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How Successfully Does Angle-resolved Photoemission Determine the Band Structure of Semiconductors?*

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Abstract

Both the calculation and the experimental determination of the band structure of simple materials using the techniques of photoemission have now reached levels of considerable sophistication and maturity. Indeed, it is often claimed that the determination of the detailed electronic band structure of semiconductors, for example, is almost routine using angle-resolved photoelectron spectroscopy in conjunction with synchrotron radiation. In this paper we will discuss the extent to which this claim is justified, illustrating the discussion with recent results from a number of III/V semiconductors. We will demonstrate the model-dependent nature of current interpretations of the experimental data, and will show that the technique is presently limited due to the scarcity of information concerning excited band states well above the vacuum level.

1. Introduction

Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), when used in conjunction with synchrotron radiation, is the established technique for the experimental determination of the electronic band structure of conducting and semiconducting solids. Experimental band structures along major symmetry directions have been established for many elemental solids and for most compound semiconductors of potential technological value, for example. A useful collection of such data can be found in the new Landolt–Börnstein series (Madelung *et al.* 1989).

When such data are examined, it is usually the case that the experimental results are seen to be in very reasonable agreement with whichever calculation scheme the author of each paper has selected for comparison purposes. In the case of materials with relatively simple band structures, such as the III/V semiconductors, the choice of calculation scheme is of marginal importance since most, if not all, such schemes involve the use of a number of parameters which have by now been optimised with reference to a variety of experimentally derived results. Even so-called *ab initio* schemes usually include some adjustable parameters. The end result is that the remaining differences between calculation methods are currently smaller than the precision available from experiment. It

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is the intention of this paper to address the question of the actual precision of experimental band structure determinations available via the photoemission method, and to demonstrate that the agreement obtained is often a result of the interpretative model employed.

The current methodology used for the interpretation of ARUPS data will be examined as it applies to normal and off-normal emission, and the limitations of the method will be illustrated. An alternative strategy for the determination of critical point energies well above the Fermi energy, namely constant initial state (CIS) spectroscopy, will then be discussed. It will be asserted that the occupied band structure of III/V semiconductors, and of many metals, is known from theory with adequate precision for most purposes and that future efforts should be aimed at the calculation and measurement of unoccupied states. Consequently, it will be argued, future angle-resolved photoemission measurements should be interpreted on the basis of presumed-known initial states, with a view to elucidating the final states involved in photoinduced transitions.

2. Experimental

Normal Emission Studies

Most experimental determinations of the valence band structure of semiconductors commence with the acquisition of a series of energy distribution curves, obtained from a specified single crystal surface using a wide range of photon energies, in which the emission angle of the electrons is confined to be within a few degrees of the surface normal. A typical set of such energy distributions is shown in Fig. 1 in which a number of features (peaks) may be identified, some of which clearly disperse in energy as a function of photon energy. It is assumed that these peaks result from the emission of photoelectrons which have escaped from the material without loss of energy due to any electronic process (the small energy loss associated with phonon scattering is not relevant here, except as a broadening mechanism).

By restricting the emission energy to essentially the normal direction, it follows that the initial state for the excitation lies along the line $K_\perp$ in reciprocal space. The magnitude of $K_\perp$ external to the solid is clearly different to its internal value, due to the effect of the potential barrier at the surface. In order to determine uniquely the point in K-space associated with a particular transition, the excited band structure $[E(K_\perp)]$ should be known, together with the particular reciprocal vector $\boldsymbol{G}$ involved in that transition.

The simplest approximation to the excited band structure is that of a free electron. We may demonstrate the interpretation of photoemission data in terms of such a first-order model by reference to Fig. 2. This shows properly calculated valence bands together with a number of branches of free electron parabolas associated with certain $\boldsymbol{G}$, so that the diagram may be drawn in the reduced zone scheme. A peak in an energy distribution due to photons of energy $h\nu$ and observed at kinetic energy E_1 could, in this modeel, be assigned the value K_1 and so lead to the prediction that the transition was associated with the valence band state indicated by the filled circle. Note that in the absence of any other evidence, the observed transition could equally have been assigned to the state identified by the open circle (with the value K_2).

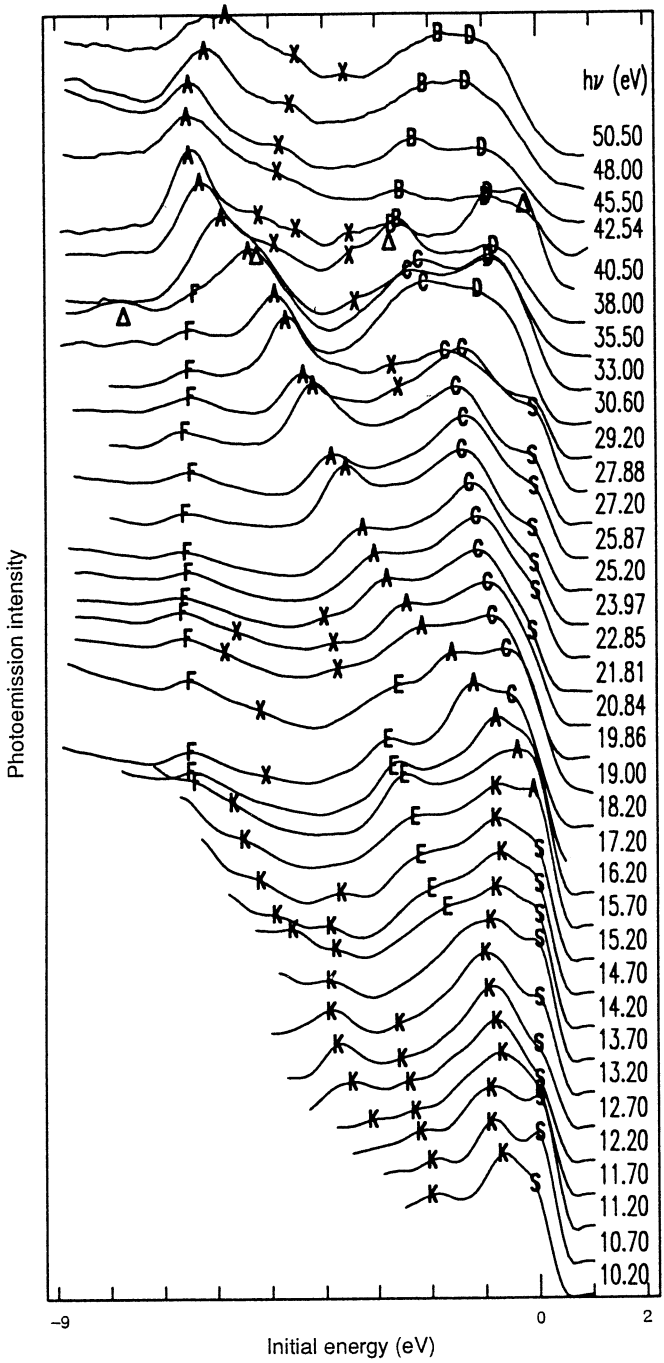

Fig. 1. Normal emission spectra taken from a GaAs(001) surface at photon energies from 10·2 to 50·5 eV. Detected peaks are marked by letter symbols. The As 3d core-level emission excited by second-order light of the monochromator is indicated by open triangles.

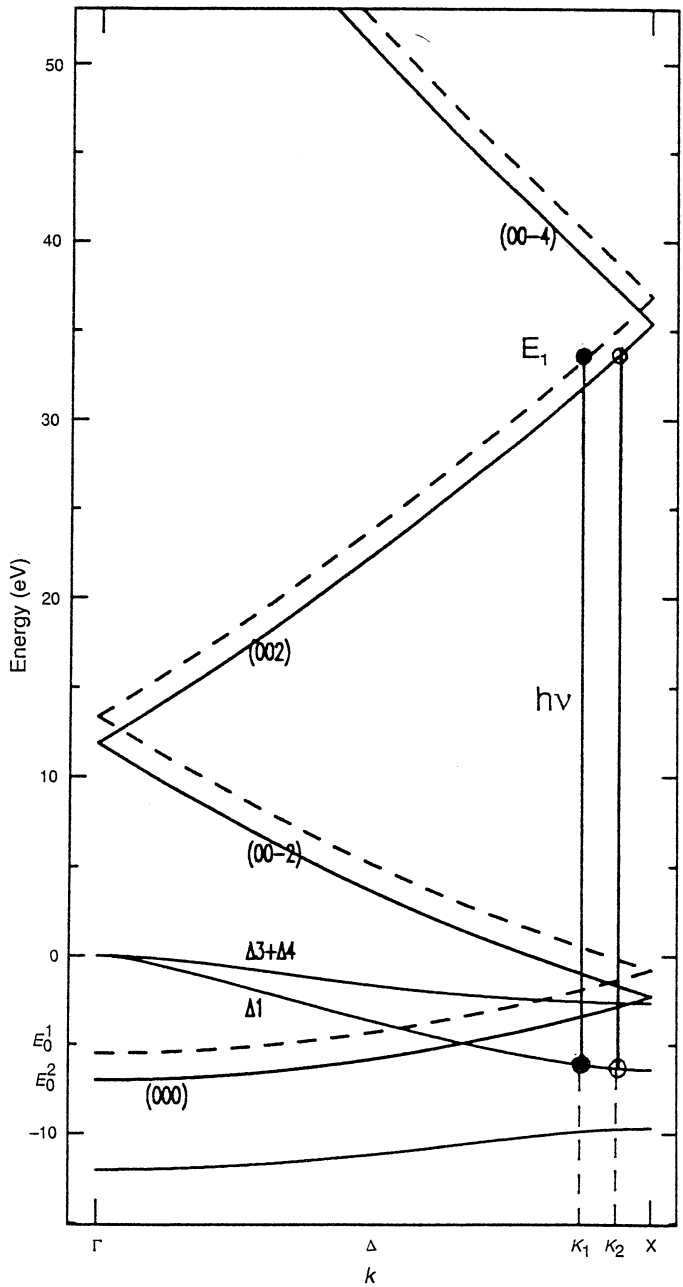

Fig. 2. LMTO valence bands and free electron final states along the Γ–Δ–X direction. Also shown are schematic representations of how the choice of the inner potential E_0 can influence the assignment of an experimental transition.

The origin of the free electron parabola (the inner potential E_0) is seldom known with certainty; indeed values differing by a few eV have been used in the literature for the same surface. It should be clear from Fig. 2 that a different choice of E_0 would result in two quite different possible assignments for the transition under consideration.

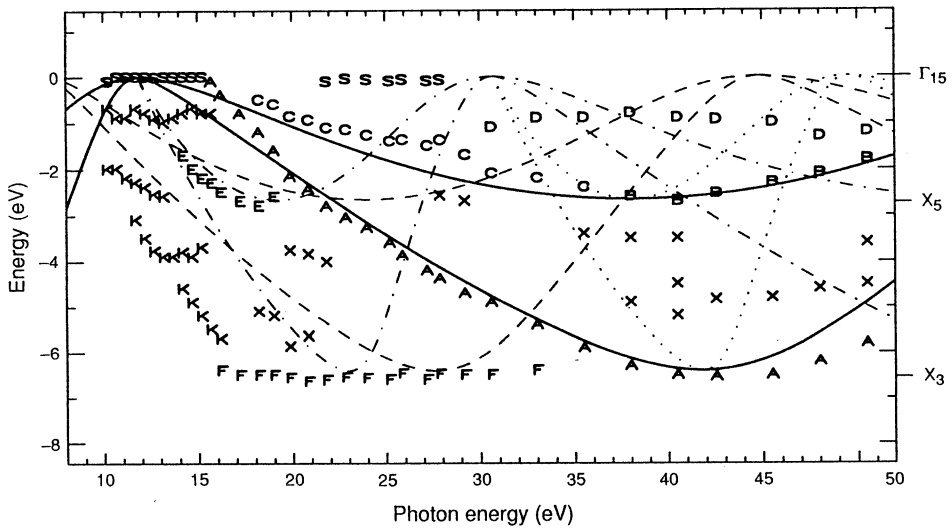

Fig. 3. Structure plot for the normal emission data shown in Fig. 1. The theoretical transition curves are generated using LMTO valence bands Δ_1 and $\Delta_{3,4}$ along the Γ–Δ–X direction and free electron bands with an inner potential $E_0 = -7{\cdot}0$ eV. The energy is measured with respect to the valence band maximum.

In order to assist with the assignment of the correct $\boldsymbol{G}$ to associate with each observed transition in a normal emission experiment, a so-called structure plot is often used. Such a plot, showing peak positions expressed in terms of binding energy as a function of photon energy, is shown as Fig. 3. The experimental values, shown as letter symbols, may be recognised as belonging to particular branches of the free-electron states by their association with particular theoretical curves. The latter have been constructed by assuming knowledge of the valence band structure (in this case from a LMTO calculation) and a selected value for the inner potential. The theoretical curves in Fig. 3 are thus the loci of allowed transitions between the calculated valence bands and the various free electron states. In many cases such a structure plot enables the experimentalist to make the proper choice between alternative assignments such as K_1 and K_2 of Fig. 2. The structure plot does not resolve all such degeneracies, nor do all experimental points have an association with such direct bulk transitions (Umklapp processes and emission from surface states must also be considered). Nevertheless, the free electron model outlined here remains the predominant model for the interpretation of angle-resolved photoemission data.

It will be apparent from the above that, in practice, the use of a free electron model relies to a considerable extent on prior knowledge of the valence band structure. The choice of E_0 in particular is likely to be influenced by the quality of agreement which then results when experimental results are compared to the

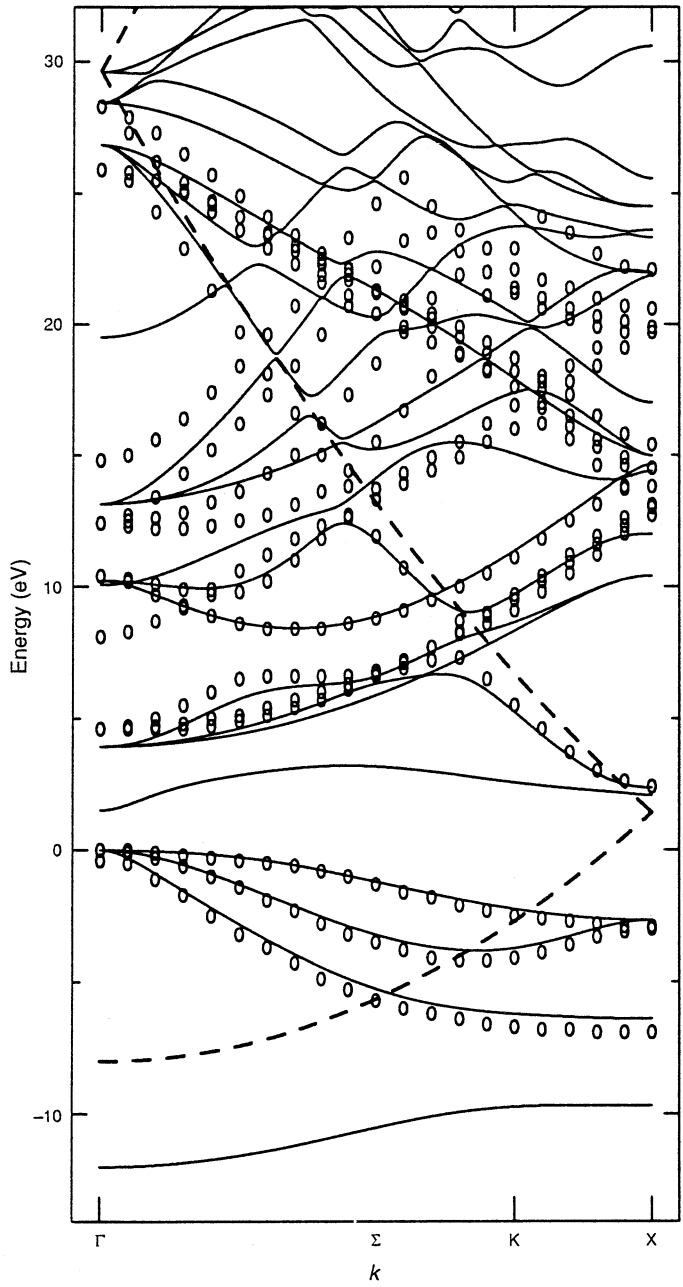

Fig. 4. LMTO bands (solid curves) along the Γ–Δ–X direction for GaAs. Experimentally derived bands (Williams *et al.* 1986) are plotted as circles. Also shown are free electron primary cone final state bands (dashed curves) with an inner potential $E_0 = -8{\cdot}0$ eV.

preselected valence band calculation. It will also be clear that the success of the method relies heavily on the ability of free-electron-like states to mimic the true excited state band structure.

Some attempts have appeared in the literature which use calculated conduction bands rather than free electron states. The calculations are, firstly, ground state calculations rather than those appropriate to the system minus one electron; secondly, few calculations include sufficient basis states to describe the band structure correctly for states more than about 20 eV above the valence band maximum.

We show a comparison between experimental data and LMTO bands for the case of GaAs(110) in Fig. 4. Here the experimental data come from the normal emission study of Williams *et al.* (1986) as modified by Stampfl (1990) to allow for a reassignment of the energy associated with the valence band minimum (VBM). The identification of the precise energy of the VBM is a point of contention among photoemission practitioners; we have given a detailed discussion of this point earlier (Leckey and Riley 1992). Superimposed on the LMTO bands in Fig. 4 we show the main branches of the free electron parabola for comparison. It is clear that experiment and theory are in reasonable agreement for quite a few of the conduction bands, especially those which are well mimicked by free electron bands. The good agreement in the case of the valence bands is to be expected as discussed above, since each observed transition has been 'identified' with a view to obtaining such agreement. It is also clear that the conduction band structure is sufficiently complex that, in many cases, no unique 'identification'

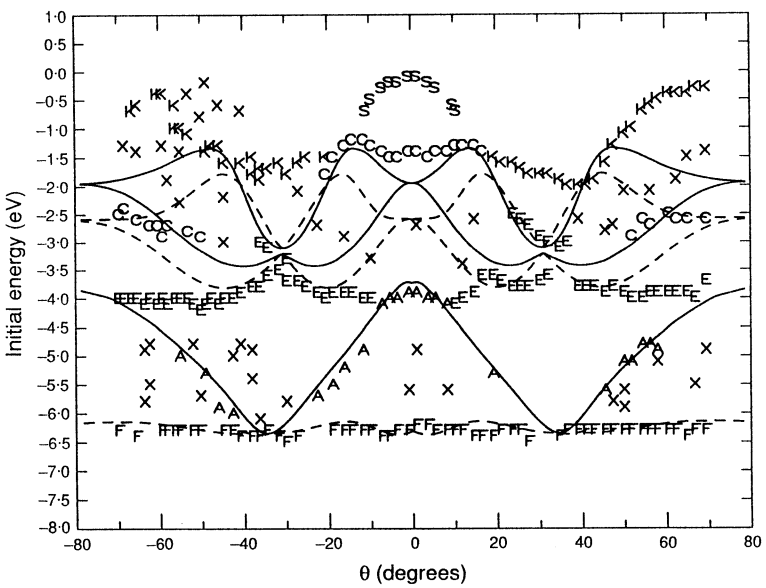

Fig. 5. Structure plot of E_i versus θ for a data set taken at a photon energy of 26·2 eV from a GaAs(001) surface. Off-normal emission was confined to a measurement plane containing the [100] azimuth. Letter symbols mark the detected peak positions in the spectra. Theoretical transition lines (solid and dashed curves) are generated using LMTO initial state bands and free electron final state bands with $E_0 = -7{\cdot}0$ eV.

can really be made, with the result that the diagram is, to a significant extent, influenced by subjective judgements.

Off-normal Studies

Whereas normal emission studies illuminate the band structure along a chosen symmetry line in reciprocal space, angle-resolved photoemission has the potential to examine all states within the Brillouin zone if off-normal emission is also considered. A typical experimental result, showing the intensity of emission over a range of kinetic (or binding) energies and covering all emission angles in a selected plane, is shown in Fig. 5 for a single photon energy. A variant of the structure plot for these data is also shown, in which the locations of peaks in the data are labelled by letter symbols. The theoretical lines in Fig. 5 are the loci of the intersection of the two surfaces $E(K_{||}, K_{\perp})$ involved in the transition (after subtraction of the photon energy). More complete analysis of such plots may be found in Cai (1992) but for the present purposes it may be seen that the data is mostly adequately explained by means of the LMTO/free-electron model used, but that there is no way of telling if the remaining discrepancies are due to inadequacies in the initial or the final states, or in both.

Constant Initial State (CIS) Spectra

If the kinetic energy of detection is increased in synchrony with increases in the photon energy used in a photoemission experiment, all observed transitions

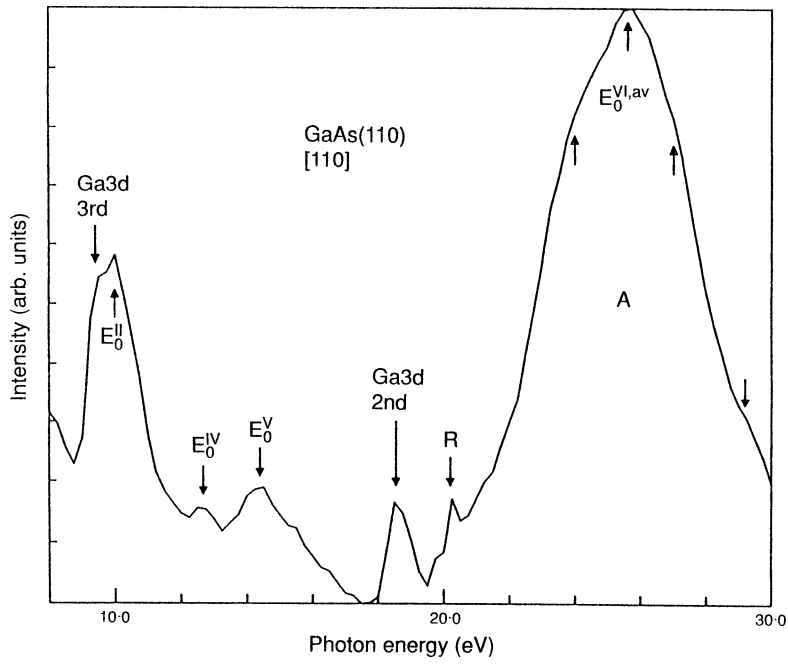

Fig. 6. A normal emission CIS spectrum taken from a GaAs(110) surface. Emissions are from Γ_{15}. Features labelled E correspond to critical-point transitions. Higher-order core-level emission is also indicated.

will originate from an initial state having a unique energy. This is known as the CIS mode of operation. If the initial state is also selected (with reference to a known band structure) and has a unique value of $\boldsymbol{K}$, then peaks in the detected intensity should enable the location of conduction band states to be determined. The process is illustrated for the case of emission from the top of the valence band [Γ_{15} for GaAs(110) in Fig. 6].

A more complete discussion of the analysis of CIS data has been presented earlier (Faul *et al.* 1993). The salient result for the present discussion is illustrated in Fig. 7, which refers to the determination of critical point energies at the Γ point for certain III/V semiconductors. In Fig. 7 the experimental critical point energies are compared with the predictions of a non-local, empirical pseudopotential method, as well as those of a simple free electron model. Although the pseudopotential calculation is clearly to be preferred to the free electron

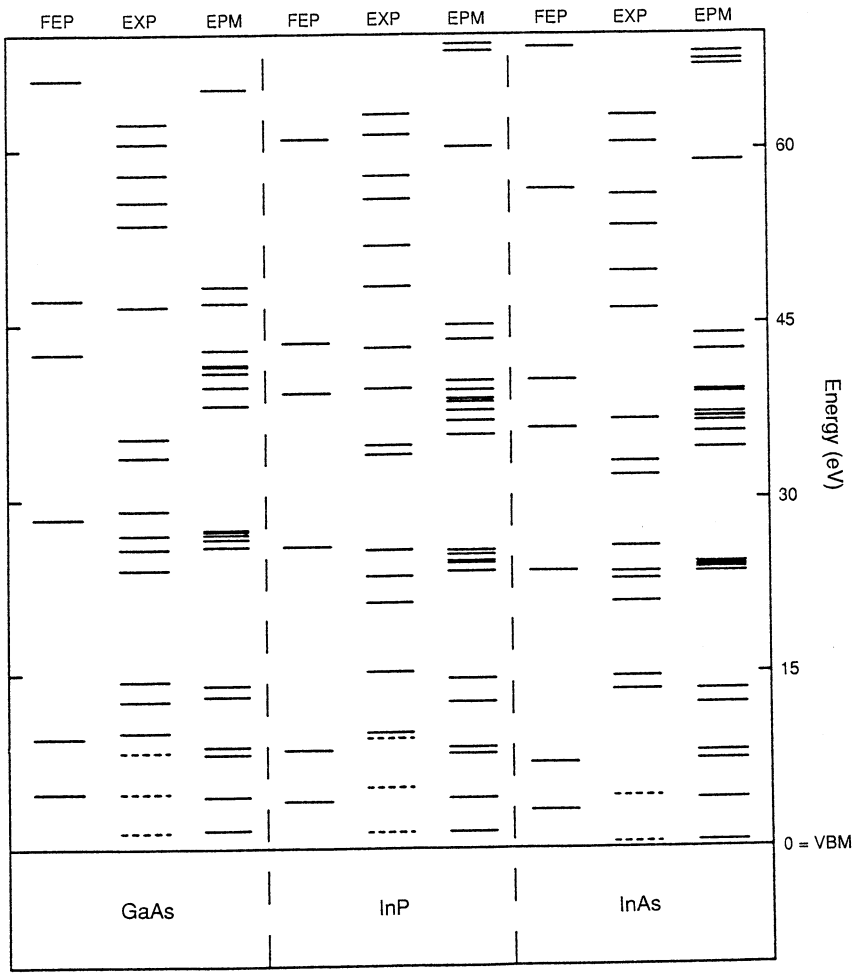

Fig. 7. Theoretical and experimental Γ-point energies for GaAs, InP and InAs. FEP stands for the free electron parabola, EXP for the experimental data and EPM for the empirical pseudopotential final states.

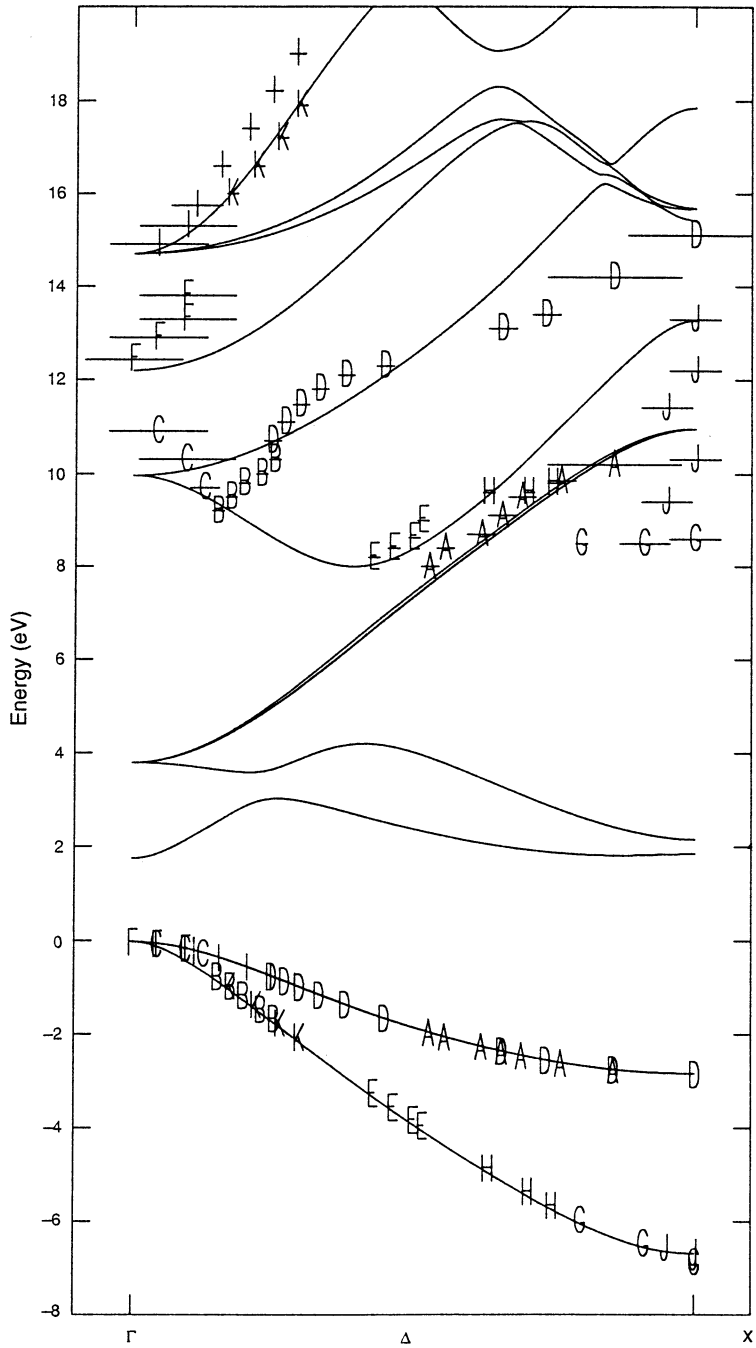

Fig. 8. Experimentally mapped band structures (letters) of GaAs along the Γ–Δ–X direction. Also shown is the LMTO-calculated band structure (solid curves) of GaAs.

model, particularly in the lower kinetic energy range, neither calculation agrees particularly well with experiment for kinetic energies well above the vacuum level.

The data used in Fig. 6 were taken under normal emission conditions using an initial state that was deliberately chosen to be single-valued in $\boldsymbol{K}$. We have also acquired angle-resolved CIS data for other initial states but the interpretation is made difficult by the many-valued nature of $\boldsymbol{K}$ for these states. Surface Umklapp processes can also complicate the interpretation in some cases, but the technique nevertheless holds considerable promise for the elucidation of conduction band states.

A preliminary study of GaAs(001), which assumes the correctness of the valence band states as given by a LMTO calculation, and which utilises both angle-resolved CIS data and a set of normal-emission energy distributions covering a wide range of photon energies, provides useful new insights into the conduction band states of relevance to the photoemission process. First results from both these methodologies are shown in Fig. 8; further details will be presented elsewhere.

3. Conclusions

Angle-resolved photoelectron spectroscopy is a good example of a technique that requires an intimate symbiotic relationship with theory before the experimental data can be usefully interpreted. Knowledge of the theoretically expected band structure is a necessary precondition for this interpretation in the sense that the occupied states should be known reasonably accurately and that the experiment should be performed at high enough photon energies (>20 eV, for example) so that the free electron approximation may be used for the unoccupied states with a reasonable chance of success. It is under conditions such as this that the majority of published band structure determinations using these techniques have been produced. Thus, discrepancies between theory and experiment have in general been deemed to be associated with initial state bands, the free electron final state bands having been implicitly assumed to be accurate. This is clearly unsatisfactory, but has been necessary to date in the absence of reliable excited-state calculations.

The shortcomings of existing conduction-band calculations have been revealed by angle-resolved CIS measurements as described above. We have also illustrated an alternative approach, one in which calculated initial states have been assumed to be accurate and photoemission energy distribution curves and CIS spectra have been combined in angle-resolved form to partially determine the true shapes of the excited states within 20 eV of the vacuum level.

We have also highlighted the urgent need for more theoretical progress towards the calculation of reliable excited state bands covering the energy range 10–50 eV above the vacuum level. It is this range which is of most importance for the interpretation of photoemission data: without such conduction band data, the photoemission experiment cannot confidently be used to verify the accuracy of valence band calculations.

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