ was calculated for both the Δ and the Λ lines and found to be isotropic at a lattice constant of 5.6532 Å. At the lattice constant 5.64 Å the M_Γ^* along the Δ direction was 8% lighter than that along the Λ direction.

As an added note of interest to the work presented here, a series of papers by Phillips and Van Vechten[30,31] give a model in agreement with our results of GaAs. In their work they used dielectrically defined average covalent and ionic energy gaps obtained from experiment to predict band energies. The value for the X_{1c} energy above the top of the valence band was 2.37 eV and the value for the L_{1c} energy above the top of the valence band was 1.89 eV. This is in fair agreement with our values of 2.57 and 1.99 eV obtained from the SCOPW method.

IV. CONCLUSION

The results of the GaAs energy-band calculation using the SCOPW method with Slater's exchange

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[27] See O. Madelung, *Physics of III–V Compounds* (Wiley-Interscience, Inc., New York, 1964), Chap. 6, p. 287.

[28] I. Balslev, Phys. Rev. **173**, 762 (1968).

[29] A. R. Hutson, A. Jayaraman, and A. S. Coriell, Phys. Rev. **155**, 786 (1966).

[30] The authors are indebted to J. A. Van Vechten for sending reports prior to publication to them.

[31] J. C. Phillips and J. A. Van Vechten, Phys. Rev. (to be published).

approximation agree well with experiment. It appears the correlation and relativistic effects can be ignored. They are either small or somehow the Slater exchange approximation accounts for them. This compensation is not as strange as it may at first appear. For example the use of free atomic potentials with Kohn-Sham exchange produces Γ-point eigenvalues very near the SCOPW values using Slater's exchange term.

The agreement with experiment would be outstanding if one reinterpreted the photoemission results as was discussed in Sec. III. That is one has three conduction-band minima; the lowest minimum occurs at the Γ point; the next higher minimum is located at L, 0.38 eV above the Γ-point minimum; and the third minimum is located on the symmetry line Δ, occurring 0.82 of the way from Γ to X at an energy value of 0.82 eV above the Γ-point minimum. However, the SCOPW model does not give any identification to the structure observed by James *et al.*[22] Aside from this everything else fits, even the ratio of the effective masses of the Γ and L minima calculated along Λ agree well with estimates used in transport calculations.

If one assumes that the location of the X_{1c} and L_{1c} are correctly given by Ref. 5, one finds that the direct energy differences (values located at the same k value in the Brillouin zone) are very close to experiment, while the indirect energies are correct only to about 0.5 eV. If this is true this discrepancy is thought to be related to the fact that the model uses a local exchange approximation.

Note added in proof. The many-body work of L. Hedin, S. Lundquist, and B. Lindquist support the use of Slater's exchange in deriving excitation energies.[32]

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[32] See review article by L. Hedin and S. Lindquist, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, to be published).

PHYSICAL REVIEW B VOLUME 1, NUMBER 2 15 JANUARY 1970

Low-Temperature Non-Ohmic Electron Transport in GaAs

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(Received 17 January 1969; revised manuscript received 18 July 1969)

The electric field dependence of the electrical conductivity and Hall effect in n-type epitaxial GaAs crystals was measured between 1.2 and 300°K. Some of the samples showed donor freeze-out, while others showed none down to the lowest temperatures. The non-Ohmic transport below 77°K was explained by a theory that included ionized-impurity and acoustic-phonon scattering, where the electron-phonon interaction was assumed to involve screened piezoelectric and deformation potentials. A treatment assuming an electron temperature and a second theory involving a direct calculation of the electron distribution function were compared with experiment. Only the theory involving a direct distribution-function calculation appears to explain the observations. A new model was proposed for the current-controlled negative resistance observed at low temperatures. This model depends upon the screening of impurity scattering and the electron-phonon interaction.

I. INTRODUCTION

A SUBJECT which has been studied in detail is non-Ohmic transport and the behavior in Ge at high electric fields, for example, is well understood.[1,2] The interaction of the electrons with phonons plays an important role in such studies. In GaAs, however, there are electron-phonon interactions not found in Ge. There is a strong polar interaction with the optical phonon. Furthermore, the absence of a center of inversion symmetry permits a strong interaction with acoustic phonons via the piezoelectric coupling.

Considerable effort has been devoted to the study, in the vicinity of room temperature, of non-Ohmic transport in the region near and above the Gunn effect field.[3,4] However, because of the strong interaction between electrons and optical phonons, other interactions may be neglected in explaining the observed behavior. There has been less investigation at low temperatures,[5–8] where other interactions are important. Oliver[6,7] analyzed his low-temperature non-Ohmic transport measurements by assuming the electron energy distribution was Maxwellian with an electron temperature different from the lattice temperature. This model is the electron-temperature model (ETM).[9] He assumed that acoustic- and optical-phonon

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[1] E. G. S. Paige, in *Progress in Semiconductors*, edited by A. F. Gibson and R. E. Burgess (John Wiley & Sons, Inc., New York, 1964), Vol. 8, Chap. 6.

[2] E. M. Conwell, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York, 1967), Suppl. 9, Chap. 2.

[3] J. B. Gunn, Solid State Commun. **1**, 88 (1963).

[4] Reference 2, pp. 80–99.

[5] R. A. Reynolds, Solid State Electron. **11**, 385 (1968).

[6] D. J. Oliver, Phys. Rev. **127**, 1045 (1962).

[7] D. J. Oliver, in ***Proceedings of the International Conference on the Physics of Semiconductors. Exeter, July, 1962***, edited by A. C. Strickland (The Institute of Physics and The Physical Society, London, 1962), p. 133.

[8] R. S. Crandall and P. Gwozdz, Bull. Am. Phys. Soc. **13**, 406 (1968).

[9] R. Stratton, Proc. Roy. Soc. (London) **A242**, 355 (1957).