# Conduction-band minima of InP: Ordering and absolute energies

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Since the conduction-band structure of InP is still controversial, we perform an *ab initio* linear muffin tin orbital (LMTO) band structure calculation to obtain the valence bands with high accuracy. The LMTO is based on the local density approximation (LDA) which suffers from the well known "band-gap problem." We therefore combine our calculated valence-band energies with carefully evaluated optical data from the literature and confirm the interconduction-band separation energies $\Delta E_{\Gamma L}=0.86\pm0.02$ eV and $\Delta E_{\Gamma X}=0.96\pm0.02$ eV. We also give new empirical local pseudopotential form factors adjusted to reproduce these experimental values.

InP is an important material for optoelectronic devices.[1] With its low conduction-band mass (only slightly larger than for GaAs) it also has a potential for electrical high-speed–low-power applications. It has been found that higher electron velocities can be attained in InP over a longer distance than in GaAs for higher fields and launching energies, mainly because the subsidiary conduction-band minima at $L_1^c$ and $X_1^c$ are located at higher energies in InP (anion at the origin). This gives a distinct advantage to InP, because higher applied voltages can be used in device applications.[2]

For detailed simulations of InP-based devices, its conduction-band structure has to be known precisely. A lot of work has been done in the early 1970's,[3–9] but even today the location of the subsidiary minima is controversial.[10–14]

In order to solve this controversy, we have performed an *ab initio* band-structure calculation using the linear muffin tin orbital (LMTO) method, based on the atomic sphere (ASA) in conjunction with local density approximation (LDA), in order to obtain the valence-band energies at $\Gamma^v$, $X^v$, and $L^v$ with high accuracy. The self-consistent potentials are created with a *scalar relativistic* Hamiltonian, i.e., all relativistic effects except the spin-orbit coupling are included.[15,16] The valence-band energies thus obtained are given in Table I. Results of a recent *ab initio* pseudopotential calculation[17] are also given in Table I.

LDA band structures of semiconductors suffer from the well known "band-gap problem": the gap is calculated too small by 50–100%, but experience shows that the valence bands nevertheless agree well with photoemission data (see Table I and Ref. 18). These difficulties can be overcome by calculating the quasi-particle energies of the screened electron-hole pair in the GW approximation,[19,20] but to our knowledge no such calculation has been performed for InP. We therefore use optical data to find the energies of the higher lying conduction-band minima.

The energy gap $E_1$ between the highest valence and lowest conduction bands along the $\Lambda$ direction can be found from modulation spectroscopy with high accuracy. Lautenschlager *et al.*,[21] e.g., report $E_1=3.355\pm0.005$ eV at 30 K (spin-orbit splitting removed). Using this along with the value $E(L_3^v)=-0.98$ eV obtained from the band-structure calculation or photoemission data[18] and the low-temperature band-gap value of $E_0=1.46$ eV (see Ref. 21, spin-orbit splitting removed), we obtain $\Delta E_{\Gamma L}=0.91$ eV (see Fig. 1), in rather good agreement with the result of Alekseev and co-workers,[13] who found $\Delta E_{\Gamma L}=0.86\pm0.02$ eV from hot luminescence experiments under uniaxial strain.[22]

Dumke *et al.*[9] have performed infrared absorption measurements in *n*-type InP at 77 K. They find a sharp rise in the absorption coefficient at $0.91\pm0.01$ eV which is attributed to transfer of electrons to a satellite valley. After subtracting the energy of the phonon involved in the indirect transition (40 meV), their data agree with those of Ref. 13. We therefore conclude that the $L_1^c$ minimum at about 0.86 eV is the lowest side valley in InP. Similar transmission measurements have found the energy of the lowest side valley in GaAs.[23] On the other hand, Onton and co-workers[3] observed indirect interconduction-band transitions in wavelength-modulated absorption at $0.483\pm0.015$ eV (GaAs) and $0.960\pm0.005$ eV (InP), after subtraction of the intervalley phonon energies. In analogy with GaAs ($\Delta E_{\Gamma X}=0.480$ eV) we assign $\Delta E_{\Gamma X}=0.96\pm0.01$ eV for InP. This also explains the origin of the shoulder just below 1 eV observed by Alekseev *et al.* in their hot-electron luminescence measurements.[13] We conclude that the gap at $X$ between the highest valence band and the lowest conduction band is 4.82 eV. Although this gap cannot be observed in ellipsometry, its energy should be close to that of $E_2$ which was found at 4.96 eV by Lautenschlager *et al.*[21] Onton *et al.*[3] also found a structure near 0.86 eV which they associated with donor levels associated with $X_1^c$, but which could also be due to transitions to $L_1^c$.

This assignment is in disagreement with other experiments; Wada *et al.*[14] obtain $\Delta E_{\Gamma L}=0.39$ eV from an analysis of capacitance measurements. Using photoemission with very high-energy resolution,[24] $\Delta E_{\Gamma L}=0.52$ and 0.64 eV have been found in Refs. 4 and 11. These results, how-

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TABLE I. Valence-band energies for InP from LMTO and EPM band-structure calculations and photoemission experiments (in eV, without spin-orbit splittings).

| InP | $\Gamma_1^v$ | $\Gamma_{15}^v$ | $L_1^v$ | $L_2^v$ | $L_3^v$ | $X_1^v$ | $X_3^v$ | $X_5^v$ | $\Gamma_1^c$ | $\Gamma_{15}^c$ | $L_1^c$ | $L_3^c$ | $X_1^c$ | $X_3^c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LMTO[a] | −11.59 | 0.0 | −9.89 | −5.93 | −0.98 | −9.24 | −5.93 | −2.40 | 0.50 | 4.23 | 1.30 | 4.94 | 1.68 | 2.30 |
| EPM | −11.34 | 0.0 | −10.16 | −5.02 | −0.73 | −9.73 | −5.23 | −1.83 | 1.45 | 4.83 | 2.32 | 5.54 | 2.43 | 3.22 |
| ARPES[b] | −11.4 | 0.0 | −10.0 | ··· | −1.0 | −9.6 | −5.9 | −2.45 | 1.46 | 5.3 | ··· | ··· | 2.8 | |
| PSP[a,c] | −11.16 | 0.0 | −9.73 | −5.54 | −0.85 | −9.14 | −5.59 | −2.12 | 0.98 | ··· | 1.60 | ··· | 1.68 | ··· |

[a]Straight LDA calculation (uncorrected).
[b]Angular-resolved photoemission and inverse photoemission data, see Ref. 18.
[c]*Ab initio* norm-conserving pseudopotential calculation from Ref. 17.

ever, can be directly ruled out by comparison with ultrafast luminescence,[12] hot-electron luminescence,[13] and infrared transmission.[9]

Extrapolations of the energy position of the $X_1^c$ point from $Ga_xIn_{1-x}P$ alloys[8] agree with the assignment given above, but are not very reliable as these materials are direct for $x<0.7$, in which case indirect transitions from $\Gamma_{15}^v$ to $X_1^c$ are not observable. By applying hydrostatic pressure,[25] it is possible to determine the energy of $X_1^c$ for an alloy with $x$ as low as 0.36. In pure InP, however, the pressure for the direct-indirect crossover is close to a phase transition, therefore $E(X_1^c)$ cannot be found with accuracy.[26] Pitt and co-workers[5–7] have performed Hall-effect measurements under high pressure. Their analysis depends on many parameters that were not well known, like the masses in the subsidiary minima and the pressure coefficients of the interconduction-band separations. From *ab initio* pseudopotential[27,28] and LMTO[29] calculations based on the LDA, these pressure coefficients are now well established ($4.0\pm0.5\times10^{-2}$ and $-1.5\pm1.0\times10^{-2}$ eV/GPa for $L_1^c$ and $X_1^c$ relative to the position of the valence-band maximum). With the interconduction-band separations given above, the data of Pitt and co-workers can only be explained if one assumes that the mass at $L$ in InP is a multiple of that in Ge, which is not reasonable. We therefore believe that the data of Pitt have to be analyzed in a different way.

The inversion asymmetry splitting $\delta=E(X_3^c)-E(X_1^c)$ (heteropolar gap) at the $X$ point in the conduction band (see Fig. 1) has been estimated in *ab initio* band-structure calculations[29,30] to be about 0.5 eV, but this value may be influenced by the band-gap problem inherent to the LDA. Recent photoemission measurements[11] suggest that this splitting could be lower (about 0.2 eV). On the other hand, InP ($f_i=0.53$) is much more ionic than GaAs ($f_i=0.31$). Here, $f_i$ is Phillips's ionicity[31] as calculated in Ref. 32. As $\delta$ is a measure of $f_i$ (see Ref. 33), $\delta$ should be much larger in InP than in GaAs ($\delta=0.4$ eV, see Ref. 34).

The density-of-states mass at the $L_1^c$ point in InP (for one valley) is probably[35] similar than that in GaAs and Ge ($0.22m_0$), if one discards the results of Pitt.[5] The mass in the $X_1^c$ valley is probably higher than in the $L_1^c$ valley, probably between 0.5 and $1.0m_0$, based on experiments by Pitt[5] and on the results for GaAs.[2]

In order to facilitate device simulations, we have adjusted the empirical pseudopotential (EPM) form factors for InP (Ref. 36) to coincide with the most reliable experimental transition energies. The interconduction-band energies have been weighted higher in the fitting procedure than the valence energies. The band energies thus obtained are also given in Table I (EPM). We suggest the following pseudopotential form factors for InP (compare Ref. 36):

$$V_S(3)=-0.2397$$

$$V_S(8)=0.0091$$

$$V_S(11)=0.0722$$

$$V_A(3)=0.0632$$

$$V_A(4)=0.0633$$

$$V_A(11)=V_A(12)=0.0207.$$

These form factors are meant to be used in the Cohen–Bergstresser scheme with a cutoff of $E_1=E_2=14$ (see Ref. 36), corresponding to 4.5 Ry or about 60 plane waves. From these form factors we obtain a value of $\delta=0.79$ eV, which may seem rather large. However, alternative sets of form factors that give smaller values of $\delta$ *and* the correct values of $\Delta E_{\Gamma L}$ and $\Delta E_{\Gamma X}$ will shift the lowest valence band down (i.e., increase the heteropolar gap in the valence band) and overestimate the conduction-band mass at $\Gamma_1^c$. With our pseudopotential form factors this mass is $m=0.08m_0$, in reasonable agreement with experiment ($m=0.077m_0$). Note that the EPM calculations confirm that the $\Gamma_1^c$ mass of InP is larger than that of GaAs although the $E_0$ gap is smaller.

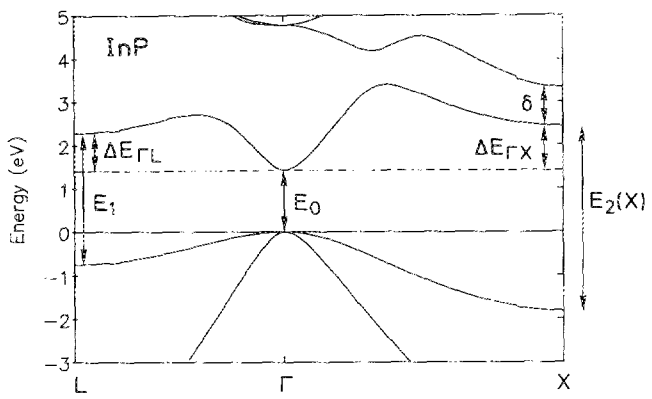


FIG. 1. Band structure of InP, calculated with the EPM form factors given here. The discontinuities are due to the finite cutoff.

We conclude that the interconduction-band separations in InP are $\Delta E_{\Gamma L}=0.86$ eV and $\Delta E_{\Gamma X}=0.96$ eV. We have shown that first-principles band-structure calculations for the valence bands can be used in conjunction with ellipsometric data for optical interband transitions to reach conclusions about the conduction-band structure of semiconductors. This information will be useful for future simulations of intervalley scattering in optical or electrical devices based on InP.


[1] See, e.g., H. C. Casey and M. B. Panish, *Heterostructure Lasers* (Academic, New York, 1978).
[2] K. Brennan and K. Hess, Solid State Commun. **27**, 347 (1984).
[3] A. Onton, R. J. Chicotka, and Y. Yacoby, in *11th International Conference on the Physics of Semiconductors*, edited by M. Miasek (Elsevier, Amsterdam, 1972), p. 1023.
[4] L. W. James, J. P. Van Dyke, F. Herman, and D. M. Chang, Phys. Rev. B **1**, 3998 (1970).
[5] G. D. Pitt, J. Phys. C **6**, 1586 (1973).
[6] G. D. Pitt, Solid State Commun. **8**, 1119 (1970).
[7] G. D. Pitt and J. Lees, Phys. Rev. B **2**, 4144 (1970).
[8] A. W. Mabbitt, Solid State Commun. **9**, 245 (1971).
[9] W. P. Dumke, M. R. Lorenz, and G. D. Petit, Phys. Rev. B **1**, 4668 (1970).
[10] O. Madelung, ed., *Numerical Data and Functional Relationships in Science and Technology* (Springer, Berlin, 1987), Vol. 22; G. P. Williams, F. Cerrina, G. J. Lapeyre, J. R. Anderson, and J. Hermanson, Phys. Rev. B. **34**, 5548 (1986); S. Sorba, V. Hinkel, H. U. Middelman, K. Horn, *ibid.* **36**, 8075 (1987).
[11] J. Peretti, H.-J. Drouhin, and D. Paget, Phys. Rev. Lett. **64**, 1682 (1990).
[12] J. Shah, B. Deveaud, T. C. Damen, W. T. Tsang, A. C. Gossard, and P. Lugli, Phys. Rev. Lett. **59**, 2222 (1987).
[13] M. A. Alekseev, I. Ya. Karlik, D. N. Mirlin, V. F. Sepega, and A. A. Sirenko, in *19th International Conference on the Physics of Semiconductors*, edited by W. Zawadzki (Institute of Physics, Polish Academy of Sciences, Warsaw, 1988), Vol. 2., p. 1423.
[14] O. Wada, A. Majerfeld, and A. N. M. M. Choudhury, J. Appl. Phys. **51**, 423 (1980).
[15] The spin-orbit interaction can be added as a formal perturbation term in the Hamiltonian, or a fully Dirac-relativistic LMTO scheme can be applied. Details of the band splittings caused by the spin-orbit coupling in zinc blende type crystals are discussed in Ref. 16.
[16] M. Cardona, N. E. Christensen, and G. Fasol, Phys. Rev. B **38**, 1806 (1988).
[17] S. Massidda, A. Continenza, A. J. Freeman, T. M. de Pascale, F. Meloni, and M. Serra, Phys. Rev. B **41**, 12079 (1990).
[18] O. Madelung, ed., *Numerical Data and Functional Relationsships in Science and Technology* (Springer, Berlin, 1989), Vol. 23, pp. 60–65.
[19] R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. B **35**, 4170 (1987).
[20] S. B. Zhang, D. Tomanek, M. L. Cohen, S. G. Louie, and M. S. Hybertsen, Phys. Rev. B **40**, 3162 (1989); M. S. Hybertsen and S. G. Louie, *ibid.* **34**, 5390 (1986).
[21] P. Lautenschlager, M. Garriga, and M. Cardona, Phys. Rev. B **36**, 4813 (1987) and references therein.
[22] By applying uniaxial strain, it is possible to distinguish between valleys in different directions.
[23] W. G. Spitzer and J. M. Whelan, Phys. Rev. **114**, 59 (1959); J. S. Blakemore, J. Appl. Phys. **53**, R123 (1982).
[24] H.-J. Drouhin, C. Hermann, and G. Lampel, Phys. Rev. B **31**, 3859 (1985); **31**, 3872 (1985).
[25] A. R. Goñi, K. Syassen, K. Strössner, and M. Cardona, Phys. Rev. B **39**, 3178 (1989).
[26] H. Müller, R. Trommer, M. Cardona, and P. Vogl, Phys. Rev. B **21**, 4879 (1980).
[27] K. J. Chang, S. Froyen, and M. L. Cohen, Solid State Commun. **50**, 105 (1984).
[28] P. E. Van Camp, V. E. Van Doren, and J. T. Devreese, Phys. Rev. B **41**, 1598 (1990).
[29] J. Gorczyca, N. E. Christensen, and M. Alouani, Phys. Rev. B **39**, 7705 (1989).
[30] R. M. Wentzcovitch, M. Cardona, M. L. Cohen, and N. E. Christensen, Solid State Commun. **67**, 927 (1988).
[31] J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).
[32] N. E. Christensen, S. Satpathy, and Z. Pawlowska, Phys. Rev. B **36**, 1032 (1987).
[33] P. Vogl, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids **44**, 365 (1983).
[34] D. E. Aspnes, Phys. Rev. B **14**, 5331 (1976).
[35] From k·p arguments, the transverse mass should be proportional to $E_1$, but little can be said about the longitudinal mass.
[36] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).