Predicted Modifications in the Direct and Indirect Gaps of Tetrahedral Semiconductors

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The charge density of GaAs was studied at various k points and for various bands by the augmented–spherical-wave method, using muffin-tin spheres at the Ga, the As, and, additionally, the interstitial sites. The lowest X_c conduction-band points were found to be unique in having a high "charge" density in the interstitial spheres. It has therefore been predicted and verified that the X_c points move up in energy relative to the Γ_c point when closed-shell atoms (like He) are substituted at the interstitial sites. The calculations also indicate indirect-direct conversion for SiHe.

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Although the electronic band structures of tetrahedral semiconductors, i.e., Si, Ge, GaAs, GaP, and ZnSe, have been calculated successfully by many different methods, the physics underlying the fact that some are direct-gap semiconductors and others indirect has not been evident. Therefore methods to modify a particular semiconductor to alter its direct-indirect gap have not been proposed, except for band folding with superlattices which imparts some direct-gap characteristics to pairs of indirect-gap semiconductors[1] and for effects of isoelectronic dopants.[2] The physics responsible for a specific semiconductor being intrinsically direct or indirect and possible modification thereof is an important problem of the solid state.

The purpose of the present Letter is to show theoretically for tetrahedral semiconductors the basic difference between the direct conduction-band edge Γ_c and the indirect conduction-band edges $X_c{}^1$ and L_c, and to use these differences to predict a new class of semiconductors and metallic compounds. Our detailed calculations and predictions are for GaAs; extension to other semiconductors will be reported later.

Our calculations are based on the augmented spherical-wave (ASW) method, developed by Williams, Kübler, and Gelatt[3] for metallic compounds. In order to take account of the open structure (diamond or zinc blende) of tetrahedral semiconductors, we include extra spheres at the tetrahedral interstitial sites, in addition to atomic spheres at the Ga and As sites. This idea has been used with the linear muffin-tin orbital (LMTO) method by Jarlborg and Freeman[4] for GaAs and by Glötzel, Segall, and Andersen[5] for elemental semiconductors. For half-metallic ferromagnets this method has been used by de Groot *et al.*[6] The interstitial spheres are treated as if they were atoms, but with zero nuclear charge. We shall refer to them as Z spheres. They are subdivided as Z_a and Z_c such that each cation is completely surrounded by nearest-neighbor anions (As and Z_a) while each anion is surrounded by cations (Ga and Z_c).

Thus in this notation GaAs becomes a novel quaternary compound: GaAsZ_cZ_a with the structure shown in Fig. 1. All four types of spheres are chosen to have the same radius, with its value fixed by the condition that the total volume of the spheres be equal to the volume of the unit cell. The basis-set wave functions for the ASW calculation are s, p, and d functions centered on the four types of sites. The calculation is nonrelativistic; the local-density approximation (LDA) is used to take account of exchange and correlation; the core functions are allowed to relax in each iteration of the self-consistent calculation. The lattice constant used, 5.73 Å, minimizes the total energy (more precisely the pressure was made equal to zero). In addition to calculating the valence- and conduction-band structure we extract for the first time from an ASW

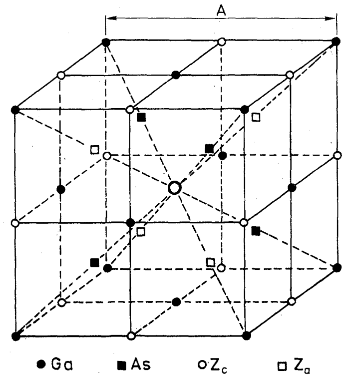

FIG. 1. Crystal structure for GaAs including the Z_c and Z_a spheres, as used in our calculations. The coordinates of the centers of the four spheres, in units of the lattice parameter A, are Ga, (0,0,0); As, $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$; Z_c, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; Z_a, $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$.

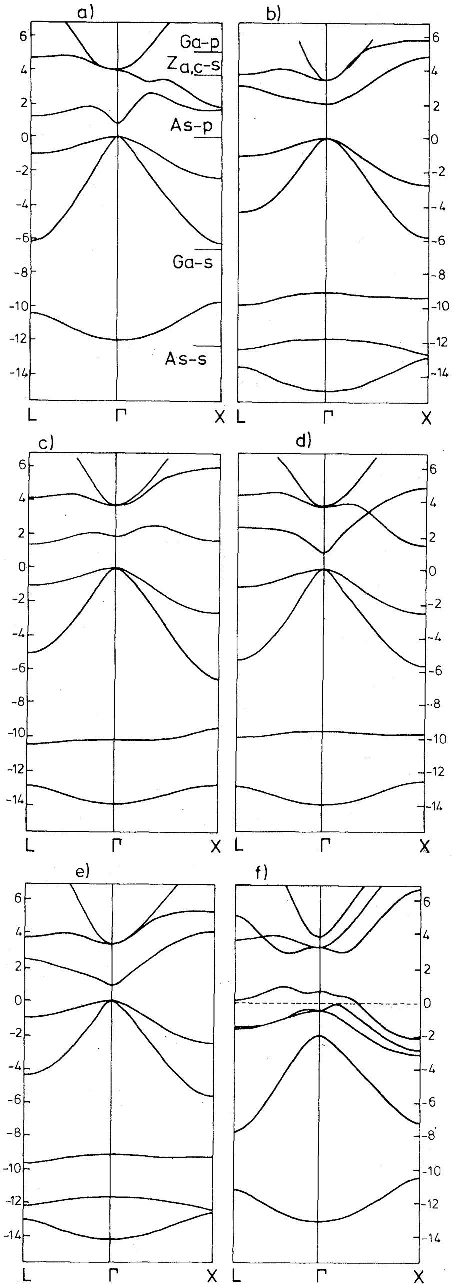

FIG. 2. Band structures along the symmetry lines L-Γ and Γ-X. Energies are in electronvolts with respect to the top of the valence band, except for (f) where they are measured with respect to the Fermi level (indicated by the dashed line). All band structures are displayed for a lattice parameter of 5.73 Å except for (e) which is at 5.95 Å. (a) $\mathrm{GaAs}Z_cZ_a$, (b) $\mathrm{GaAsHe}_c\mathrm{He}_a$, (c) $\mathrm{GaAs}Z_c\mathrm{He}_a$, (d) GaAsHe_cZ_a, (e) $\mathrm{GaAsHe}_c\mathrm{He}_a$ relaxed, (f) $\mathrm{GaAsH}_c\mathrm{H}_a$.

calculation the *radial charge densities within each of the four spheres, for states at different points in the Brillouin zone.*

Some results of the calculation for $\mathrm{GaAs}Z_cZ_a$ are shown in Figs. 2(a) and 3. On the right-hand side of Fig. 2(a) the Hankel energies of the ASW calculation are indicated. These can be described as site energies for the compressed atoms; the precise definition is in Ref. 3. In the limit of infinite lattice constant these energies equal the free-atom eigenvalues. We note two features of the Hankel energies: (1) The energy difference between the p and s states of both Ga and As is 12 eV, approximately *twice that for the free atoms* (this change arises from the atoms being compressed in the solid so that the s function is perturbed by a larger effective nuclear charge, compared to the p function, than is the case for the free atom), and (2) the *p state of the Ga lies above the s states of Z_c and Z_a.*

Our computed band structure for $\mathrm{GaAs}Z_cZ_a$ is shown in Fig. 2(a). It compares well with the LMTO bands of Jarlborg and Freeman,[4] which are in good agreement with other *ab initio* theoretical results, as well as with experiment. Our valence-band width of 12 eV agrees very well; our gaps —direct and indirect— are too small. This is a well-known deficiency of the LDA; cf. Perdew.[7] Incidentally, to test our program we have calculated the band structure of Si and have obtained results in good agreement with the linear augmented plane-wave (LAPW) calculation of Hamann,[8] with the LMTO calculations of Glötzel, Segall, and Andersen,[5] and with the self-consistent pseudopotential analysis of Zunger and Cohen.[9] In the $\mathrm{GaAs}Z_cZ_a$ calculation the Z_a and Z_c spheres have accumulated 0.65 and 0.79 electron of the eight valence electrons, mainly near the surface of their spheres, showing that the interstitial region is almost empty. This is quite in contrast to the situation for the conduction-band states. Figure 3 shows the charge densities $\rho_\nu(r)$, or more precisely the squared wave-function moduli, decomposed among the spheres, as a function of the distance r from the center of each sphere, for different points in the Brillouin zone. The charge densities have been spherically integrated and normalized such that $\sum_\nu 4\pi\int_0^k dr \times r^2\rho_\nu(r)=1$, where ν denotes the sphere index. The region near the nucleus is omitted since the density oscillates wildly there and we do not want to stress this part.

The crucial point, however, is that the Γ_c point has a total 18% occupancy in Z_c and Z_a, whereas the X_c^1 point has a total 57% occupancy of Z_c and Z_a with that occupancy rather uniform throughout the spheres. In other words, the X_c^1 point is

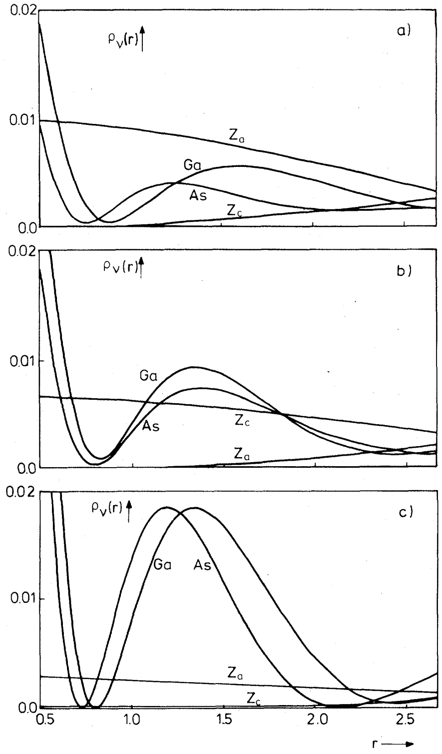

FIG. 3. Charge densities as a function of radial distance (in Bohr radii) for each sphere. The region between 0 and 0.5 has been omitted. (a) $X_c^{\,1}$ point, (b) $X_c^{\,3}$ point, (c) Γ_c point.

more describable as being itinerant, whereas the Γ_c is more completely describable in terms of tight binding. We know from symmetry that Γ_c involves s-s combinations of Ga and As orbitals and from the Hankel energies we observe that these lie well below the Z s states; on the other hand, from symmetry and the Hankel energies we find that $X_c^{\,1}$ involves combinations of anion s states and cation p states and the Gap orbital lying above the Z_a s state then clearly facilitates occupancy of the Z_a s state. The next higher X_c point, $X_c^{\,3}$, involves combinations of cation s states and anion p states. The As p state is lower in energy than the Z_c s state. Consistently the Z spheres have only 43% occupancy. The L_c-point occupancy is in between the X_c and Γ_c occupancy in that it amounts to 17% and 14% for the Z_c and Z_a spheres, respectively. The next higher Γ_c point has a total 28% occupancy of the Z_a and Z_c states. For completeness we mention that a scalar relativistic calculation does not essentially alter the above results; the charge densities change by less than 1% for Γ_c, L_c, X_c.

At this point a brief digression on the theoretical point of view taken above may be enlightening. The very use of empty spheres and corresponding s, p, and d states allows for more variational freedom in the determination of the states of the system. The "charge" accumulation at the X_c points is a natural outcome of this procedure. It is a result which will never be produced by a tight-binding calculation with s, p, and d functions centered only on the anions and cations of the true crystal, simply because of lack of variational freedom. Of course this would be remedied by inclusion of a complete set of basis functions. For the conduction-band states there has been a lot of discussion on whether or not d states and/or next-nearest-neighbor interaction should be included in a tight-binding analysis to describe the conduction band. Clearly the above self-consistent calculation shows that even this will not be sufficient. One could, of course, include basis states centered on interstitial sites, but the strength of empirical tight binding being an approach with few adjustable parameters may then be lost. Self-consistent pseudopotential calculations involving a sufficiently large number of plane-wave states should be able to produce the above interstitial "charge" effect.

With the Γ_c and X_c points clearly distinguishable by different occupancies of Z spheres, modifications of the band structure of GaAsZ_cZ_a, and for that matter of tetrahedral semiconductors in general, are expected to result from substitution of other atoms and/or molecules at the Z-sphere sites. We thus expected that substitution of closed-shell atoms or molecules at both Z_c and Z_a would force, by orthogonalization, charge away from these spheres, thus selectively perturbing the X_c point to higher energy. Because of its small size, closed shell, and simple structure, He was chosen. In Fig. 2(b) the calculated band structure is shown for the same lattice parameter as in GaAsZ_cZ_a: *The X_c minimum has been eliminated.* Other effects are evident: (1) The direct gap has somewhat more than doubled; (2) the valence-band width has increased from 12 to 15 eV and the rather flat 1s He states are clearly evident within the valence band; (3) different from GaAsZ_cZ_a, the lower $X_c^{\,1}$ point consists of cation s and anion p states, the higher $X_c^{\,3}$ point of anion s and cation p states. In addition to the band structure the valence-band charges within the He$_c$ and He$_a$ spheres were calculated and found to be 0.66e and 0.52e, respectively (charge in excess of the 2e neutralizing the He^{2+} nucleus), 0.13e below the 0.79e and 0.65e for Z_c

and Z_a. The total energy was also calculated: $+1.8$ eV per GaAsHe$_c$He$_a$, compared to GaAsZ_cZ_a $+2$ He atoms, both at the equilibrium lattice constant of the latter. If the lattice constant of GaAsHe$_c$He$_a$ is allowed to relax we find the equilibrium lattice constant to be 4% larger than that of GaAsZ_cZ_a. Figure 2(e) shows the band structure for this case. The dramatic upshift of X_c^1 and X_c^3 is still present but the direct gap returns to close to the GaAsZ_cZ_a gap. The positive energy of formation decreases from 1.8 to 1.4 eV. In order to explore further modifications of the band structure caused by substitution, the band structures with He only at one of the Z sites were calculated; that is, of GaAsHe$_c Z_a$ and of GaAsZ_cHe$_a$. The latter was predicted to have the smaller positive energy of formation because the He atom is nearer to the Ga atom which is smaller than As: The calculation yielded 0.75 eV compared to 0.85 eV for its isomer GaAsHe$_c Z_a$. The band structures for these two cases are shown in Figs. 2(c) and 2(d). For GaAsZ_cHe$_a$ the conduction-band X point with anion s contribution in GaAsZ_cZ_a is perturbed upward and for GaAsHe$_c Z_a$ the X_c with cation s contribution in GaAsZ_cZ_a moves up. Relaxation does not essentially alter these results. The major conclusion is that it is necessary that *both* Z_c *and* Z_a *be occupied by closed-shell atoms or molecules* in order to convert indirect-gap tetrahedral semiconductors into direct-gap semiconductors.

From Fig. 2 it is clear that the L_c points follow basically the behavior of the X_c points. Clearly we are now in a position *to indicate theoretically how to make indirect semiconductors direct.* We have verified, for example, that SiHe should be a direct semiconductor. Calculations on other materials are in progress.

Non-closed-shell atoms were then considered and because of its small size H was selected. Substitution in both Z_c and Z_a results in a negative energy of formation of 1 eV (formation from atomic H) and yields the band structure shown in Fig. 2(f): The upshift is present but GaAsH$_c$H$_a$ is a metal! This effect is expected and is so large that probably all tetrahedral semiconductors in which Z_c and Z_a are fully replaced by atomic H are metals. Calculations with H_2 molecules at Z_c and Z_a sites in GaAs are in progress.

The experimental preparation of this new class of semiconductors and semimetals does not appear at present to be easy. We have estimated the pressure necessary to force the He stoichiometrically into both Z-sphere sites of GaAs as a few hundred kilobars, assuming a fixed lattice constant. One can envisage an ingenious pressure experiment so as to put a substantial amount of He into GaAs.

Ion implantation of He, preferably along the channelling directions of GaAs with low kinetic energies, is going to be explored. Other tetrahedral semiconductors are being considered theoretically: for example AlSb and even grey Sn with their larger unit cells.

Experiments with H incorporation into GaAs appear to be more feasible. The GaAsH$_c$H$_a$ is thermodynamically stable with respect to GaAsZ_cZ_a $+2$H, metastable with respect to GaAs$Z_cZ_a+H_2$. Ion implantation is going to be explored; electrolytic incorporation can also be considered.[10]

In conclusion, we have calculated the band structure of GaAs using the ASW method applied to tetrahedral semiconductors by including muffin-tin spheres on interstitial empty sites. From the computed charge distribution in the four different types of spheres in the unit cell for different points in k space we have found a qualitative difference between the Γ_c point involved in the direct gap and the X_c point involved in the indirect gap. Guided by this result, we calculated the band structures for GaAs with He either fully or partly substituted for the empty spheres. The direct-indirect character can thus be predictably modified. The substitution of H in GaAs for the empty spheres results in a metal. These conclusions are believed to apply qualitatively to other tetrahedral semiconductors.

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