PHYSICAL REVIEW B VOLUME 31, NUMBER 2 15 JANUARY 1985

Relativistic and core-relaxation effects on the energy bands of gallium arsenide and germanium

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(Received 17 July 1984)

Relativistic self-consistent band-structure calculations using either norm-conserving pseudopotentials or the linear-muffin-tin-orbital method (LMTO) demonstrate that relativistic effects on some conduction bands of gallium arsenide, if qualitatively not unexpected, are however, surprisingly large (the direct gap is reduced by one-half), despite the relatively light atoms. This is discussed in terms of a simple bonding-antibonding picture: Relativistic effects may either be depressed or amplified, with respect to free atoms, by the formation of bands and bonds. The gallium $3d$ core states are known to be shallow, i.e., not far enough from the $4s$ and $4p$ energies to allow them to be treated as completely frozen-core states. Therefore, in a new self-consistent LMTO calculation we treat them on the same footing as the other valence-band states. The most evident effects of the Ga $3d$ core-relaxation are a further, sizable shrinkage of the gaps, and a clear improved agreement of the valence bands with photoemission experiments. We stress the influence of relativistic and core-relaxation effects on the bands of GaAs, and also show, for the first time, that the intrinsic failure of the local-density approximation as far as gaps are concerned is much larger for third-row semiconductors than for, e.g., the better-known case of Si. This is emphasized by our calculation for the neighboring elemental semiconductor, germanium, where almost no gap is found, i.e., metallization has occurred one row too early. The calculated gaps are a necessary reference for the development of the density-functional theory of the energy gap.

I. INTRODUCTION

Relativistic effects are known to produce measurable spin-orbit splittings[1] and shifts[2] in the energy bands of elemental and compound semiconductors. Theoretical investigations have included both aspects[2,3] since the early years of solid-state physics; but at that time the most attention was paid to a correct description of the excitation spectra of semiconductors.[4] The degree of sophistication and accuracy of the calculations, on the other hand, were not sufficient to demonstrate where the most severe approximations in the physical models could possibly be hidden.[5] As a result, even in the pioneering self-consistent orthogonalized-plane-wave (OPW) calculations by Herman and co-workers,[6] which were later extended to include relativistic corrections,[7] the conduction bands were often adjusted to reproduce the experimentally measured gaps.[8] This fact made the discussion of relativistic effects on the gaps somewhat difficult. Another complication in that respect arose because relativistic corrections were sometimes simulated by means of core-state shifts introduced *ad hoc*, rather than directly obtained from the calculations.[2,6] Nevertheless, in the few nonadjusted calculations,[7] the relativistic effects were clearly visible. The fact that they tend to decrease the direct gap of tetrahedral semiconductors, as recently re-emphasized by Wang and Klein[9] and by Glötzel *et al.*,[10] was qualitatively well known.[7] Less was known about another factor which can influence the gaps of many important semiconductors, namely those containing gallium. The gallium $3d$ states are corelike, but nevertheless they are so close to the $4s$ states that treating them as "frozen-core" states may result in a slightly inaccurate description of the binding process.[11,12] Although the role of orthogonalization to inner $3d$ states was known,[13] little attention was paid, to our knowledge, to the *large* influence of their relaxation on selected bands and $\vec{k}$ points.

The main purpose of this work is to study these two effects—relativistic shifts and core relaxations—from a qualitative as well as quantitative point of view. As an example, we chose GaAs, for which a series of self-consistent calculations are performed. They are based on two different computational schemes, the linear-muffin-tin-orbital[14] (LMTO) method and norm-conserving pseudopotentials.[15] Different levels of approximation are treated—nonrelativistic, scalar-relativistic, and fully relativistic band structures are calculated, with the Ga $3d$ states treated both as "frozen" and "relaxed" states. Our results show that this quantitative investigation is indeed necessary. Neither of the effects is negligible. As far as the gaps are concerned, they introduce corrections of the same order of magnitude as the gaps themselves. Within the local-density approximation (LDA) for exchange and correlation, this also means that the absolute values of the calculated gaps turn out to be much worse than already believed for GaAs: Once all effects are included, the completely first-principles gap of GaAs within the LDA equals 0.25 eV (or $\sim\frac{1}{6}$ of the experimental value). This leads us to check the situation for the neighboring elemental semiconductor (germanium) also, since, experimentally, its gap is about half the GaAs gap, and furthermore it is different in character (indirect versus direct). In Ge there is no need to relax the $3d$ core states, but relativistic effects are as important[10] as they are in GaAs. The investigation was performed using relativistic norm-conserving pseudopotentials[16] as well as the LMTO method,[14,17] and it was found, in fact, that the LDA gap of germanium is practically zero and closes at Γ. In nature, this occurs in the next row, for Sn ($Z=50$). Our results then reach a twofold goal: a quantitative estimate of relativistic and core-relaxation effects in GaAs, and a revised opinion about the magnitude of the discrepancy between experimental and local-density gaps for third-row semiconductors.

The paper will follow these following lines: In Sec. II we describe the comparison of relativistic and nonrelativistic LMTO calculations for GaAs using the same potential for both calculations, in order to demonstrate the net effect of relativistic equations on the gaps. We also discuss therein the results of relativistic atomic shifts on different bands and at different $\vec{k}$ points with the help of a very simple bonding-antibonding model. In Sec. III we present the results of two self-consistent scalar-relativistic band calculations for GaAs using LMTO (Refs. 14 and 17) and norm-conserving pseudopotentials (Refs. 15 and 16). This provides an excellent comparative test of the two methods. The relaxation of the Ga $3d$ states is investigated in Sec. IV, and in Sec. V we describe the band structure of germanium within the LDA. Some conclusions are given in Sec. VI.

II. RELATIVISTIC SOLID-STATE SHIFTS

Relativistic effects in the free atom have a twofold result: a downward shift of the $1s$ state, which, in turn, propagates to all higher s states through mutual orthogonality (so that also higher and higher s states are shifted down by decreasing amounts), and a splitting of the $l \neq 0$ states into spin-orbit doublets.[18] Both effects increase with atomic number. The spin-orbit splitting has received more attention in the past for its implications on the semiconductor bands and their symmetry classification.[1,3,7,19] The scalar-relativistic effects[20] have also been known to cause important modifications of the band structure of metals[17,21] and semiconductors.[5–8,10] The latter effects have recently explained, for example, the remarkable insulating nature of the intermetallic compound CsAu.[22] We are therefore not dealing with qualitatively unknown effects, but rather making a quantitative point concerning third-row tetrahedral semiconductors such as GaAs and Ge ($Z=31$, 32, and 33). We will show that although relatively unimportant for the valence bands and the total charge density [hence, nonrelativistic calculations of the structural properties of GaAs (Refs. 11 and 12) and Ge (Ref. 23) are not seriously affected], relativistic effects have a major influence on some selected conduction-band edges. The reason for the large difference in the effects on occupied and empty states can be qualitatively explained in terms of renormalization arguments,[21,17] together with the particular spatial extent of Bloch functions at different band-index and $\vec{k}$ points for tetrahedral semiconductors.[24] We recall this in the simple bonding-antibonding model of Fig. 1. Relativistic corrections to the Hamiltonian can be approximately represented by potential terms $[\Delta V^{\mathrm{rel}}(r)]$ which are extremely localized near the nucleus,[18] in a region where the wave function is practically energy independent and thus—apart from a constant factor—identical for the bonding (B) and antibonding (A) states. Within perturbation theory, the relativistic corrections are

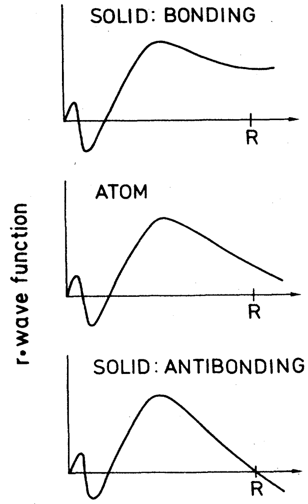

FIG. 1. Radial wave functions associated with bonding (top) and antibonding states (bottom), respectively. The distance R is the "atomic-sphere radius." The wave function in the middle is a sketch of an atomic wave function, or the radial wave function in the solid at the band center (see also Ref. 17).

$$\Delta E_i = \frac{\langle \psi_i \mid \Delta V \mid \psi_i \rangle}{\langle \psi_i \mid \psi_i \rangle}, \quad i=A,C,B \tag{1}$$

where A and B denote the antibonding and bonding states, and C denotes the state at the band center. Then, $|\Delta E_A| > |\Delta E_C| > |\Delta E_B|$ follows simply because the numerator is practically always the same, while the denominator is smallest for antibonding and largest for bonding. This reflects the fact that ψ^2 is larger at the nucleus for the (empty) antibonding state, which must have a node between the atoms, than for the (full) bonding state, where part of the charge has been transferred from the nuclear to the bonding region (Fig. 1).

Obviously, the actual wave function in a tetrahedral semiconductor is more complicated than the simple scheme of Fig. 1, and we need additional symmetry considerations to complete our picture. The character of the wave function at the top of the valence bands is mostly p-like on the atoms and bonding, whereas the $\Gamma_{2'}$ conduction state (Γ_1 in III–V materials), which for Ge and GaAs is the lowest conduction state at the Γ point of the Brillouin zone, is s-like on the atoms and antibonding. Figure 3 clearly shows these features for the case of GaAs. Its uppermost valence state (left) and the lowest conduction state (right) at $\vec{k}=0$ (top panels) are plotted in the (110) plane, which contains the chain of the bonds. The plots refer to the square of the wave function. For the empty conduction state at Γ (top right), the strong localization near the nuclei, due to the s character and enhanced by the existence of a node between the atoms, is clearly visible. We now look at the same quantities for the X and L points (middle and bottom panels, respectively), and observe that (right panel) while the wave function corresponding to the X_1 conduction minimum is almost completely delocalized and sits in the interstitial regions,[25,26] with no amplitude on the nuclei, the L_1 minimum is in a somewhat intermediate situation between the Γ_1 and X_1 conduction minima. Its wave function has a large amplitude on the nuclei but also a nonzero amplitude in the interstitial regions. The left-hand column, where the corresponding uppermost valence states are shown, only tells us that the X and L valence edges, being lower and lower in energy, have a wave-function character which resembles more and more the total valence charge density (which is the intuitive reason that one[27] or a few[28] special points are enough to accurately describe the charge density of a semiconductor).

With the help of Figs. 1 and 2, we then easily understand that the relativistic atomic shift of the s state with respect to the p states is enhanced at Γ (and slightly less at L) for the lowest conduction states, while it has no apparent effect at the X conduction edge and little effect upon the valence states. This is what is found in previous calculations for Ge (Ref. 10) and shown for gallium arsenide in Fig. 3 of this work.

The results shown in Fig. 3 are based on the LMTO method[14] and its fully relativistic version.[17] The von Barth—Hedin exchange-correlation potential[29] was used within the local-density approximation of the density-functional theory[30] for the self-consistent non-relativistic calculation (dashed lines). The same potential was then used for the fully relativistic bands (solid lines). Empty spheres were placed at the tetrahedral interstitial sites.[31,10] The purpose of showing this figure, (as opposed to the corresponding Table I, where *self-consistent* eigenvalues are listed at some high-symmetry points) is to emphasize the very large value of the purely relativistic shifts, and to check the detailed validity of the qualitative ideas discussed above.

The Ga, Ge, and As free atoms have relativistic shifts of the 4s states of 0.3—0.4 eV. The average 4p level remains approximately constant (see Fig. 4, where calculated atomic eigenvalues are shown). In view of the previous discussion, we then expect that the direct gap *decreases* by *more* than 0.3—0.4 eV. The top of the valence bands, p-like, does not move, except for a small amount due to its spin-orbit splitting. The Γ_1 ($\Gamma_{2'}$ for Ge) conduction edge, s-like and antibonding, will amplify the atomic drop of the 4s states. The valence-band width will also *increase*, but by *less* than 0.3—0.4 eV: the bottom of the valence bands at Γ is also s-like, but bonding, and this fact reduces the atomic drop of the 4s states. Moreover, a very small increase of the bandwidth will be contributed by the spin-orbit splitting of the top of the valence bands. This is, in fact, what the (self-consistent) calculation gives, as shown in Table I. The direct gap is decreased by 0.7 eV, while the valence-band width increases by just 0.2 eV. The Γ-X gap remains practically unchanged, following our previous considerations on the nature of the conduction wave functions.[24–26]

The qualitatively known relativistic effects on the band structure of heavier semiconductors are then quantitatively very significant in a first-principles description of the conduction bands, even for Z as small as 30. In other words, shifts of the same order of magnitude as the gap can occur for GaAs and Ge.

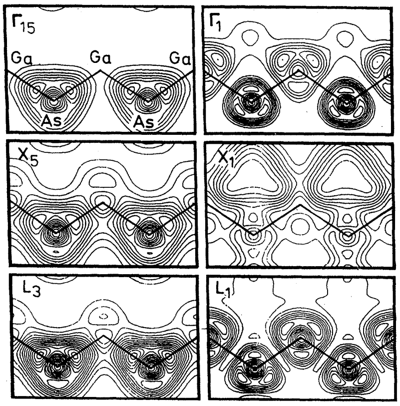

FIG. 2. Probability amplitude calculated from the pseudo wave functions for states at the top of the valence band (left-hand panel) and states in the lowest conduction band (right-hand panel) at Γ, X, and L in GaAs.

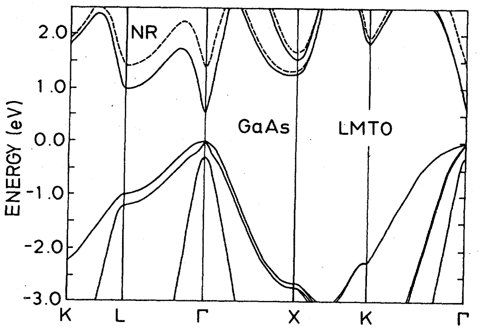

FIG. 3. GaAs. Solid line: self-consistent fully relativistic LMTO band structure. Dashed curve: nonrelativistic band structure calculated with the *same potential* as the relativistic bands. The nonrelativistic bands (only conduction states shown) are adjusted to the relativistic ones at the valence-band top.

TABLE I. Self-consistent nonrelativistic and scalar-relativistic LMTO calculations for GaAs. Energies in eV at symmetry points with respect to the top of the valence bands. The description of exchange correlation as given by von Barth and Hedin (Ref. 29) is used. (SO denotes spin-orbit splitting.)

	Nonrelativistic self-consistent	Relativistic self-consistent (without SO)
Γ_1^c	1.26	0.59
X_1^c	1.37	1.36
L_1^c	1.38	1.03
Γ_{15}^v	0	0
X_5^v	−2.54	−2.52
L_3^v	−0.95	−0.94
Γ_1^v	−12.22	−12.51

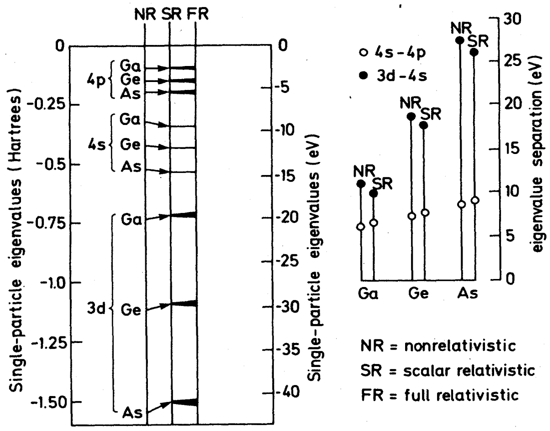

FIG. 4. Comparison of $3d$, $4s$, and $4p$ atomic energy levels in Ga, Ge, and As ($Z=31$, 32, and 33). Three sets of local-density calculations are represented: NR, nonrelativistic; SR, scalar relativistic (i.e., without spin-orbit coupling); and FR, fully relativistic. The $4s$-$4p$ and $3d$-$4s$ separations are indicated for each atom on the right-hand side of the figure.

III. SELF-CONSISTENT SCALAR-RELATIVISTIC BANDS OF GALLUIM ARSENIDE

The band structure of GaAs has been a source of continuous interest[32] since the early days of semiconductor physics.[33] Several models, adjusted to provide very good fits to optical data, have been presented,[32] but truly parameter-free calculations have been few. Computational schemes using different techniques for solving the Schrödinger equation in the crystal have only recently reached the level of sophistication needed to yield results which are in quantitative agreement with each other.[34] In conjunction with the local-density approximation,[30] these methods have allowed detailed theoretical predictions of the structural properties of materials.[35] Simultaneously, it has also become clear that the discrepancy between the calculated semiconductor gaps and the measured optical threshold is a systematic[34–37] feature of the LDA rather than an accident. In view of the standing debate on the origin of these discrepancies and the attempts to develop a new density-functional theory of the energy gap,[36,37] it is important to determine the magnitude of the errors for semiconductors other than the better-known example of silicon.[34]

TABLE II. Comparison of first-principles local-density band structures of GaAs and experiment at some high-symmetry points in the Brillouin zone.

	LMTO[a]	LCGO[b]	NCP + PW[c]	NCP + PW[d]	LMTO[e]	LMTO[f]	Expt.[g]
Γ_1	−12.3	−12.35	−12.33	−12.55	−12.47	−12.85	−13.1
Γ_{15}	0	0	0	0	0	−0.36 0	−0.34 0
Γ_1	1.1	1.21	1.10	0.64	0.64	0.25	1.42(1.52)
Γ_{15}	4.5	3.78		3.77			
X_1	−10.42	−9.79	−9.88	−10.23	−10.47	−10.49	−10.75
X_3	−6.20	−6.60	−6.62	−6.72		−7.06	−6.70
X_5	−2.43	−2.64	−2.61	−2.60	−2.57	−2.90 −2.83	−2.80
X_1	2.07	1.61	1.51	1.41	1.35	1.05	1.81(1.98)
X_3	2.31	1.88		1.62		1.28	2.38
X_5		10.26		10.15			
L_1	−11.06	−10.56	−10.64	−10.91	−11.14	−11.20	−11.24
L_1	−6.09	−6.49	−6.46	−6.53		−6.94	−6.70
L_3	−1.02	−1.12	−1.11	−1.09	−0.98	−1.39 −1.18	−1.30
L_1	1.55	1.37	1.30	1.05	1.06	0.67	1.72(1.82)
L_3	4.91	5.15		4.64			5.41
L_1		8.39		7.70			

[a] Linear-muffin-tin—orbital calculation by Jarlborg and Freeman, Ref. 38. Scalar relativistic. The "combined-correction term" is not included (see text and Ref. 39).

[b] Linear combination of Gaussian orbitals by Wang and Klein, Ref. 9. The calculation is nonrelativistic.

[c] Norm-conserving pseudopotentials (Ref. 15) with a converged plane-wave basis set, as obtained by Froyen and Cohen (Ref. 12). The calculation is nonrelativistic.

[d] This work, similar to footnote c, but relativistic pseudopotentials (Ref. 16) are used here.

[e] This work, similar to footnote a, but with the "combined-correction term" included. Form for the local exchange-correlation potential identical to footnote d is adopted (Refs. 41 and 42). Here, and in the preceding columns the frozen-core approximation is used (also Fig. 5 and text, Sec. III).

[f] This work, fully relativistic calculation with relaxed Ga $3d$ cores.

[g] Experimental band structure of GaAs. Sources are listed in Refs. 32 and 46. The numbers in parentheses are 0-K values measured for Γ and extrapolated at X and L [D. E. Aspnes, Phys. Rev. B **14**, 5331 (1976)].

The only existing relativistic calculation for GaAs (Ref. 38) is based on the LMTO method, and it makes use (as ours also does) of "empty spheres."[31] It does not, however, include the so-called "combined-correction term,"[14] which corrects for the truncation of the angular momentum and the spherical approximation to the atomic cells. We have found, in agreement with Glötzel *et al.*,[10] that this correction is particularly important[39] for the gap states Γ_1^c and Γ_{15}^v. The former (Γ_1^c) is just where the relativistic effects are most important, and, in fact, omission of the combined-correction term in Ref. 38 completely wipes out the relativistic shifts. This follows from a comparison of the first column of Table II to two recent, accurate, but nonrelativistic calculations[9,12] in the second and third columns.

The direct gap of the relativistic calculation (Table II, first column) is within 0.1 eV of the nonrelativistic direct gaps (second and third columns). On the contrary, recent relativistic calculations using first-principles pseudopotentials[40] seemed to point out that, for GaAs, a sizable shrinkage of the direct gap does result from the inclusion of relativistic effects, in agreement with the qualitative discussion as well as with the non-self-consistent study described in Sec. II and shown in Fig. 3 of this paper.

In order to examine this point, we perform a relativistic self-consistent calculation which does not suffer from the problems of Ref. 38 and, thus, can provide useful information on the actual amount of solid-state relativistic shifts in GaAs. To avoid possible uncertainties due to the choice of a particular band-calculation method, we perform, in fact, two parallel calculations using the same expression for the local exchange-correlation potential:[41,42] one based on relativistic LMTO's,[14] and the other on relativistic norm-conserving pseudopotentials[15,16] with a plane-wave basis set. In both calculations we only include scalar-relativistic effects,[20] since we wish (later) to consider spin-orbit coupling separately.

A few details of these independent calculations may be of interest before we discuss their results, which are summarized in Fig. 5 and Table II. For the eigenvalue convergence of the pseudopotential calculation, we found it necessary to include about 300 plane waves (or a cutoff of 14.57 Ry), in agreement with the general experience with norm-conserving pseudopotentials.[43] The LMTO calculation was optimized by the choice of equal atomic spheres for Ga and As (radius $S=3.000$ a.u.) and slightly smaller, $S=2.110$ a.u., for the empty interstitial spheres E_1 (surrounded by four As atoms) and E_2 (surrounded by four Ga atoms). Three energy panels[14] were needed to obtain accurate bands over the entire energy range of interest. Panel 1 contains the As *s* band, panel 2 the remaining valence states, and panel 3 the conduction bands.

Under these conditions the agreement between the two calculated band structures is excellent, as can be seen from Fig. 5, where the LMTO results are represented by a solid line and the pseudopotential results by dots, and from Table II, where, in the fourth and fifth columns, the eigenvalues are listed at some symmetry points. Tables I and II clearly demonstrate that relativistic effects are responsible for a large reduction of the direct gap (0.5 eV), a less pronounced reduction of the Γ-*L* gap (0.2 eV), and practically no effect on the Γ-*X* gap. The small increase of the valence-band width (0.2 eV) due to the relativistic drop of the bonding Γ_1 state is also evident, and everything, contrary to the results of Ref. 38, fits together with the modifications expected on the grounds of the simple picture discussed in Sec. II.

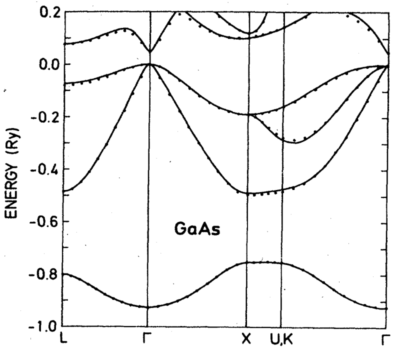

FIG. 5. GaAs. Scalar-relativistic self-consistent band structures obtained by the LMTO (solid lines) method and from norm-conserving relativistic pseudopotentials (dots). The same approximation to exchange-correlations is used in the two calculations (Ceperley-Alder), and in both cases the Ga 3*d* states are treated as "frozen" core states.

We could conclude that the local-density gap of GaAs is less than 50% of the experimental value [1.51 at 0 K (Ref. 32)], being equal to 0.65 eV in both of our independent calculations (Table II). This finding would already show that the common statement, according to which the LDA gives gaps which are typically 30—40 % off the experimental value,[9,12] is an optimistic one. However, before concluding our study, the effects of relaxing the Ga 3*d* states must be examined.

IV. RELAXATION OF THE Ga 3*d* CORE

Our two independent calculations make both use of an approximation which, for this particular material, could lead to some inaccuracies: the Ga 3*d* states are included in the "frozen core." From the pictorial compilation of atomic (LDA) eigenvalues for Ga, Ge, and As contained in Fig. 4, it is seen that the Ga 3*d* states are not far from the Ga 4*s* states, and very close (~5 eV) to the As 4*s* states. This fact (which is slightly increased by relativistic effects, Fig. 4) is reflected by the experimental ionization potentials as well: the fourth ionization potential of Gallium (i.e., the energy required to strip away the first 3*d* electron from the Ga^{3+} ion) is almost equal to the fifth ionization potential of arsenic (the energy required to strip away the last 4*s* valence electron from the As^{4+} ion).[44]

The frozen-core approximation is necessary in any pseudopotential approach, but it is not essential in full-core band-structure methods (such as LMTO), although it is often conveniently adopted. Its application when calculating the structural properties of GaAs has been estimated to cause very small problems,[12] but the effect on individual band edges is hard to predict in a quantitative fashion. This fact, together with the independent development of GaAs linearized—augmented-plane-wave (LAPW) calculations,[45] has led us to examine the effects of the Ga 3*d* core relaxation on the gaps. A relativistic LMTO calculation is performed with the Ga 3*d* states fully relaxed, i.e., treated as normal band states. The results are listed in the sixth column of Table II. This calculation is fully relativistic, i.e., all relativistic effects, *including* spin-orbit coupling, are considered.

The band structure is also shown in Fig. 6. Two features immediately appear: one is that the Ga 3*d* core relaxation has resulted in a nearly uniform drop of the entire first conduction band (relative to the valence-band edge) by about 0.4 eV. The other is that relaxation of the 3*d* cores by itself yields a further drop of all valence-band minima relative to the valence-band top. (In addition, the spin-orbit splitting reduces the gap by a small amount.) *A priori,* it is not easy to interpret how the 3*d* core relaxation (which results in the charge transfer of 0.04 electrons from the Ga to the As sphere) can cause both the overall drop of the first conduction band, and, at the same time, lower all the valence-band minima. Our experience with relativistic shifts and with the different character of conduction wave functions at different $\vec{k}$ points (Fig. 2, right-hand panels) would suggest that potential corrections which act on the Γ_1 states should have almost no influence on the X_1 conduction state.

A comparison of band structures where the upper valence-band edges are lined up does not provide the correct point of view for discussion of the effects of relaxation of the 3*d* states. In fact, we immediately understand the actual situation if it is assumed that it is just the Γ_{15}^{v} state (i.e., the top of the valence bands, mostly As *p*-like but with some *d* character) that is pushed upwards. In GaAs this state must be orthogonal to the 3*d* state, while the Γ_1^v and Γ_1^c states are automatically orthogonal to it by symmetry.[13] Thus the Γ_{15}^{v} state is pushed upwards in energy with respect to the bottom of the valence bands, as well as with respect to the conduction-band bottom as a result of the relaxation of the 3*d* states. This is what causes the reduction of all gaps by approximately the same amount, and simultaneously increases all valence-band widths (sixth column of Table II and Fig. 6).

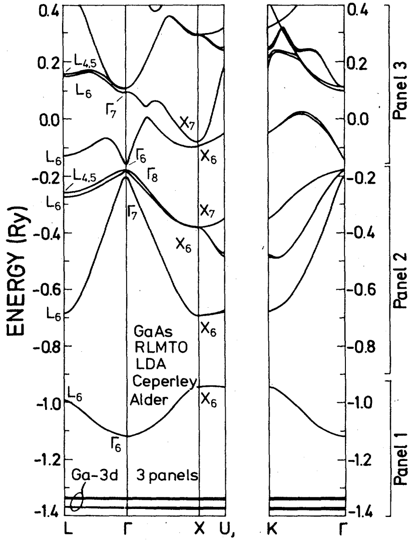

FIG. 6. Fully relativistic LMTO band calculation for GaAs. Three energy panels were used (indicated on the figure), and the Ga 3*d* states are treated self-consistently as band states on the same footing as the other valence-band states.

A comparison of the results of the different calculations in Table II (columns 1—6) to the experiments (column 7) shows that the valence bands of our last calculation, which included fully relativistic and core-relaxation effects, are much closer to the experimental results of angle-resolved photoemission,[46] listed in the last column, than all previous *ab initio* calculations which disregarded those effects.

In particular, the calculated valence-band width (12.85 eV) is very close to the experimental value, 13.1 eV, while the bandwidths obtained from nonrelativistic calculations keeping the Ga 3*d* states frozen are closer to 12 eV. Also, for most valence states, the agreement is markedly improved.

On the other hand, the calculated minimum gap is now far from experiment [0.25 versus 1.51 eV at 0 K (Ref. 32)], and the rest of the conduction band is shifted downwards with respect to experiments by an amount which (unlike, e.g., the case of silicon[34]) has a considerable $\vec{k}$ dependence, so that also effective masses, contrary to nonrelativistic calculations,[9] are in flagrant disagreement with experimental ones.[47] It seems fair to observe at this point that no matter which direction the improvements of the local-density-functional theory will take,[24,34—37,48,49] they will have to face much larger errors than previously thought, for the important case of GaAs.

The local-density band-structure calculation yields Ga 3*d* bands which are located 15.90 eV below the valence-band edge (Fig. 6). This is in agreement with the calculation by Wang and Klein,[9] but 3 eV higher than the spectral position of the Ga 3*d* peak in the experimental photoemission spectra obtained by Ley *et al.*[46] The reason for this large difference is that the energy eigenvalues for states which are very localized, as are the Ga 3*d* states, differ very much from the total-energy difference $E(N-1)-E(N)$. This difference between the energy $E(N-1)$ of the system with one photoelectron emitted, and the initial *N*-electron system, is measured by photoemission, and only for truly extended initial one-electron states is it well described by one-electron energy differences. We have tried to estimate the effects of screening of the localized *d* hole created by the photoexcitation process from atomic calculations alone. We simply calculate, within the LDA, the total energy of the Ga atom $[E(N)]$ and the energy of the ion $[E(N-1)]$, where one *d* electron is removed. The calculated binding energy $E(N-1)-E(N)$ is found to be 8.5 eV larger than the negative of the 3*d* eigenvalue. Thus, the atomic calculation shows that the localization effect is indeed large, but it overestimates the error in the solid, which was only 3 eV. Although the Ga 3*d* states in GaAs are very localized, the contributions from the (other) valence electrons (*s* and *p*) in the crystal to the relaxation around the core hole are large.

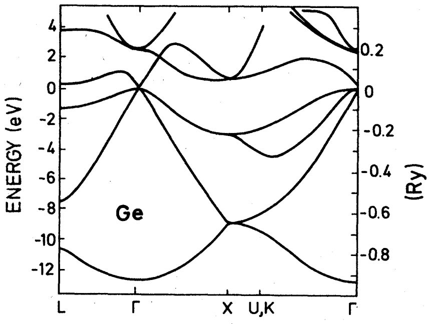

FIG. 7. Scalar-relativistic pseudopotential band structure of Ge derived within the local-density approximation. The gap is direct (at Γ) and almost equal to zero in this approximation.

V. GERMANIUM RELATIVISTIC BANDS

Since GaAs has such a small direct gap, and Ge, the neighboring elemental semiconductor, is experimentally known to have a gap which is half of that in GaAs and indirect (Γ-L) in character, we want to check the results of Ref. 10, where a relativistic LMTO calculation had found, for Ge, a very small, but still indirect (Γ-L), gap. Since the germanium $3d$ cores are very far from the $4s$ valence states (Fig. 4), and thus can safely be included in the frozen core, we are left with relativistic effects only. We can then use relativistic pseudopotentials[16] without problems. The same number of plane waves is used as for GaAs, which, in view of the equal lattice constant and equal core, ensures the same degree of convergence. The results, shown in Fig. 7 and Table III, suggest that the gap practically closes at Γ as a result of the relativistic drop of the $\Gamma_{2'}$ state. Thus, in addition to the very large absolute error in the gap, the LDA also leads to an incorrect topology of the first conduction band in Ge. This also implies that the metallization trend, encountered in nature for Sn, occurs practically one row too early within the local-density approximation. We obtained the same results by means of LMTO calculations, and independent calculations of Skriver[50] and Schlüter[51] are consistent with this. It is tentatively suggested that even in Ref. 10 the combined-correction term was not completely converged, giving rise to small overestimates of the direct gaps (as for GaAs, the valence-band top is particularly sensitive to this correction). The differences discussed here are small, however ($\sim$0.1 eV), and on this scale even the difference between two choices of the local exchange-correlation potential could play some role.

TABLE III. Germanium bands calculated from first principles using relativistic norm-conserving pseudopotentials (Ref. 16) and a converged plane-wave basis (text), within the local-density approximation for exchange and correlation. Spin-orbit effects are not included. Note that the gap shrinks to almost zero at Γ, so that the *order* of the conduction-band minima, in addition to the absolute gap values, does not correspond to the experimental situation (Fig. 7 and Sec. V).

Γ_1	-12.70
$\Gamma_{25'}$	0.0
$\Gamma_{2'}$	0.09
Γ_{15}	2.57
X_1	-8.84
X_4	-3.05
X_1	0.70
X_3	9.46
$L_{2'}$	-10.62
L_1	-7.56
$L_{3'}$	-1.38
L_1	0.19
L_3	3.74
$L_{2'}$	7.04

VI. CONCLUSION

We have performed a series of nonrelativistic, scalar-relativistic, and fully relativistic self-consistent band-structure calculations for GaAs. We have also allowed the shallow $3d$ states of gallium to fully relax. This work has told us that the scalar-relativistic shifts yield a reduction of $\sim$0.5 eV of the direct gap, and that the core-relaxation and spin-orbit effects reduce it by another $\sim$0.3 eV. The relativistic and core-relaxation effects also lead to modifications of the valence bands which show a markedly improved agreement in relation to the photoemission data. However, the gap has been squeezed to the unacceptable[45] value of 0.25 eV [the experimental value is 1.51 eV at 0 K (Ref. 32)] within the local-density approximation.

Relativistic calculations for germanium confirm that for third-row semiconductors the calculated gaps in this approximation (Ge:0.09 eV, direct) are much less than 50% of the experimental value, and the dispersion is also incorrect for the first conduction band. We proved that for these materials the size of the relativistic shifts (and of the core-relaxation effects, in the case of the $3d$ states of gallium) on the gap is of the order of the gap itself, and that although they can be neglected for the calculation of some ground-state properties,[11,12,52] they cannot be disregarded in the description of semiconductor gaps.

Note added. Dr. H. Krakauer has informed us that they [H. Krakauer, S.-H. Wei, B. M. Klein, and C. S. Wang, Bull. Am. Phys. Soc. **29**, 391 (1984), and unpublished] found the gap in GaAs to be 0.27 eV, and that they indeed did allow the core states to relax self-consistently. Furthermore, they obtained in their LAPW calculations good agreement with the experimental bulk modulus (within 10%) and lattice parameter (within 1%).

ACKNOWLEDGEMENTS

We would like to thank O. K. Andersen, M. Cardona, O. Gunnarsson, D. R. Hamann, J. Menendez, W. E. Pickett, and L. Viña for helpful discussions. We also thank H. Krakauer for communicating details of unpublished work (Ref. 45 and *Note added*).

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