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Electronic properties under pressure of the cubic binary Ga compounds

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Results of a calculation of ground-state electronic properties of the binary Ga compounds in the zinc-blende structure are given. These properties are derived from the total crystalline energy, which is evaluated in the local-density approximation using *ab initio* norm-conserving nonlocal pseudopotentials. The calculated properties are the lattice constant, the bulk modulus, and its pressure derivative. Also given are the first- and second-order coefficients of the main energy gaps as a function of the pressure and of the relative change of the lattice constant. Furthermore, the transition pressures from the direct to the indirect band gap are determined. All the results are compared with recent measurements and with other *ab initio* calculations.

Recently,[1] results have been published of the pressure coefficients of the direct and indirect optical absorption in GaAs. In these experiments the absorption edge is measured instead of the luminescence or photoreflectance peaks as was done earlier. It is claimed by these authors that due to the thickness of the samples (≤ 3 μm) the recent measurements are more accurate than the previous ones.

In the present paper the above-mentioned experimental results are compared with *ab initio* calculations. These calculations have been performed not only for the widely studied semiconductor GaAs, but also for the other binary Ga compounds, GaN, GaP, and GaSb. All four materials have been treated in the cubic, i.e., zinc-blende, structure although under normal conditions, i.e., zero pressure and room temperature, GaN crystallizes in the wurtzite structure. As a matter of fact, GaN has not been observed in the zinc-blende structure while the other three compounds GaP, GaAs, and GaSb do not have a wurtzite phase in the experimental range of pressure and temperature. GaP and GaSb transform to the β-tin structure at 240 and 76.5 kbar, respectively, and GaAs to an orthorhombic distorted NaCl structure at 209 kbar. Besides the total energy of the crystal, the lattice constant, the bulk modulus, and its pressure derivative, the *ab initio* calculations of electronic properties include the first- and second-order coefficients of the pressure and lattice parameter dependence of the Γ, X, and L gap, the hydrostatic deformation potential, and the crossover pressure from direct to indirect band gaps.

TABLE I. Calculated and experimental values of the lattice constant (a) (in Å), the bulk modulus (B_0) (in Mbar), and the pressure derivative of the bulk modulus (B_0').

		Experiment	Present work	Ref. 4	Ref. 5	Ref. 6	Ref. 7	Ref. 8	Ref. 9
GaN	a		4.4401						
	B_0		1.5833						
	B_0'		2.8446						
GaP	a	5.4505[a]	5.3585	5.16		5.34	5.79	5.832	
	B_0	0.8819[b]	0.8582	0.92		0.897	0.87	0.81	
	B_0'	4.79[b]	4.0394					4.4	
GaAs	a	5.6532[c]	5.5779		5.617	5.570			5.55
	B_0	0.7466[d]	0.7090		0.81	0.725			0.73
	B_0'	4.67[d]	3.9373						
GaSb	a	6.0959[e]	6.0234						
	B_0	0.570	0.5220						
	B_0'	4.8	4.4417						

[a]Reference 10.
[b]Reference 11.
[c]Reference 12.
[d]Reference 13.
[e]Reference 14.

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TABLE II. Calculated and experimental direct and indirect band gaps (in eV).

	Calculation		Experiment	
	Direct	Indirect	Direct	Indirect
GaN	1.401	2.712		
GaP	2.272	1.379	2.895[a]	2.350[b]
GaAs	0.810	1.059	1.43[c]	1.85[d]
GaSb	0.444	0.494	0.822[e]	1.095[f]

[a]Reference 15.
[b]Reference 16.
[c]Reference 1.
[d]Reference 17.
[e]Reference 18.
[f]Reference 19.

The theory and main approximations used in these calculations have been given before.[2] For the exchange contribution to the electron energy the Kohn-Sham expression has been used and for the correlation contribution the Wigner interpolation formula. The ionic potentials are represented by the norm-conserving nonlocal pseudopotentials of Bachelet, Hamann, and Schlüter.[3] The kinetic energy of the electrons is cut off at 16.5 hartrees for GaN, 12 hartrees for GaP, 10.5 hartrees for GAs, and 9.5 hartrees for GaSb, which corresponds to an expansion of the electron wave functions in, respectively, 537, 609, 537, and 609 plane waves. The lattice constants a, bulk moduli B_0, and their pressure derivatives B'_0, calculated from the Murnaghan equation of state, are given in Table I, together with the experimental data and the results of other *ab initio* calculations. For GaN in the zinc-blende structure comparison with experiment is not possible. Neither do other *ab initio* calculations of this material exist. For the other three compounds, the present calculations agree with experiment within 2% for a, 8.5% for B_0, and within 16% for B'_0. In general the trend shown by the results is that the agreement improves as the element of column V in the Ga compound becomes heavier: the heavier the element, the larger the lattice parameter and the lower the kinetic energy cutoff for the same number of plane waves. Experience with similar calculations on the IV-IV covalent semiconductors has shown that, as a general rule, the convergence is better for heavier materials.[2] Other *ab initio* calculations have been performed only for GaP and GaAs. The results of Bachelet *et al.*[4] and Christensen[8] have been obtained, respectively, with a linear combination of local orbitals and linearized augmented plane waves (APW's). Ihm[5] and Nielsen[9] used a plane-wave expansion with a Löwdin perturbation

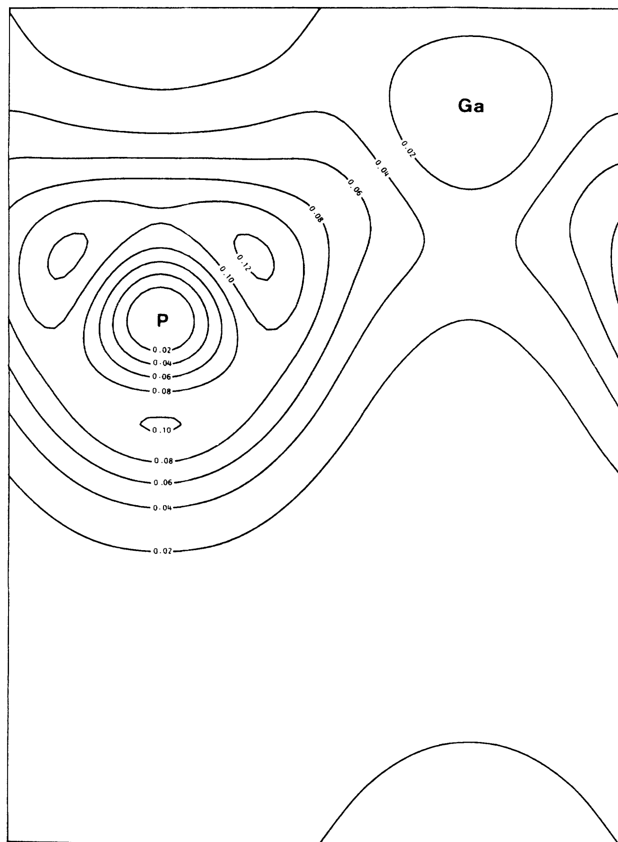

FIG. 2. Valence charge density of GaP in the (110) plane. Units are $e/\mathrm{a.u.}^3$. The contour step is 0.02 $e/\mathrm{a.u.}^3$.

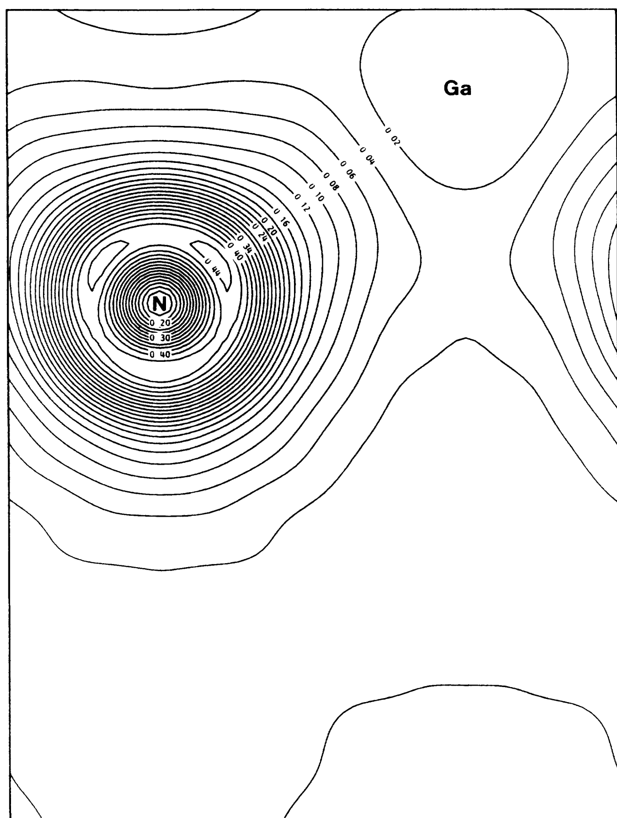

FIG. 1. Valence charge density of GaN in the (110) plane. Units are $e/\mathrm{a.u.}^3$. The contour step is 0.02 $e/\mathrm{a.u.}^3$.

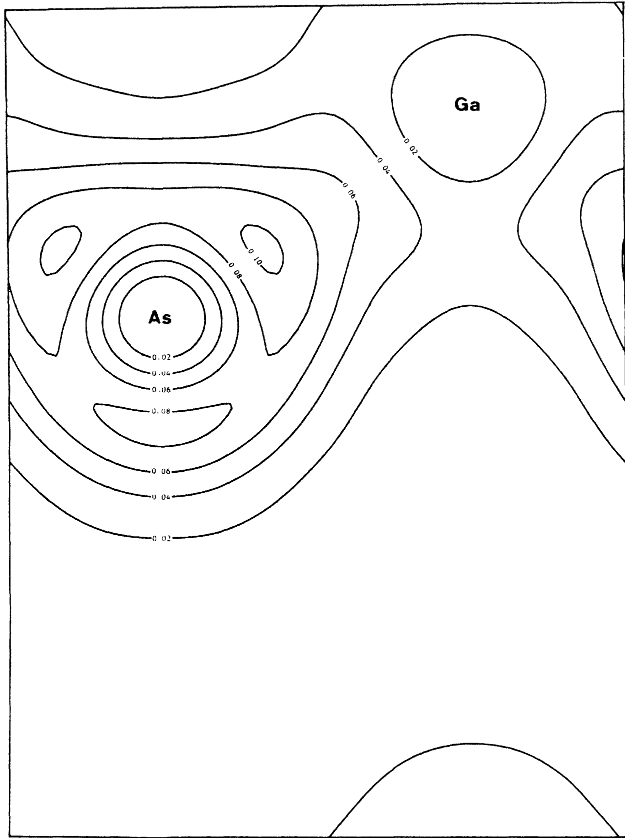

FIG. 3. Valence charge density of GaAs in the (110) plane. Units are $e/\text{a.u.}^3$. The contour step is 0.02 $e/\text{a.u.}^3$.

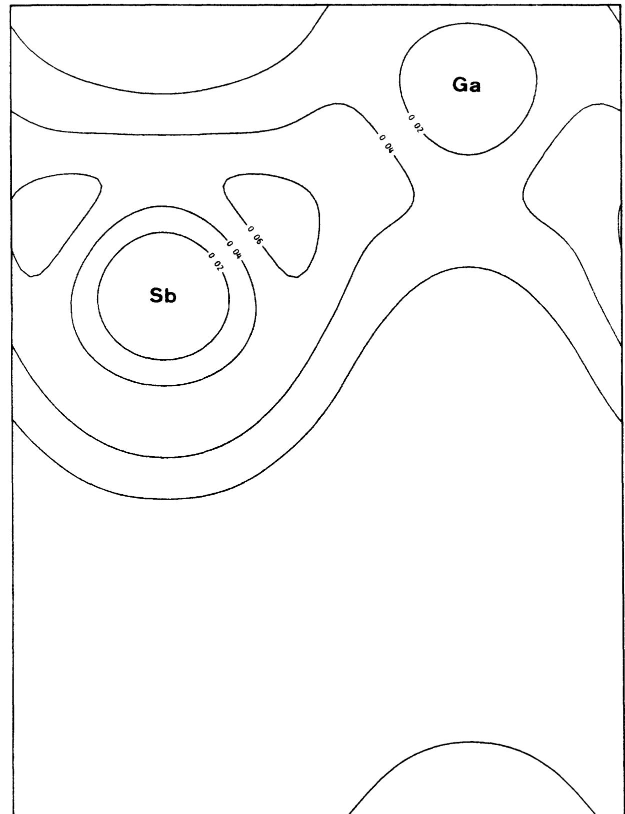

FIG. 4. Valence charge density of GaSb in the (110) plane. Units are $e/\text{a.u.}^3$. The contour step is 0.02 $e/\text{a.u.}^3$.

scheme totaling, respectively, 280 and 550 waves. The cutoffs in the calculation of Froyen[6] were 6 hartrees and of Rodriguez[7] 140 plane waves. It should be noted that in the present work a substantially larger basis (537–609 plane waves) than in the older calculations is used. The present calculation shows the best agreement with those of Froyen and Nielsen for a and B_0 to within about 4%, while B_0' has not been calculated by these authors.

Table II gives the calculated and experimental values of the direct (Γ_{15} valence band to Γ_1 conduction band) and of the indirect (Γ_{15} to X_1 for GaN and GaP and Γ_{15} to L_1 for GaAs and GaSb) band gaps. These gaps are underestimated by a factor less than 2 except in the case of GaSb where this factor increases to 2.5 for the indirect gap. Of course, the present calculation is nonrelativistic. Experimentally the spin-orbit splitting in GaSb has been determined as 0.747 eV.[20] It should also be noted that the calculated value of the band gap can be improved by extending the theory beyond the local density approximation.[21]

Figures 1–4 show contour maps of the valence charge density of the four compounds in the (110) plane with a contour step of 0.02 $e/\text{a.u.}^3$. The density of the lines around the anions shows that in GaN more charge is concentrated around the anion N than in GaSb around Sb, i.e., the heavier the anion, the less polar the crystal.

Figure 5 shows the valence charge density in between two atoms in the [111] direction. It is clear that going from GaN to GaSb, the charge density gradually becomes more symmetric, an indication of the fact that GaSb is more covalent than GaAs, which in turn is more covalent than GaP, etc. According to Phillips's ionicity scale, GaN is one of the most ionic III-V semiconductors.

Table III gives the first- and second-order pressure coefficients b and c of the energy difference between the Γ_1, X_1, and L_1 states and the top valence band Γ_{15}. These coefficients are determined by fitting the equation

$$E_0(p)-E_0=bp+cp^2 \qquad (1)$$

to the calculated energy differences for six different pressures between 0 and 1 Mbar. The results are compared with existing experimental data. For GaP and GaAs, respectively, four and five measurements are available while for GaSb only one measurement of the first-order coefficient b of the energy difference in the Γ point was found. These coefficients have been determined by fitting the experimental results at pressures between 0 and the transition pressure of the crystal which is less than 175 kbar for the four compounds, far below the 1 Mbar used in the theoretical fit. Whereas the calculated first-order coefficients b agree quite well with the experimental re-

sults, the second-order coefficients c are quite different in the case of GaP. For the X_1-Γ_{15} energy difference in GaP the coefficients c even differ in sign (1.60 eV/Mbar^2 versus -4.8 eV/Mbar^2). The agreement between theoretical and experimental second-order coefficients is better in GaAs. The only other calculation based on *ab initio* methods has been performed by Christensen[8] for the gap in the Γ point of GaAs. His results are $b=12.02$ eV/Mbar and $c=-36.3$ eV/Mbar^2. However, in his article he mentioned that Syassen found -18 eV/Mbar^2 for c.

Table IV gives the first- and second-order coefficients of the same energy differences as before in an expansion with respect to the relative change of the lattice constant $\Delta a/a$, where $\Delta a = a_p - a$ and a_p and a are the lattice constants at pressure p and at equilibrium,

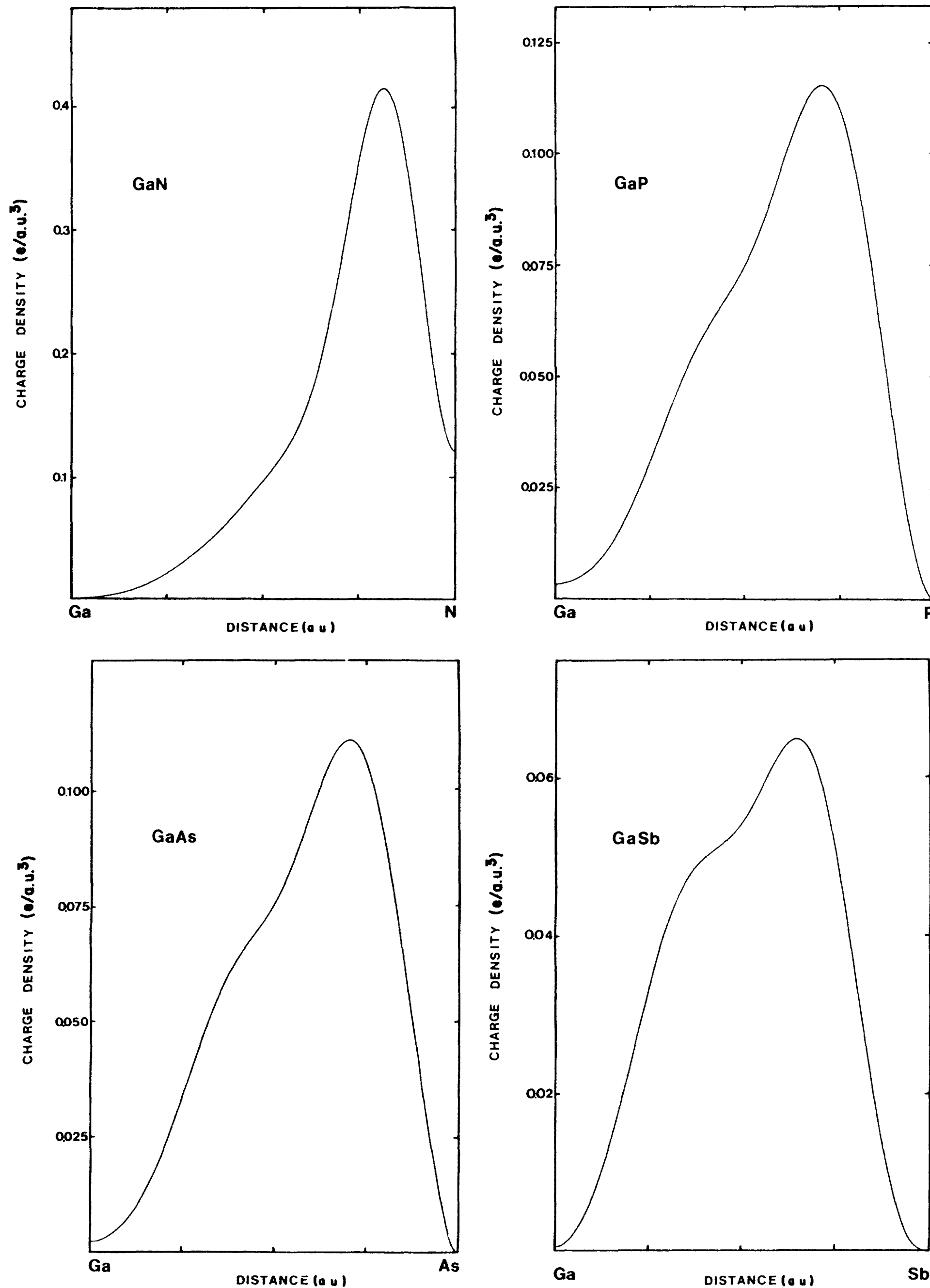

FIG. 5. Valence charge density of the Ga compounds in the [111] direction. Units are e/a.u.^{3}. Notice the different scales of the four figures.

TABLE III. Calculated and experimental linear (b) and quadratic (c) coefficients of the pressure dependence of the band gaps (b in eV/Mbar, c in eV/Mbar^2).

		Calculation	Experiment	
		GaN		
Γ gap	b	3.58		
	c	0.63		
X gap	b	−1.73		
	c	5.32		
L gap	b	2.67		
	c	3.23		
		GaP		
Γ gap	b	9.56	10.50±0.16[a];	9.7±0.8[b]
	c	−9.16		−35±6.0[b]
X gap	b	−2.18	−1.4[a];	−2.4[b]
	c	1.60		−4.8[b]
L gap	b	3.71		
	c	−3.88		
		GaAs		
Γ gap	b	11.52	12.5±0.5[c];	10.8±0.3[d]
	c	−16.83	−37±5[c];	−14±2[d]
X gap	b	−2.44	−2.7[e];	−1.35±0.13[d]
	c	2.67		
L gap	b	4.52	5.5[f]	
	c	−6.27		
		GaSb		
Γ gap	b	13.75	14.0[g]	
	c	−22.43		
X gap	b	−2.07		
	c	1.56		
L gap	b	4.45		
	c	−6.86		

[a]Reference 22. [b]Reference 23. [c]Reference 24. [d]Reference 1. [e]Reference 25. [f]Reference 26. [g]Reference 27.

TABLE IV. Calculated and experimental linear (b^*) and quadratic (c^*) coefficients of the dependence of the band gaps on the relative change in the lattice constant (in eV).

		Calculation	Experiment
		GaN	
Γ gap	b^*	−16.85	
	c^*	128.98	
X gap	b^*	8.72	
	c^*	174.18	
L gap	b^*	−12.29	
	c^*	211.78	
		GaP	
Γ gap	b^*	−26.56	
	c^*	30.02	
X gap	b^*	5.79	
	c^*	−20.37	
L gap	b^*	−10.35	
	c^*	4.21	
		GaAs	
Γ gap	b^*	−24.31	−26.0±0.8[a]
	c^*	38.52	46.0±20.0[a]
X gap	b^*	5.20	5.0±0.5[a]
	c^*	−16.97	
L gap	b^*	−9.57	
	c^*	18.19	
		GaSb	
Γ gap	b^*	−23.16	
	c^*	38.73	
X gap	b^*	3.20	
	c^*	−23.49	
L gap	b^*	−7.46	
	c^*	15.88	

[a]Reference 1.

$$E_0\left(\frac{\Delta a}{a}\right)-E_0=b^*\left(\frac{\Delta a}{a}\right)+c^*\left(\frac{\Delta a}{a}\right)^2 .$$

Experimentally only the coefficients in the Γ point and the first-order coefficient for the X_1-Γ_{15} energy difference (both for GaAs) have been determined recently by Goñi *et al.*[1] The agreement is within 7% for b^* and around 16% for c^*.

The hydrostatic deformation potentials

$$a_D=\frac{dE_0}{d\ln V}=B_0\frac{dE_0}{dp} ,$$

where E_0 is the direct band gap, are given in Table V. The agreement with the experimental values for GaP and GaAs is within 18%. In Fig. 6 the calculated difference of the direct band gap at pressure p and at zero pressure, $E_0(p)-E_0(0)$ is plotted as a function of the relative density $(\rho-\rho_0)/\rho_0$ for GaAs together with the experimental results of Ref. 1. The slope of the straight line corresponds to a deformation potential

$$\frac{dE_0}{d\ln\rho}=8.19 \text{ eV}$$

which should be compared with the value 8.5±0.1 eV obtained from a least-squares fit through the experimental data points. The discrepancy between theory and experiment is about 4%. Similar deformation potentials have been calculated for the other compounds and are given in Table VI. Measurements for the other compounds are not found in the literature.

TABLE V. Calculated and experimental values of the hydrostatic deformation potential a_D (in eV).

	Calculation	Experiment	
GaN	5.67		
GaP	8.20	9.3±1.5[a];	9.9±0.3[b]
GaAs	8.17	9.77±0.8[c];	6.7[d]
GaSb	7.18		

[a]Reference 22.
[b]Reference 28.
[c]Reference 29.
[d]Reference 30.

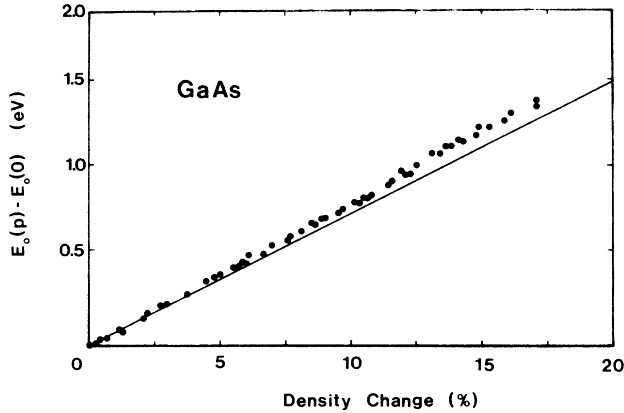

FIG. 6. Direct gap of GaAs as a function of the relative density: solid line, calculation; circles, experiment (Ref. 1).

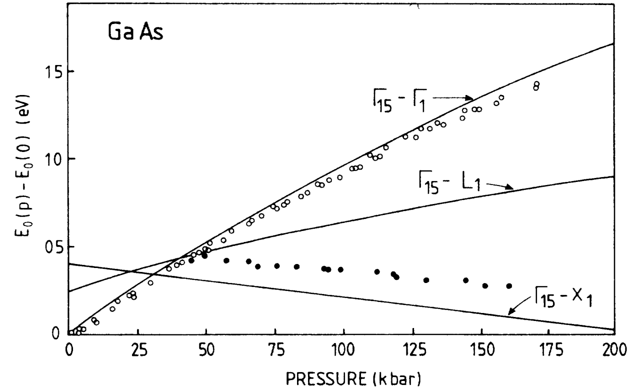

FIG. 7. Indirect and direct band gap of GaAs as a function of the pressure. Solid lines, calculation; open circles, direct gap experiment; solid circles, indirect gap experiment (Ref. 1).

In Fig. 7 the energy gaps in the Γ, X, and L points are given as a function of pressure up to 200 kbar for GaAs. The experimental data points for the Γ and X gap obtained by Goñi *et al.*[1] are shown by open and solid circles. For the Γ gap the overall agreement between theory and experiment is quite good while for the X gap the calculated curve has about the same slope as the least-squares fit through the data but the theoretical curve is shifted down by a constant over the whole experimental range from 50 to 200 kbar. As has been mentioned earlier the local-density approximation (LDA) does not reproduce the band gaps correctly and the error is not the same for different gaps. However, according to Ref. 21, the self-energy corrections to the LDA band gaps are to a good approximation k independent for GaAs as well as Si and therefore independent of the lattice parameter. The differences between the theoretical and experimental X and Γ gaps are, respectively, 0.697 and 0.62 eV. The difference between these two values is 0.077 eV which is the constant shift between theoretical and experimental Γ_{15}-X_1 curves at zero pressure.

The pressure at which GaAs makes the transition from a direct to an indirect band gap semiconductor is given at the crossing of the Γ_{15}-Γ_1 and Γ_{15}-X_1 curves. Experimentally Goñi *et al.*[1] found 42 kbar while in the present work a value of 30.9 kbar is calculated. In Fig. 7 the crossover pressure between the Γ and L gaps occurs at 36.5 kbar. Table VII gives all the crossover pressures from direct to indirect X and L gaps for the four compounds. It should be noted that these pressures are negative for GaP since this material is the only one of the series which has an indirect band gap under normal conditions.

In summary, *ab initio* calculations are presented of electronic properties under pressure for four Ga compounds in the zinc-blende structure. Crossover pressures from a direct to an indirect gap semiconductor are compared with experiment for GaAs and predicted for the other materials. At the same time the lattice constant, bulk modulus, and its pressure derivative derived from the total energy of the ground state are also given.

TABLE VI. Calculated and experimental values of the deformation potential $dE_0/d\ln\rho$ (in eV).

	Calculation	Experiment
GaN	6.73	
GaP	8.67	
GaAs	8.19	8.5±0.1[a]
GaSb	7.82	

[a]Reference 1.

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TABLE VII. Crossover pressure from direct to indirect band gap (in kbar).

		Calculation	Experiment
GaN	X gap	216.7	
	L gap	537.0	
GaP	X gap	−63.6	
	L gap	−68.2	
GaAs	X gap	30.9	30[a];40±2[b];42±3[c] 35[d]
	L gap	36.5	
GaSb	X gap	19.8	
	L gap	4.4	

[a]Reference 25.
[b]Reference 24.
[c]Reference 1.
[d]Reference 29.

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