Electronic Structure and Optical Spectrum of Boron Arsenide

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A first-principles self-consistent orthogonalized-plane-wave (SCOPW) energy-band calculation has been performed for cubic BAs using a nonrelativistic formalism and Slater's free-electron exchange approximation. These are the first fully self-consistent energy-band solutions reported for BAs. The imaginary part of the dielectric constant, spin-orbit splittings, effective masses, deformation energies, and the x-ray form factors (Fourier transforms of the electron charge density) have been calculated. The theoretical results are compared with the available experimental data.

I. INTRODUCTION

ONE of the III-V boron compounds which remains relatively unexplored because of the difficulties involved in syntheses of pure single crystals is BAs. BAs crystallizes in the cubic zinc-blende structure with a lattice constant of 4.777 Å.[1] The cubic BAs is stable in the presence of arsenic vapor up to 920°C. Above this temperature the cubic BAs transforms into a rhombohedral structure.

The purpose of this paper is to report for BAs a theoretical calculation of the band structure, the imaginary part of the dielectric constant (ϵ_2) derived from the theoretical bands, spin-orbit splittings, effective masses, deformation energies, and the form factors (the Fourier transforms of the electron charge density).

In the past couple of years a great deal of success has been attained in calculating the energy-band structures of group III–V, II–VI, and IV compounds using an unadjusted first-principles self-consistent orthogonalized-plane-wave (SCOPW) model developed here at ARL. The SCOPW programs used to calculate the electronic band structure have given surprisingly good one-electron band energies for tetrahedrally bonded compounds when Slater's exchange is used.[2–8]

II. CALCULATIONAL DETAILS

A. Self-Consistent OPW Model

The orthogonalized-plane-wave method of Herring[9] is used to calculate the electron energies. In the SCOPW model,[2,3] the electronic states are divided into tightly bound core states and loosely bound valence states. The core states must have negligible overlap from atom to atom. They are calculated from a spherically symmetrized crystalline potential.

The valence states must be well described by a modified Fourier series,

$$\psi_{k_0}(r)=\sum_{\mu} B_\mu\{\Omega_0^{-(1/2)}e^{i\mathbf{k}_\mu\cdot\mathbf{r}} -\sum_a e^{i\mathbf{k}_\mu\cdot\mathbf{R}_a}\sum_c A_{c\mu}{}^a\psi_c(|\mathbf{r}-\mathbf{R}_a|)\},$$

where $\mathbf{k}_\mu=\mathbf{k}_0+\mathbf{K}_\mu$, $\mathbf{k}_0$ locates the electron within the first Brillouin zone, $\mathbf{K}_\mu$ is a reciprocal-lattice vector, $\mathbf{R}_a$ is an atom location, ψ_c is a core wave function, and Ω_0 is the volume of the crystalline unit cell. The coefficients $A_{c\mu}{}^a$, are determined by requiring that $\psi_{k_0}(r)$ be orthogonal to all core state wave functions. The variation of B_μ to minimize the energy then results in the valence one-electron energies and wave functions.

The dual requirements of no appreciable core overlap and the convergence of the valence wave function expansion with a reasonable number of OPW's determines the division of the electron states into core and valence states. For B, the $2s$ and $2p$ states (for As the $4s$ and $4p$ states) are taken as the valence states. OPW series convergence is discussed in Sec. II B.

The calculation is self-consistent in the sense that the core and valence wave functions are calculated alternately until neither changes appreciably. The Coulomb potential due to the valence electrons and the valence charge density are both spherically symmetrized about each inequivalent atom site. With these valence quantities frozen, new core wave functions are calculated and iterated until the core wave functions are mutually self-consistent. The total electronic charge density is calculated at 650 crystalline mesh points covering 1/24 of the unit cell, and the Fourier transform of $\rho(r)^{1/3}$ is calculated. The new crystal potential is calculated from the old valence charge distribution and the new core charge distribution. Then new core-valence orthogonality coefficients $A_{c\mu}{}^a$ are calculated. The iteration cycle is then completed by the calculation of new valence energies and wave functions. The iteration process is continued until the valence one-electron energies change less than 0.01 eV from iteration to iteration.

The appropriate charge density to use for both the self-consistent potential calculation and the form factor calculation is the average charge density of all the elec-

[1] A. Perri, S. La Placa, and B. Post, Acta Cryst. **11**, 310 (1958).
[2] R. N. Euwema, T. C. Collins, D. G. Shankland, and J. S. DeWitt, Phys. Rev. **162**, 710 (1967).
[3] D. J. Stukel, R. N. Euwema, T. C. Collins, F. Herman, and R. K. Kortum, Phys. Rev. **179**, 740 (1969).
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[5] D. J. Stukel and R. N. Euwema, Phys. Rev. **186**, 1193 (1969).
[6] T. C. Collins, D. J. Stukel, and R. N. Euwema, Phys. Rev. B **1**, 724 (1970).
[7] D. J. Stukel and R. N. Euwema, Phys. Rev. B **1**, 1635 (1970).
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[9] C. Herring, Phys. Rev. **57**, 1169 (1940).

trons in the Brillouin zone. In the present self-consistent calculations, this average is approximated by a weighted average over electrons at the Γ, X, L, and W high symmetry points of the Brillouin zone shown in Fig. 1. The weights are taken to be proportional to the volumes within the first Brillouin zone closest to each high symmetry point. The adequacy of this approximation has been tested and the error in the energy eigenvalues has been shown to be less than 0.1 eV.[7]

The present self-consistent model neglects correlation effects and approximates the complicated Hartree-Fock exchange potential by a term proportional to the electron charge density to the one-third power. The best known exchange potentials are Slater's[10]:

$$V_{x\mathrm{S}}=-6[(3/8\pi)\rho(r)]^{1/3},$$

and Kohn and Sham's[11] and Gaspar's[12]:

$$V_{x\mathrm{KSG}}=-4[(3/8\pi)\rho(r)]^{1/3}.$$

We have experimented with the constant of proportionality. When calculating the energy-band structure of tetrahedrally bonded semiconductors with our SCOPW model, we have found that Slater's exchange always gives results that agree most closely with experiment. For compounds such as Si and ZnS, band gaps and ϵ_2 peak positions agree to within 0.1 eV. For compounds such as ZnSe and Ge, the differences between theory and experiment are as bad as 0.5 eV, but again Slater's exchange gives results in closest agreement with experiment. To give a feeling for which transitions are most sensitive to the value of the exchange constant, both Slater's and Kohn, Sham, and Gaspar's energies are tabulated in Table I for selected high symmetry point values.

TABLE I. Self-consistent energy eigenvalues for cubic BAs based on Slater's and Kohn and Sham's exchange and on a four-point (Γ, X, L, and W) zone sampling. 537, 411, and 259 OPW's were used at Γ and a comparable member of OPW's at X, L, and W. The zero of energy has been placed at the top of the valence band (Γ_{15v}). All entries are in eV.

Level	Slater's exchange 537 OPW's	Slater's exchange 411 OPW's	Slater's exchange 259 OPW's	Kohn-Sham exchange 259 OPW's
Γ_{1c}	4.69	4.65	4.57	5.08
Γ_{15c}	3.56	3.54	3.56	3.12
Γ_{15v}	0.0	0.0	0.0	0.0
Γ_{1v}	−15.08	−15.10	−15.17	−15.44
X_{1c}	2.19	2.19	2.17	1.21
X_{3c}	1.89	1.85	1.75	0.92
X_{5v}	−3.83	−3.84	−3.87	−4.22
X_{3v}	−8.29	−8.35	−8.49	−8.74
X_{1v}	−11.10	−11.09	−11.08	−11.01
$X_{1c}-X_{5v}$	6.02	6.03	6.04	5.43
$X_{3c}-X_{5v}$	5.72	5.69	5.62	5.14
L_{3c}	5.23	5.17	5.20	4.57
L_{1c}	2.93	2.89	2.81	2.73
L_{3v}	−1.66	−1.72	−1.72	−1.86
L_{1v}	−8.37	−8.43	−8.53	−9.06
L_{1v}	−12.34	−12.38	−12.42	−12.43
$L_{3c}-L_{3v}$	6.89	6.89	6.92	6.43
$L_{1c}-L_{3v}$	4.59	4.61	4.53	4.59
W_{4c}	6.50	6.56	6.70	6.39
W_{2c}	5.86	5.90	5.94	5.07
W_{3v}	−4.77	−4.80	−4.82	−5.43
W_{2v}	−5.10	−5.13	−5.18	−5.80
W_{1v}	−7.88	−7.95	−8.10	−8.22
W_{4v}	−10.96	−10.95	−10.94	−10.81
$W_{2c}-W_{4v}$	10.63	10.70	10.76	10.50

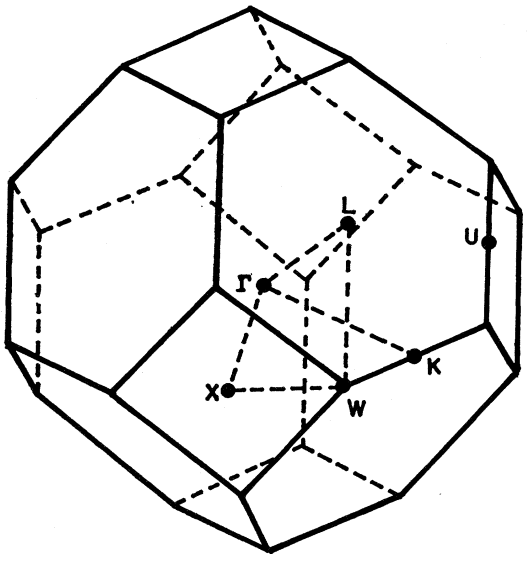

FIG. 1. Zinc-blende Brillouin zone with high symmetry points labeled.

In order to calculate the absorptive part of the dielectric constant, 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.[13] In our experience, this procedure gives the ϵ_2 peaks at the correct energies. However, the relative peak heights do not match experiment because of their dependence upon the poor pseudopotential wave functions, and because of complicated electron-hole and electron-phonon interactions which are ignored in our model.

One way of taking relativistic effects into account within the framework of nonrelativistic band calculations is with first-order perturbation theory. The perturbing Hamiltonian obtained for the spin-orbit splitting is

$$\hat{H}_{\mathrm{so}}=-\tfrac{1}{4}iq^2\boldsymbol{\sigma}\cdot[\nabla V(r)\times\nabla],$$

where $V(r)$ is the potential, $\boldsymbol{\sigma}$ is the Pauli spin operator,

[10] J. C. Slater, Phys. Rev. **81**, 385 (1951).
[11] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[12] R. Gaspar, Acta Phys. Acad. Sci. Hung. **3**, 263 (1954).
[13] R. N. Euwema, D. J. Stukel, T. C. Collins, J. S. DeWitt, and D. G. Shankland, Phys. Rev. **178**, 1419 (1969).

and q is the fine-structure constant. The Γ_{15v} SCOPW valence wave functions are used in this calculation.

B. OPW Series Convergence

A major problem involved in an OPW calculation of BAs is the very slow convergence of the OPW series expansion of the valence and conduction wave functions. In the OPW expansion, all **k** vectors are used whose magnitudes are smaller than some value $k_{\max}$. The minimum distance that can be defined by the plane-wave terms in the OPW series is thus roughly

$$d_{\min}\approx\tfrac{1}{2}\lambda_{\min}=\frac{\pi}{k_{\max}}=a/2(m^2+n^2+l^2)^{1/2},$$

where a is the lattice constant and (m,n,l) are integers defining the largest k vector. The dependence of the BAs valence and conduction band energies upon $d_{\min}$ is shown for two different OPW models in Figs. 2 and 3. In Fig. 2, Herman's overlapping free atomic potential model[14] is used in which the potential is calculated from free-atom charge densities which are packed in the crystal lattice. In Fig. 3, SCOPW results are presented for different $d_{\min}$. For both figures, the B and As core charge densities ($4\pi r^2\rho(r)$) are also shown.

As we discuss at length in another paper,[15] the series convergence depends upon two factors. One is the relative core size of anion and cation. $d_{\min}$ depends upon the lattice constant which depends upon the sum of anion and cation core sizes. The penetration into the smaller core is thus least when the core size ratio is most extreme. It is clear from the figures that BAs has an extreme core size ratio and thus a relatively poor penetration into the B core. The second factor involves the presence or absence of core wave functions in the symmetrized OPW's. If no core wave functions are present in an OPW expansion, it becomes a pure plane-wave expansion (Fourier series) with consequently poorer convergence. B has no p states in the core, and thus the Γ_{15v} wave function contains no B core states to aid convergence. The only saving factor is that Γ_{15v} convergence depends much more critically upon penetration into the anion than upon cation penetration. But it can be seen from the figures that convergence of the energies is still not complete by 1000 OPW's. This lack of convergence can also be seen more quantatively in Table I where SCOPW energies are given for 259, 411, and 537 OPW's. In going from 411 OPW's to 537 OPW's the Γ_{1v}, Γ_{15v}, Γ_{15c}, and Γ_{1c} changed by 0.05, 0.07, 0.06, and 0.03 eV, respectively. We estimate a maximum uncertainty of 0.3 eV in our most converged 537 SCOPW results due to lack of OPW convergence.

III. RESULTS

The SCOPW model involves no adjustable parameters. However, one must supply the lattice constant. In these calculations the lattice constant used was 4.777 Å determined by Perri, LaPlaca, and Post.[1] Ku[16] has reported a lattice constant of 4.7778 Å. Self-consistent calculations were also made with lattice constants of 4.767 Å and 4.787 Å to determine the effects of pressure.

The energy bands based on Slater's exchange, a

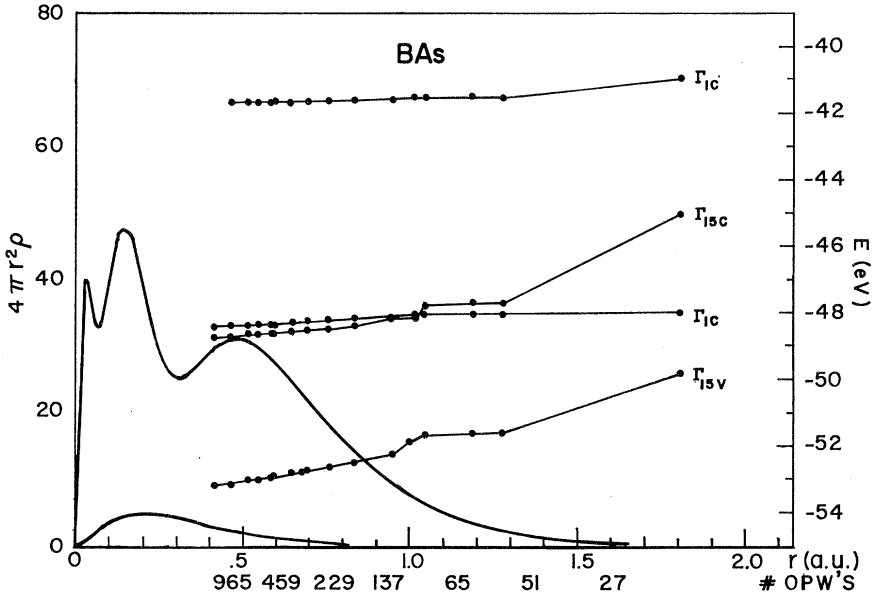

FIG. 2. Convergence study of non-self-consistent energy levels at Γ point in cubic BAs.

[14] F. Herman and S. Skillman, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Publishing House of Czechoslovak Academy of Science, Prague, 1961), p. 20.
[15] R. N. Euwema and D. J. Stukel, Phys. Rev. (to be published).
[16] S. M. Ku, J. Electrochem. Soc. **113**, No. 8, 813 (1966).

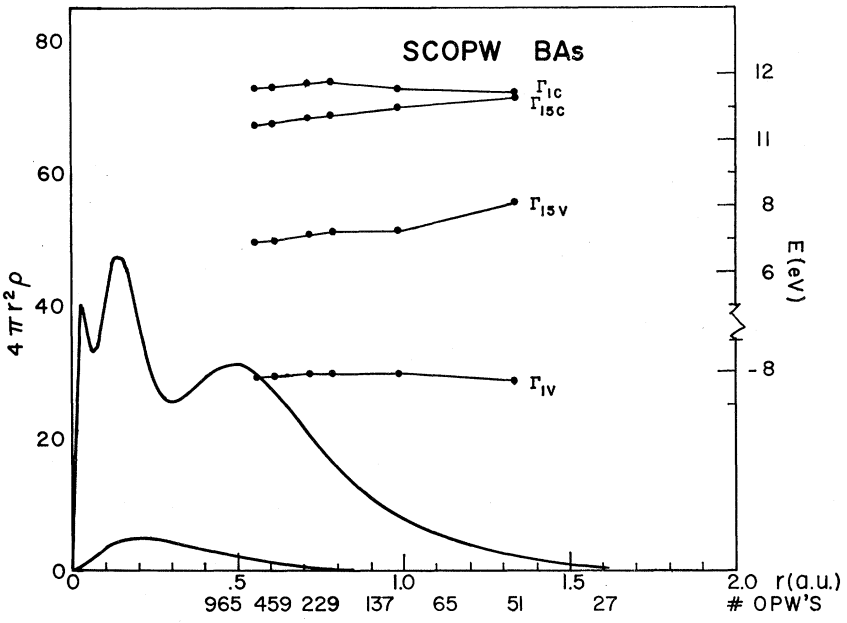

FIG. 3. Convergence study of SCOPW energy levels at Γ point in cubic BAs.

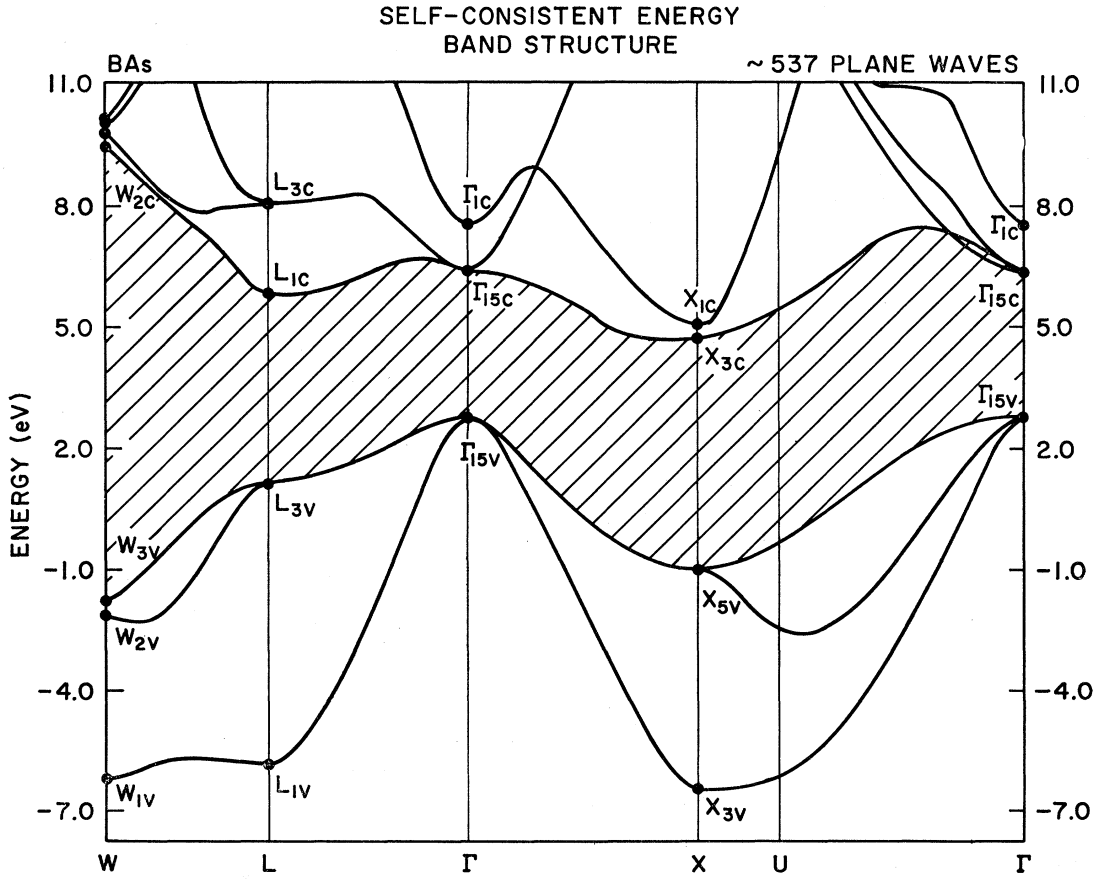

FIG. 4. SCOPW energy-band structure of BAs. The solid dots denote SCOPW energy levels. The solid lines were obtained by fitting a pseudopotential-type interpolation scheme to the SCOPW energy levels.

TABLE II. Self-consistent energy eigenvalues for BAs based on four-point zone sampling. Slater's exchange, 259 OPW's, and a lattice constant of 4.777 Å are given in column 2. The changes in the eigenvalues when self-consistency was obtained at 4.767 Å and 4.787 Å are given in columns 3 and 4. The resulting average deformation energies appear in column 5. The energies are in eV. Deformation energies are in eV per unit dilation.

Level	Energy (4.777 Å)	$E_{4.777}-E_{4.787}$	$E_{4.767}-E_{4.777}$	D. E.
Γ_{1v}	−8.046	0.037	0.044	6.5
Γ_{15v}	7.127	0.090	0.099	15.0
Γ_{15c}	10.684	0.093	0.104	15.7
Γ_{1c}	11.706	0.175	0.191	29.1
X_{1v}	−3.955	0.070	0.075	11.5
X_{3v}	−1.364	0.056	0.069	9.9
X_{5v}	3.260	0.064	0.073	11.1
X_{3c}	8.878	0.082	0.095	14.1
X_{1c}	9.299	0.087	0.090	14.2
L_{1v}	−5.290	0.059	0.066	10.1
L_{1v}	−1.404	0.047	0.056	8.2
L_{3v}	5.408	0.079	0.088	13.3
L_{1c}	9.941	0.129	0.140	21.4
L_{3c}	12.323	0.097	0.105	16.1
W_{4v}	−3.816	0.078	0.078	12.4
W_{1v}	−0.968	0.068	0.074	11.3
W_{2v}	1.949	0.060	0.061	9.6
W_{3v}	2.300	0.065	0.062	10.1
W_{2c}	13.072	0.103	0.100	16.2
W_{4c}	13.830	0.170	0.134	24.0

lattice constant of 4.777 Å, and 537 OPW's at Γ (and a comparable number of OPW's at X, L, and W) are given in Fig. 4. The energy eigenvalues are given in the fourth column of Table I.

There are two minima in the bottom conduction band which are lower than the minimum at Γ. The lowest minimum occurs at 0.81 of the distance from the Γ point to the x point. The indirect gap which is measured to this point, $\Delta_{1c}{}^{m}-\Gamma_{15v}$, is 1.6 eV. The next lowest minimum occurs at the L point where $L_{1c}-\Gamma_{15v}$ is 2.93 eV. The direct gap $\Gamma_{15c}-\Gamma_{15v}$ is 3.56 eV.

Ku[16] has made transmission-versus-wavelength measurements at room temperature on powdered samples to estimate the optical energy gaps for BAs. The optical energy gap was estimated by extrapolation of the slope of the optical transmission-versus-wavelength plot to zero transmission. The value he obtained was 1.46 eV. Vorob'ev, Medvedeva, and Sobolev[17] concluded from reflection spectra studies of BAs that either their samples were severely contaminated with impurities or that there are indirect transitions in the range of 0.8 to 2.0 eV.

TABLE III. Theoretical BAs structure factors in electron per crystallographic unit cell. The RHF values are relativistic free atomic Hartree-Fock results. KSG and Sl refer to the use of the Kohn-Sham-Gaspar or Slater exchange approximation. Sl-RHF, for example, refers to structure factors calculated using SCOPW valence electron densities and RHF free atomic core densities. 259 and 537 refer to the number of OPW's used in the wave function expansion.

		259 OPW's				537 OPW's	
hkl	RHF	KSG	KSG-RHF	Sl	Sl-RHF	Sl	Sl-RHF
111	108.39	109.00	109.10	110.26	109.81	110.27	109.81
200	92.87	92.62	92.72	93.64	93.07	93.50	92.93
220	99.07	98.61	98.81	99.98	99.05	100.12	99.19
311	85.02	84.44	84.62	85.64	84.56	85.67	84.59
222	75.81	75.88	76.03	77.01	75.92	76.95	75.85
400	82.97	82.45	82.69	83.79	82.54	83.87	82.63
331	72.50	72.68	72.87	74.05	72.79	74.06	72.81
420	64.66	64.74	64.86	65.99	64.76	65.93	64.70
224	72.29	72.18	72.42	73.63	72.33	73.70	72.40
115	63.40	63.36	63.54	64.71	63.47	64.71	63.47
333	63.40	63.26	63.44	64.60	63.36	64.60	63.35

To calculate the effects of hydrostatic pressure on the band energies, we iterated to self-consistency using lattice constants of 4.787 Å and 4.767 Å in addition to the equilibrium lattice constant of 4.777 Å. The results are presented in Table II. The two sets of energy differences give one a feeling for the accuracy involved in taking small differences of quantities from different sets of iteration. Since the lattice constant was changed by 0.2% on each side of the equilibrium lattice constant these two sets of energy differences also give one a feeling of the linearity present. The deformation energies are defined as

$$\text{D. E.}=\delta E/(\delta V/V)=-\delta E/(3\delta a/a)$$

and are given in units of eV per unit dilation. a is the lattice constant.

The imaginary part of the dielectric constant (ϵ_2) is given in Fig. 5. The location of some of the major transitions are also indicated. It should be remembered that the detailed ϵ_2 shape is unreliable, while the peak positions are much more reliable. Vorob'ev *et al.* found a reflection peak at 4.77 eV which agrees very well with our $L_{1c}-L_{3v}$ transitions around 4.6 eV. They did not report any structure at higher energies. Our peak at around 5.8 eV is due to transitions occurring in the outer part of the zone in the U-K region. The theoretical peak around 7 eV is due primarily to transitions near the L point, $L_{3c}-L_{3v}$.

The spin-orbit splitting at $k=0$ of the top Γ_{15v} valence band into Γ_7 and Γ_8 bands has been found by the use of first-order perturbation theory on the self-consistent Slater Γ_{15v} wave functions to be 0.33 eV.

Effective masses have been calculated for the top valence band at the Γ point and for the bottom conduction band at the $\Gamma-X$ minimum. For the Γ_{15v} valence band (where spin-orbit splitting has been neglected) $m_\Gamma{}^{*}=0.71$ (heavy hole) and 0.14 (light hole) for the (1,1,1) direction and $m_\Gamma{}^{*}=0.31$ (heavy hole) and 0.26 (light hole) for the (1,0,0) direction. For the conduction band minimum in the (1,0,0) direction, the effective mass in the parallel direction is about 1.2.

In Table III theoretical Fourier components of the charge density (the x-ray form factors) are given. The Fourier components in the column headed RHF are obtained by the superposition of relativistic Hartree-Fock free atoms placed in the crystalline lattice. The columns are headed with the exchange potential used in the SCOPW model. From Table III it can be seen that for the higher reflections the RHF results agree

[17] V. G. Vorob'ev, Z. S. Medvedeva, and V. V. Sobolev, Izv. Akad. Nauk SSSR, Neorgan, Mat. **3**, 959 (1967).

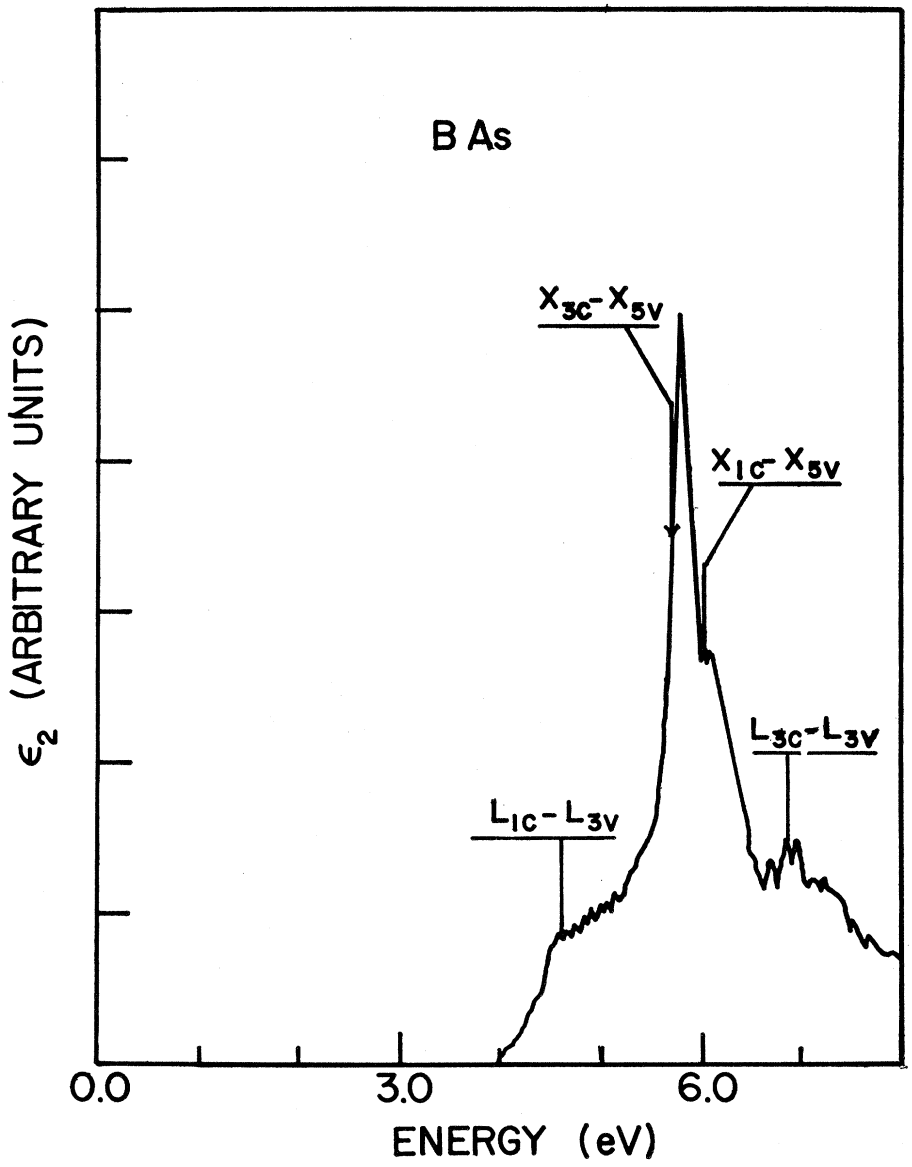

FIG. 5. Theoretical ϵ_2 curve for BAs with the location of the high-symmetry-point transitions shown.

with the results obtained using Kohn and Sham's exchange potential. This good agreement illustrates the well known general result that the Kohn-Sham wave functions are very good for free atom calculations. For the low reflections the RHF results are generally too small in semiconductors. The opposite result applies in metals where the valence charge spreads out. The Slater results generally give slightly better agreement with experiment for lower reflection.[18]

IV. CONCLUSIONS

The validity of these calculations cannot be fully judged because of the absence of comprehensive experimental results. It should be remembered that these results are based almost completely on first principles with no adjustment to fit experiment. The only experimental data used is the lattice constant. Correlation is neglected and Slater's exchange approximation is made. In the final analysis the validity of these results depends upon the applicability of Slater's exchange approximation and the validity of the SCOPW model. Past experience on many tetrahedral compounds gives us considerable faith in the validity of these results.

ACKNOWLEDGMENT

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[18] P. M. Raccah, R. N. Euwema, D. J. Stukel, and T. C. Collins, Phys. Rev. B 1, 756 (1970).