PHYSICAL REVIEW B VOLUME 52, NUMBER 7 15 AUGUST 1995-I

First-principles calculation of Ga-based semiconductors

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(Received 3 October 1994; revised manuscript received 30 December 1994)

The physical properties of the III-V semiconducting compounds, GaP, GaAs, and GaSb, have been calculated by employing a scalar relativistic version of the first-principles full-potential self-consistent linearized-muffin-tin-orbital method. The calculated values of the lattice parameters of the compounds are reproduced well within 2.6% of the measured values. The computed dispersion curves and the electronic density of states are in excellent agreement with the available photoemission data for all the compounds. The predicted bulk modulus and the elastic constants are in close agreement with the experimental data where available. The frequencies of the frozen phonons at symmetry points are in good agreement with the available measured data.

I. INTRODUCTION

Electronic, structural, and lattice-dynamical properties can be determined by *ab initio* methods with reliable accuracy if one knows the electronic structure and the energy of the solid as a function of the atomic positions. Recently, the linear-muffin-tin-orbital (LMTO) method has been utilized for the study of the electronic structure of molecules as well as of crystalline solids. There are several attractive features associated with the method, such as the requirement of only a minimal basis set enabling its application to large unit cells with high efficiency, its applicability to atoms with a large number of core states and also to atoms having prominently d or f character, and its transparency and accuracy.

Usually, to make the LMTO method efficient, an atomic-sphere approximation (ASA) is used. This has its own limitations, such as the discarding of the nonspherical parts of the electron density and its use of spherical Hankel functions with vanishing kinetic energy only.

In the present method, the potential matrix elements are separated into two parts, one contribution coming from the atomic spheres and the other from the complicated interstitial region. The first part is evaluated by expanding it in terms of the usual spherical harmonics. The interstitial quantities are expanded in terms of spherical Hankel functions. The three-center intergrals involved are assumed to be linear combinations of two-center integrals and the coefficients are evaluated by a numerical method. These two-center integrals involving Hankel functions can easily be evaluated analytically by converting them into surface integrals.

In the present article, we have investigated the various properties of the Ga-based III-V semiconductors. These materials have been studied earlier by several workers using different *ab initio* techniques. Chelikowsky and Cohen[1] have investigated the electronic structure and other properties of Ga-based semiconductors by employing a nonlocal-pseudopotential scheme. Weyrich, Brey, and Christensen[2] have calculated the phonon frequency of GaAs by using the LMTO-ASA method. Min, Massidda, and Freeman[3] used the full-potential linearized augmented-plane-wave (FLAPW) method to study the energy bands, density of states, and total energy of GaAs. Bachelet and Christensen[4] employed the LMTO-ASA and norm-conserving pseudopotential methods to investigate the electronic structure of GaAs. Causa, Dovesi, and Roetti[5] have made a pseudopotential Hartree-Fock linear combination of atomic orbitals study of III-V and IV-IV semiconductors including the Ga-based semiconductors. They have calculated the binding energy, lattice parameter, bulk modulus, and $k=0$ transverse-optical phonon frequencies. Giannozzi *et al.*[6] have calculated the total energy and force in the framework of the local-density approximation using a pseudopotential method for GaAs. First-principles, norm-conserving, pseudopotential calculations[7-9] have also been performed for some frozen-phonon frequencies in semiconductors. We have made a comprehensive study of the lattice parameter, elastic constant, electronic structure, density of states, frozen frequencies, and electronic charge density for three Ga-based semiconductors (GaP, GaAs, and GaSb).

A number of experimental measurements have been reported in the literature. For earlier review of the experimental work we refer to the articles of Blakemore[10] and of Cardona and Harbeke.[11] Polarization-dependent angle-resolved photoelectron spectroscopy (ARPES) has been employed by Williams *et al.*[12] for the study of Ga-based and In-based compounds. The measurements were made for the dispersion curves in the [110] direction. More recently, Zhang *et al.*[13] have determined the conduction-band structure along the Γ-K-X and Γ-Δ-X directions by using ARPES.

Earlier, the present LMTO method has been seen to produce quite good results for II-VI semiconducting compounds like ZnS, ZnSe, ZnTe, and CdTe.[14,15] The influence of structural relaxation of the atoms on the valence-band offset at the lattice-matched interfaces of II-VI and III-V semiconductors ZnTe/GaSb(110) and the lattice-mismatched interface ZnS/ZnSe(001) has been investigated.[16] Very recently, the method has been utilized for the study of the parent superconductor $CaCuO_2$,[17] and the role of van Hove singularities in Hg-based superconductors[18] (revealing the highest value of T_c of about

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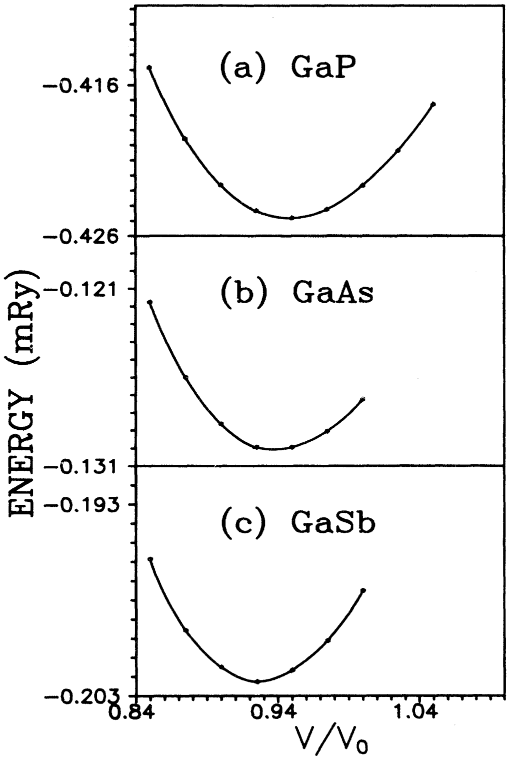

FIG. 1. Variation of crystal energy (mRy) with the ratio of unit-cell volumes. V_0 and V are the experimental and calculated volumes for (a) GaP, (b) GaAs, and (c) GaSb.

165 K) at high pressure.

For detailed information about the method used, we refer to earlier articles.[14–19] The results for the three prototypes of III-V semiconductors, i.e., GaP, GaAs, and GaSb, are presented in Sec. II. The main conclusions are included in Sec. III.

II. CALCULATION AND RESULTS

The chosen values of the radii of atomic spheres for GaP, GaAs, and GaSb are 2.210, 2.295, and 2.475 a.u., respectively. For more technical details, see Refs. 14 and 17.

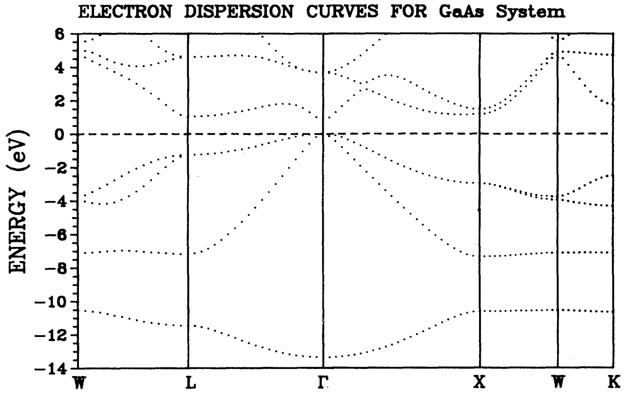

FIG. 3. Dispersion curves for GaAs.

The effects of the semicore $3d$ or $4d$ states on top of the valence band are investigated in a two-panel calculation. For all the systems, we consider Ga($4s,4p,4d$) as valence states in the first panel and the semicore Ga($3d$) states in the second panel. For anions, we consider P($3s,3p,3d$), As($4s,4p,4d$), and Sb($5s,5p,5d$) as the valence states. In the second panel of GaAs and GaSb, we include As($3d$) and Sb($4d$) as the semicore states.

Figure 1 depicts the variation of the total electronic energy with the relative volume of the crystal, V/V_0, where V_0 is the experimental unit-cell volume of the solid. For GaP [Fig. 1(a)], the energy minimum appears at a lattice parameter equal to 5.3581 Å which is very close to the experimental value[20] of 5.4505 Å. For GaAs and GaSb [Figs. 1(b) and 1(c)] the minimum energy appears at 5.508 and 5.939 Å, respectively, which are also very near to the experimental values,[20] 5.653 and 6.095 Å. The discrepancies for the lattice parameter are of the order of 1.7%, 2.57% and 2.57%, for GaP, GaAs, and GaSb, respectively.

The electronic charge out of the muffin-tin (MT) sphere for Ga and P in GaP is 1.68 and 1.64, respectively, and for Ga and As in GaAs 1.55 and 1.79, respectively. The values for Ga and Sb in GaSb are 1.14 and 2.34. The to-

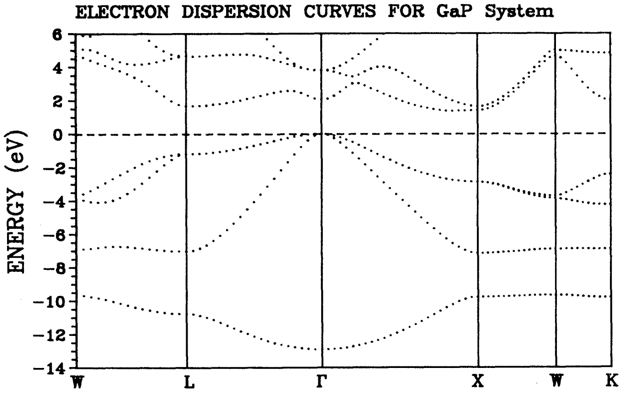

FIG. 2. Dispersion curves for GaP.

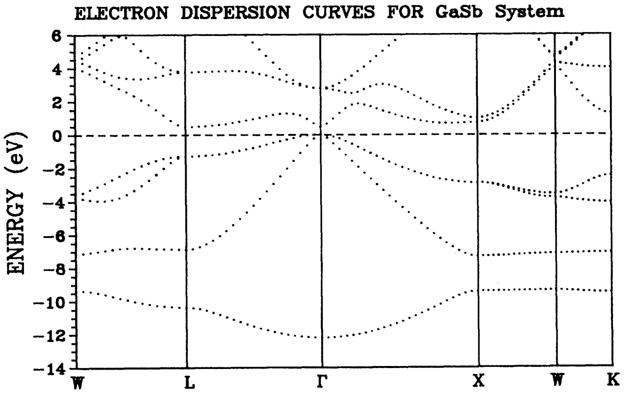

FIG. 4. Dispersion curves for GaSb.

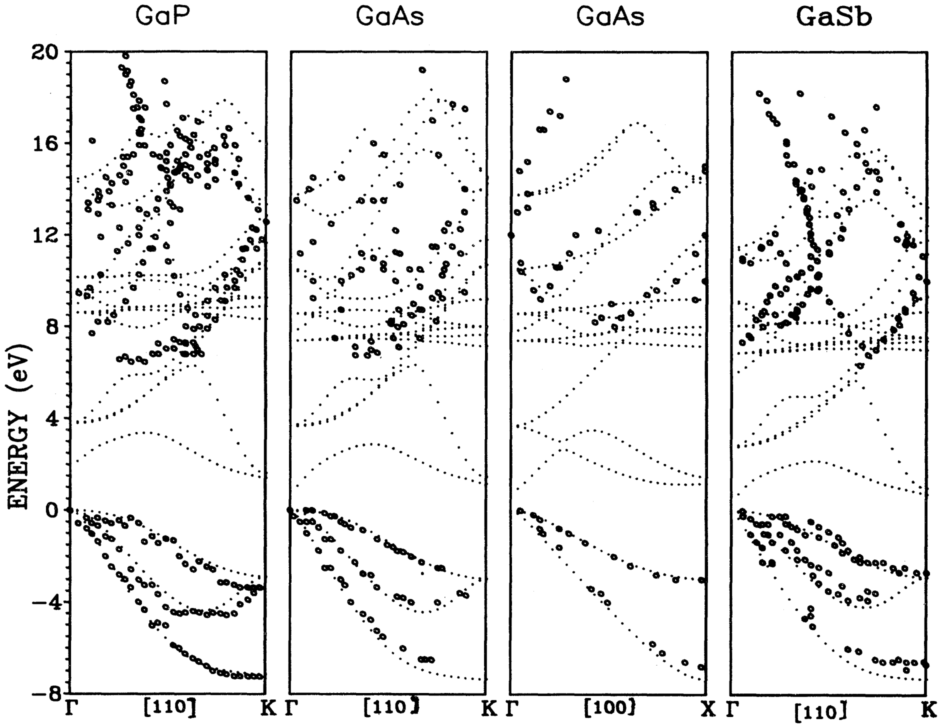

FIG. 5. Dispersion curves for GaP and GaSb in the [110] direction and for GaAs in the [110] and [100] directions, along with experimental data (Refs. 12 and 13) shown by small circles and calculation by dots.

TABLE I. Comparison of the *ab initio* band structure results and experiment at some symmetry points in the Brillouin zone in GaAs.

	LMTO[a]	LCGO[b]	NCP+PW[c]	NCP+PW[d]	LMTO[e]	LMTO[f]	LMTO[g]	Expt.[h]	Expt.[i]
Γ_1	−12.3	−12.35	−12.33	−12.55	−12.47	−12.85	−13.37	−13.1	
Γ_{15}	0	0	0	0	0	−0.36 0	0	0	0
Γ_1	1.1	1.21	1.10	0.64	0.64	0.25	0.83	1.42	
Γ_{15}	4.5	3.78		3.77			3.67		
X_1	−10.42	−9.79	−9.88	−10.23	−10.47	−10.49	−10.61	−10.75	
X_3	−6.20	−6.60	−6.62	−6.72		−7.06	−7.34	−6.70	−6.56
X_5	−2.43	−2.64	−2.61	−2.60	−2.57	−2.90 −2.83	−2.97	−2.80	−3.0
X_1	2.07	1.61	1.51	1.41	1.35	1.05	1.16	1.01	
X_3	2.31	1.88		1.62		1.28	1.47	2.38	
X_5		10.26		10.15			10.7	10.7	10.2
L_1	−11.06	−10.56	−10.64	−10.91	−11.14	−11.20	−11.47	−11.24	
L_1	−6.09	−6.49	−6.46	−6.53		−6.94	−7.18	−6.70	
L_3	−1.02	−1.12	−1.11	−1.09	−0.98	−1.18	−1.27	−1.30	
L_1	1.55	1.37	1.30	1.05	1.06	0.67	1.02	1.72	
L_3	4.91	5.15		4.64			4.59	5.41	
L_1		8.39		7.70			7.49		

[a] LMTO-ASA (Ref. 22).

[b] Linear combination of Gaussian orbital method (Ref. 23).

[c] Norm-conserving pseudopotential (Ref. 24).

[d] Similar to c but relativistic pseudopotential (Ref. 25).

[e] Similar to a but with the combined correction term (Refs. 26 and 27).

[f] Similar to a, fully relativistic with relaxed Ga(3*d*) cores (Ref. 2).

[g] Present work, scalar relativistic full LMTO with relaxed Ga(3*d*) and As(4*d*) cores.

[h] Experimental band structure (Refs. 10, 11, and 28).

[i] Reference 13.

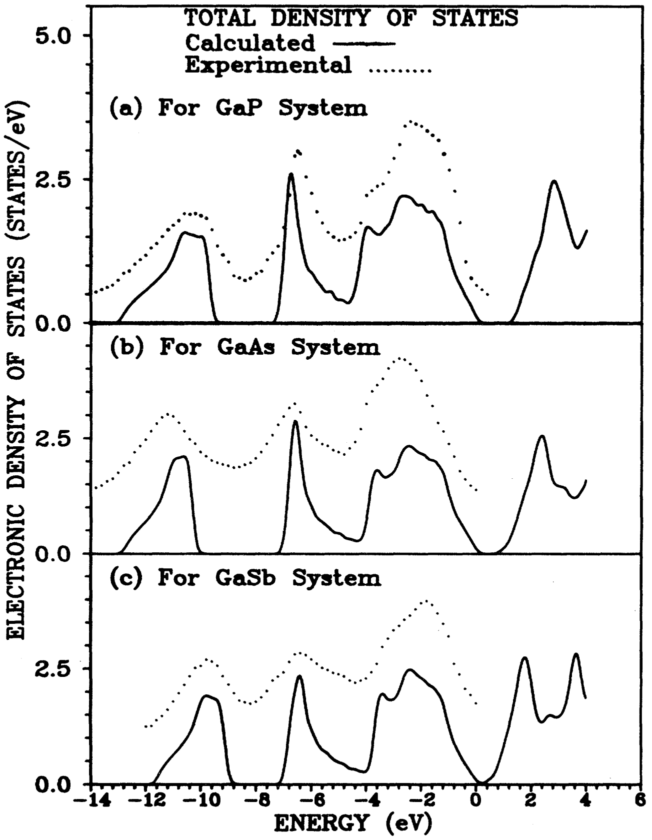

FIG. 6. Total density of states for (a) GaP, (b) GaAs, and (c) GaSb, along with the experimental data (Ref. 21).

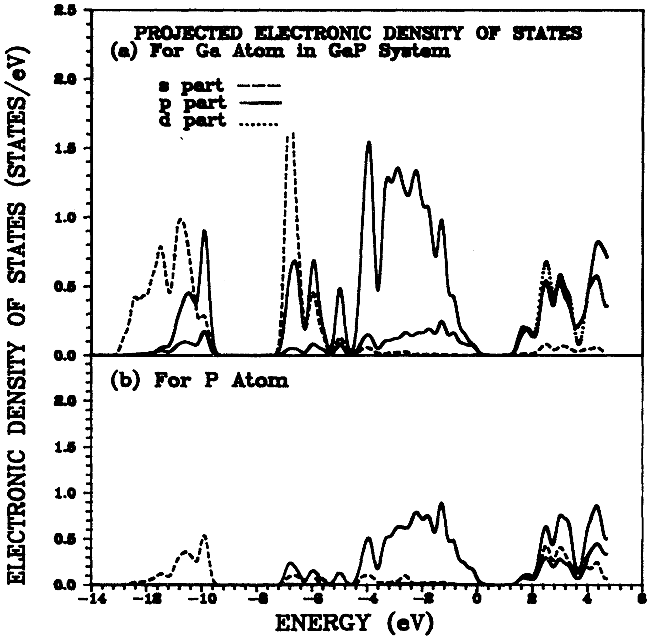

FIG. 7. Projected electronic density of states at different atoms for GaP.

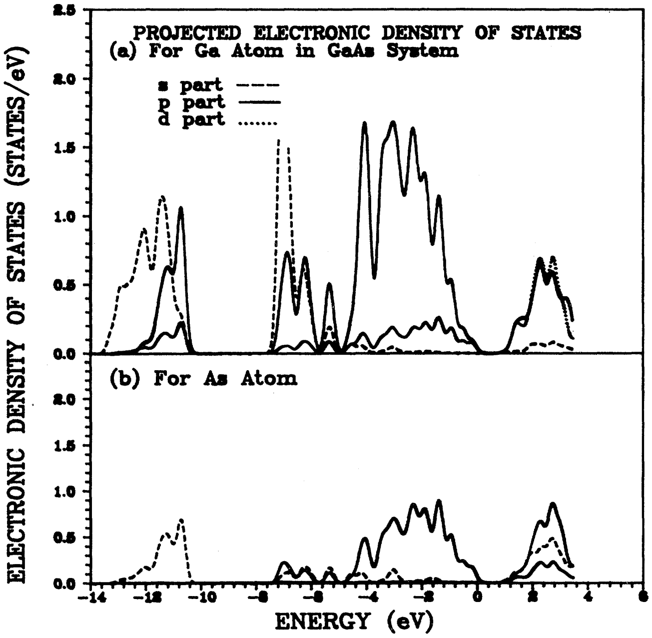

FIG. 8. Projected electronic density of states at different atoms for GaAs.

tal charge per unit cell outside the MT spheres is 2.48e in GaP, 2.50e in GaAs, and 2.62e in GaSb.

A. Electronic structure

The calculated dispersion curves for GaP, GaAs, and GaSb are shown in Figs. 2–5. For more technical details, see Ref. 15.

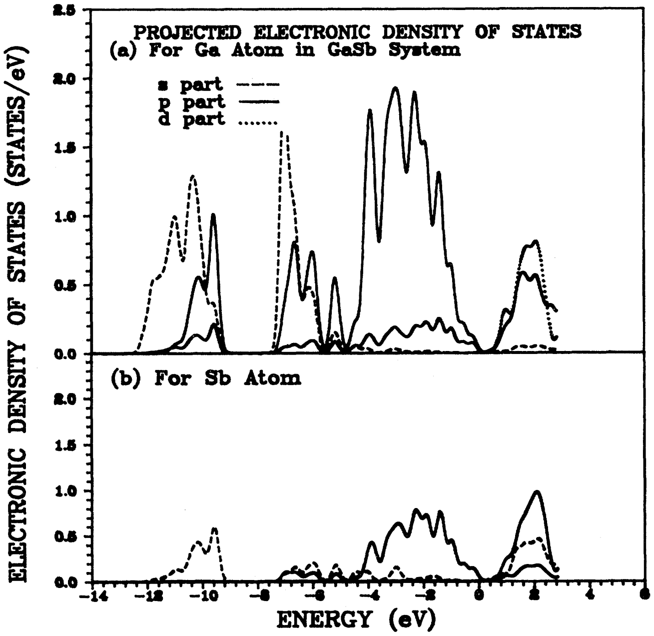

FIG. 9. Projected electronic density of states at different atoms for GaSb.

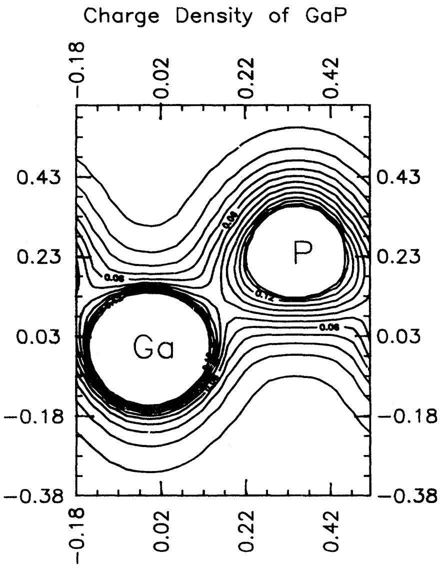

FIG. 10. Contour plots of the self-consistent charge density for the $(1,\bar{1},0)$ plane of GaP. The plots are in steps of 0.012 electron/$(\text{a.u.})^3$ up to a maximum of 0.14 $e/(\text{a.u.})^3$.

In GaP (Fig. 2) the lowest conduction state appears near the X point at $\mathbf{k}=(0.84,0,0)$ and the fundamental gap is thus indirect in conformity with experiment. For GaAs (Fig. 3) the bottom of the conduction band appears at the Γ point and the gap 0.83 eV is thus direct. The gap is also direct for GaSb (Fig. 4). The value of the direct band gap decreases with the atomic number of the anion.

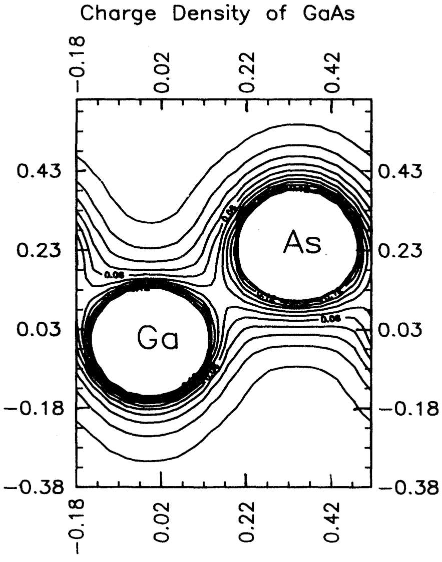

FIG. 11. Same as Fig. 10 but for GaAs.

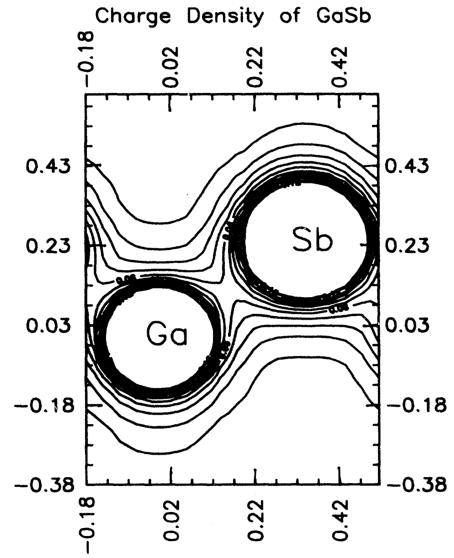

FIG. 12. Same as Fig. 10 but for GaSb.

Polarization-dependent angle-resolved photoemission data are available for these Ga-based semiconductors in one symmetry direction of the wave vector, i.e., in the [110] direction.[12,13] We have included these data in Fig. 5 from the lowest valence-band region (−8.0 eV) to the conduction-band region up to 20.0 eV. For GaAs, the figure includes more recent photoemission data[13] available for two symmetry directions, i.e., [110] and [100].

The experimental data are in overall good agreement with the calculated dispersion curves. Unfortunately, there are no measured data available just at the bottom of the conduction-band region, especially in the 0–6 eV region. The calculated dispersion curves lying in the valence-band region are in general in very good agreement with the experimental data except for some small discrepancies near the critical points K and X. In the higher conduction-band region, the comparison between the theory and experiment is not very clear because of the complexity of the dispersion curves and the experimental data. However, most of the experimental points are seen to lie on the computed dispersion curves.

In Table I, we make a comparison of the results of

TABLE II. Computed physical quantities for GaP. The lattice parameter is in units of Å. The elastic data are in units of Mbar and the phonon frequencies in cm^{-1}.

Quantity	Other calculations	Present	Expt.
Lattice parameter		5.3581	5.4505[a]
Bulk modulus	0.95[b]	0.9783	0.91[c]
C_{11}		1.5778	
C_{12}		0.6785	
C_{44}		0.3664	
TO(Γ)	377[b]	359	367[c,d]
TA(X)		142	106[d]
LA(X)		237	249[d]
LO(X)		355	366[d]
TO(X)		304	354[d]

[a] Reference 20.
[b] Reference 5.
[c] Reference 29.
[d] Reference 30.

TABLE III. Computed physical quantities for GaAs. The lattice parameter is in units of Å. The elastic data are in units of Mbar and the phonon frequencies in cm^{-1}.

Quantity	Other calculations	Present	Expt.
Lattice parameter		5.508	5.653^{a}
Bulk modulus	$0.77^{b}, 0.63^{c}, 0.78^{d}$ $0.73^{f,g,h}, 0.81^{i}$ 0.76^{d}	0.771	0.77^{e}
C_{11}		1.205	
C_{12}		0.554	
C_{44}		0.674	
TO(Γ)	$273^{b,j}, 276^{j}$ $270^{l,m}, 271^{n}$	264	$267^{k}, 270^{e}$
TA(X)	$82^{n}, 62^{j}$	85	$79^{k}, 80^{o}$
LA(X)	223^{n}	207	227^{k}
LO(X)	$240^{n}, 240^{j}$	214	$241^{k}, 230^{o}$
TO(X)	$254^{n}, 265^{j}$	266	$252^{k,o}$

[a] Reference 20.
[b] Reference 5.
[c] Reference 3.
[d] Reference 31.
[e] Reference 29.
[f] Reference 32.
[g] Reference 33.
[h] Reference 34.
[i] Reference 35.
[j] Reference 8.
[k] Reference 36.
[l] Reference 9.
[m] Reference 2.
[n] Reference 6.
[o] Reference 37.

first-principles local-density-approximation (LDA) band structure of GaAs and experiment at some symmetry points in the Brillouin zone. A comparison has already been made by Bachelet and Christensen.[4] For completeness, we reproduce it. Our results, especially in the valence-band region, are in better agreement with the experimental values than the other calculated results.

B. Density of states

We calculate the electronic density of states (DOS) by employing a sampling method with a Gaussian broadening of energy 0.2 eV over a mesh of 231 points in the irreducible part of the Brillouin zone. The total DOS is shown in Fig. 6(a) and the projected density of states in Fig. 7 for GaP. The low-lying peak near -12.0 eV arises from the Ga($4s$)-like orbital. The main peaks appear near -12.0, -9.9, -6.7, and -3.0 eV and originate from the Ga($4s$), bonding Ga($4p,4d$)-P($3s$), Ga($4s$), and Ga($4p$)-P($3p$) bonding orbitals, respectively. The top of the energy gap is composed of the antibonding Ga($4p,4d$) and P($3p$) states. The bottom of the conduction band is comprised of the antibonding Ga($4p,4d$) and P($3s,3p,3d$) states. The calculated value of the indirect energy gap of 1.36 eV is quite small, compared with the experimental[20] value of 2.24 eV. This underestimation of the electron energy gap is a usual result of first-principles LDA calculation of semiconductors and insulators. For more details, we refer to Ref. 15.

The total DOS and projected DOS on the two atoms for GaAs are shown in Figs. 6(b) and 8, respectively. The major peaks in the valence-states region appearing near -11.5, -7.0, -4.0, and -2.0 eV originate mainly from the bonding Ga($4s,4p,4d$)-As($4s$)-, Ga($4s$)-, Ga($4p,4d$)-, and the bonding Ga($4p,4d$)-As($4p$)-like orbitals, respectively. The calculated direct energy gap of 0.83 eV is quite small, compared to the experimental[20] value of 1.35 eV.

The total DOS and projected DOS for GaSb are shown in Figs. 6(c) and 9, respectively. The major peaks near -10.0, -7.0, -4.0, and -2.0 eV arise from the bonding Ga($4s,4p,4d$)-Sb($5s$)-, Ga($4s$)-, Ga($4p$)-, and Ga($4p,4d$)-Sb($5p$)-like bonding orbitals, respectively. The calculated direct energy gap of 0.47 eV is again small, compared to the experimental[20] value of 0.67 eV.

To make contact with experiment, we have included the photoemission data for the total DOS available[21] in the valence-band region in Fig. 6 in the various panels for

TABLE IV. Computed physical quantities for GaSb. The lattice parameter is in units of Å. The elastic data are in units of Mbar and the phonon frequencies in cm^{-1}.

Quantity	Other calculations	Present	Expt.
Lattice parameter		5.939	6.095^{a}
Bulk modulus	0.59^{b}	0.7994	0.56^{c}
C_{11}		1.1742	
C_{12}		0.6377	
C_{44}		0.2565	
TO(Γ)	$240^{b}, 230^{d}$	218	$230^{c,e}$
TA(X)	57^{d}	52	57^{e}
LA(X)	162^{d}	147	166^{e}
LO(X)	211^{d}	194	211^{e}
TO(X)	210^{d}	216	212^{e}

[a] Reference 20.
[b] Reference 5.
[c] Reference 29.
[d] Reference 6.
[e] Reference 38.

GaP, GaAs, and GaSb. The experimental density of states is in very good agreement with the present results both qualitatively and quantitatively.

C. Charge density

Contour plots of the self-consistent valence charge density for GaP, GaAs, and GaSb in the $(1,\bar{1},0)$ plane are shown in Figs. 10, 11, and 12, respectively, in steps of 0.012 electron/(a.u.)^3 up to a maximum of 0.14 e/(a.u.)^3.

D. Elastic constants

For more details see Ref. 15. The results for the elastic constants for GaP, GaAs, and GaSb along with the experimental data are included in Tables II, III, and IV, respectively. Experimental results are not available for comparison except for the bulk modulus. Excellent agreement is seen except for GaSb where the discrepancy is as large as 50%.

E. Phonon frequencies

Again, for technical details, see Ref. 15. The results for GaP, GaAs, and GaSb have been presented in Tables II, III, and IV, respectively. Only one kind of atom moves in the Brillouin zone-boundary modes LO(X) or LA(X); the mode with the heavy atom corresponds to the acoustic mode LA(X), whereas the one involving motion of light atoms is the optical mode LO(X).

For all the systems, the TO(Γ) frequency is in very close agreement with the experimental data and also with other calculated data. The other frequencies are also in reasonable agreement with measured values.

In GaSb (Table IV) no experimental data are available for comparison. Detailed experimental work needs to be performed.

III. CONCLUSIONS

The modified version of the LMTO method generates the lattice parameters, bulk modulus, electron dispersion curves, density of states, elastic constants, and phonon frequencies for the Ga-based compounds in close agreement with the experimental data wherever available.

ACKNOWLEDGMENTS

All the calculations were performed on HP 720 and DEIL 5100 computer systems available with us. The authors are thankful to the Department of Science and Technology, New Delhi and the University Grants Commission, New Delhi for their financial assistance.

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[1] James R. Chelikowsky and Marvin L. Cohen, Phys. Rev. B **14**, 556 (1976).

[2] K. H. Weyrich, L. Brey, and N. E. Christensen, Phys. Rev. B **38**, 1392 (1988).

[3] B. I. Min, S. Massidda, and A. J. Freeman, Phys. Rev. B **38**, 1970 (1988).

[4] Giovanni B. Bachelet and Niels E. Christensen, Phys. Rev. B **31**, 879 (1985).

[5] M. Causa, R. Dovesi, and C. Roetti, Phys. Rev. B **43**, 11 937 (1991).

[6] P. Giannozzi, S. de Grioncoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991).

[7] D. R. Hamann, M. Schluter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[8] K. Kunc and R. M. Martin, Phys. Rev. B **24**, 2311 (1981).

[9] O. H. Nielsen and R. M. Martin, in *Electronic Structure, Dynamics, and Quantum Structural Properties of Condensed Matter,* edited by J. T. Devreese and P. Van Camp (Plenum, New York, 1985), p. 313.

[10] J. S. Blakemore, J. Appl. Phys. **53**, R123 (1982).

[11] M. Cardona and G. Harbeke, *Semiconductors. Physics of Group IV Elements and III-V Compounds,* edited by K. -H. Hellwege and O. Madelung, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. a (Springer, Berlin, 1982), pp. 242ff.

[12] Gwyn P. Williams *et al.*, Phys. Rev. B **34**, 5548 (1986).

[13] X. D. Zhang *et al.*, Phys. Rev. B **48**, 17 077 (1993).

[14] Bal K. Agrawal and Savitri Agrawal, Phys. Rev. B **45**, 8321 (1992).

[15] Bal K. Agrawal, P. S. Yadav, and Savitri Agrawal, Phys. Rev. B **50**, 14 881 (1994).

[16] M. Methfessel, Bal K. Agrawal, and M. Scheffler (unpublished).

[17] Bal K. Agrawal and Savitri Agrawal, Phys. Rev. B **48**, 6451 (1993).

[18] Bal K. Agrawal and S. Agrawal, Physica C **233**, 8 (1994).

[19] M. Methfessel, Phys. Rev. B **38**, 1537 (1988).

[20] *CRC Handbook of Chemistry and Physics,* 70th ed., edited by R. C. Weast, D. R. Lide, M. J. Astle, and W. H. Beyer (CRC, Boca Raton, Florida, 1990), pp. E-106 and E-110.

[21] L. Ley *et al.*, Phys. Rev. B **9**, 600 (1974).

[22] T. Jarlborg and A. J. Freeman, Phys. Lett. **74A**, 349 (1979).

[23] C. S. Wang and B. M. Klein, Phys. Rev. B **24**, 3393 (1981).

[24] D. R. Herman, M. Schlûter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[25] L. Kleinman, Phys. Rev. B **21**, 2630 (1980); G. B. Bachelet and M. Schlûter, *ibid.* **25**, 2103 (1982). A compilation of relativistic norm-conserving pseudopotentials is given by G. B. Bachelet, D. R. Herman, and M. Schlûter [Phys. Rev. B **26**, 4199 (1982)] for the entire Periodic Table in terms of a few analytical functions.

[26] M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[27] H. MacDonald and S. H. Vosko, J. Phys. C **12**, 2977 (1979).

[28] T. C. Chiang, J. A. Knapp, M. Aono, and D. E. Eastman, Phys. Rev. B **21**, 3513 (1980).

[29] *Semiconductors. Physics of Group IV Elements and III-V Compounds* (Ref. 11).

[30] J. L. Yarnell, J. L. Warren, R. J. Wenzel, and P. J. Dean, *Inelastic Neutron Scattering* (IAEA, Vienna, 1968), Vol. 1, p. 301.

[31] D. M. Wood, S. H. Wei, and A. Zunger, Phys. Rev. Lett. **58**, 1123 (1987); Phys. Rev. B **37**, 1342 (1988).

[32] S. Froyen and M. L. Cohen, Phys. Rev. B **28**, 3258 (1983).

[33] D. M. Bylander and L. Kleinman, Phys. Rev. B **34**, 5280 (1986); **36**, 3229 (1987); Phys. Rev. Lett. **59**, 2091 (1988).

[34] S. Ciraci and I. P. Batra, Phys. Rev. Lett. **58**, 14 (1987); Phys. Rev. B **36**, 1225 (1987).

[35] J. Ihm and J. D. Joannopoulos, Phys. Rev. B **24**, 4191 (1981).

[36] J. L. T. Waugh and G. Dolling, Phys. Rev. **132**, 2410 (1963).

[37] G. Dolling and J. L. T. Waugh, in *Lattice Dynamics,* edited by R. F. Wallis (Pergamon, London, 1965), p. 19.

[38] M. K. Faar, J. G. Traylor, and S. K. Sinha (unpublished); M. K. Faar (private communication).