Electron Emission from Core and Valence States of Some Semiconductors

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Measurements of the energy distributions of emitted electrons from Si, GaP, and ZnS allowed the determination of the relative positions of some core levels of these materials and the optical density of states of the valence band in Si. These energy levels were determined relative to the Fermi level. The electron emission was induced by monochromatic X-rays (AlKα). These results are compared with values obtained from OPW calculations for the valence bands and selfconsistent Hartree-Fock-Slater calculations for the core states.

The useful properties of intrinsic semiconductors result in general from particular shapes of valence and conduction bands and from electronic transitions between them. It therefore has been a legitimate task for experimentalists to derive as much information as possible about these bands: mainly relative energy positions and curvatures at points of high symmetry in the Brillouin zone. Theoreticians have tried to fill in the gaps and to extrapolate, calculating higher bands, by pseudopotential calculations or to derive the band structure by first principle calculations, according to e. g. APW, OPW or KKR type calculations.

The merit of the latter calculations is based on the ultimate hope that once a "valid method" is found one could calculate the band structure for materials which have not yet been extensively studied or not even been synthesized. Presently, however, the "validity of the methods" is still to be improved and tested by comparison with the knowledge gained from experiments.

A host of experimental information is available about the relative energy positions of the upper valence and the lower conduction bands at several points in the Brillouin zone for Si, Ge and most compounds derived from III – V and II – VI group elements.

Theory has been advanced also and agrees fairly well with the observations of valence and conduction band energies. Apart from this narrow region, however, experimental checks are hard to be obtained. The usual methods of observing energy differences between bands by optical spectroscopy are limited in the far UV to about 15 eV. Besides, often ambiguities might arise, as it is not always clear whether an observed structure is to be assigned to transitions from lower valence or core states to the lowest conduction band or from the top of the valence band to higher conduction bands. To extend the energy region and in order to deal unambiguously only with valence and core states the following measurements have been made: Soft X-rays of 1486.6 eV (half-width 1.2 eV) are absorbed by the samples which consequently emit electrons. The energy distribution of the emitted electrons is analysed and – neglecting interactions within the solid – represents the binding energy of the electrons. The plot of "number of emitted electrons per time" versus "binding energy" shows peaks and structures which represent an "optical density of states". Thus one can measure energy differences with respect to the Fermi level of the valence band structure and of lower core levels.

From the theoretical viewpoint this is interesting because in OPW band structure calculation schemes, bands and core levels are first separated, treated differently and then again combined. This procedure though it may give reasonable agreement with observed band parameters may still be unrealistic as for as the description of *all* levels is concerned.

It should be pointed out that the measurements presented here were obtained in a few quick runs. They are only intended to demonstrate the procedures and the potentials of the method. It is to be expected that refined measurements in the near future will lead to improved and more reliable results.

Experimental Procedures

The phenomenon of X-ray induced electron emission, its merits and limitations have been well discussed by SIEGBAHN et al.[1], who did pioneering

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[1] K. SIEGBAHN et al., Nova Acta Reg. Soc., Sc. Ups. Ser. IV **20**, 1 [1967].

work in this area during the past decade. Applications of this method to semiconductors and comparison with band structure calculations have not yet been made.

The method is as follows: Soft X-rays of well defined energy are radiated on to a sample. In our case, the 1486.6 eV line, $\mathrm{AlK}\alpha_{12}$, which has a half-width of approximately 0.9 eV has the predominant intensity. Due to the absorption of photons electrons in the sample are excited. If they are excited to a higher energy (E_1) than the energy with which they are bound in the solid (E_2), then they are emitted from the solid. The energy difference ($E_1 - E_2$) is measurable as their kinetic energy. As Siegbahn has demoonstrated, under certain excitation conditions e. g. with the $\mathrm{AlK}\alpha$ line, by far the largest number of emitted electrons have not lost any part of their energy by interactions in the process of emerging from the solid. Thus the measurable kinetic energy spectrum represents truely the binding energies of the emitted electrons.

An electrostatic spherical analyser has been used which has an ultimate resolution of 0.2 eV over the total energy range when using appropriate retardation potentials. It is assumed that there is no energy difference between the Fermi levels of the sample and the electron analyser. Furthermore the difference between the Fermi level and the vacuum level of the sample has been determined with a calibration on carbon, assuming that 284 eV [2] is the correct binding energy of the C_{1s} electrons. Several details in this connection may require further investigation (e. g. whether Fermi levels of samples change appreciably due to the intense X-ray radiation) but the energy differences between peaks due to core states and the structure due to the valence band will not be affected.

The experimental apparatus used for these measurements was developed and built by Dr. J. HELMER and Dr. N. WEICHERT of Varian Associates. It was the prototype of an Induced Electron Emission Spectrometer, which soon will be commercially available.

Results

For the initial measurements three compounds (Si, GaP, ZnS) were selected for which results for core and valence states were available according to a non-relativistic first principle calculation and for which, because of their light weight, the influence of relativistic corrections is considered to be small. The calculations were made in this laboratory by Drs. EUWEMA, COLLINS and STUKEL. They used a selfconsistent OPW method for the calculation of valence and conduction bands. The core states were calculated according to the self-consistent Hartree-Fock-Slater method, using Slater's exchange parameter and with frozen valence charge density and coulomb potentials which both were spherically symmetrized about the core in question.

For Si we were able to make a detailed study of the valence band shown in Fig. 1. Compared are three experimental curves (1 – 3) with density of states derived from two calculations (4, 5). Curve 1 is the one measured by induced electron emission in this work. Curve 2 represents results of SAGAWA [3] from his measurements of the Si L_2L_3 soft X-ray emission band. Curve 3 is a measurement of AMELIO [4] using Auger electron spectroscopy and secondary emission. Curve 4 had been calculated by EUWEMA, COLLINS and STUKEL [5] and curve 5 represents the results of KANE's [6] calculations. Zero energy is at the top of the valence band in all cases. It is to be noted that the general features, namely three wide bands, are observable in all three experiments

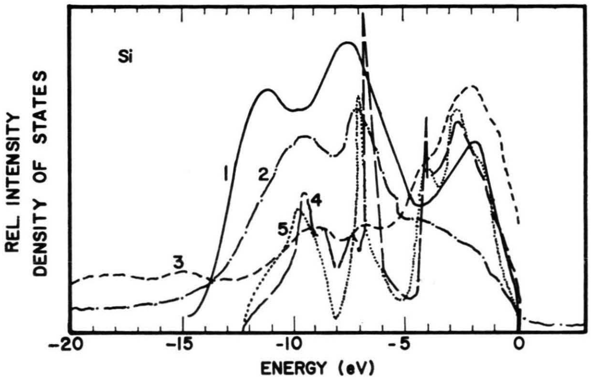

Fig. 1. The valence band of Si. Zero energy refers to the top of the valence band. (1) Relative intensity distribution of X-ray induced electron emission (present work). (2) Sagawa's $L_{2,3}$ soft X-ray emission band. (3) Amelio's secondary electron emission. (4) Calculated density of states by Euwema et al. (5) Calculated density of states by Hane.

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[2] S. HAGODRÖM and S. E. KARLSSON, Arkiv Fysik **20**, 451

[3] T. SAGAWA, private communication.

[4] G. F. AMELIO, PhD Thesis, Georgia Institute of Technology, Atlanta, Ga., 1968.

[5] R. EUWEMA, T. COLLINS, and D. STUKEL, private comunication.

[6] E. O. KANE, Phys. Rev. **159**, 624 [1967].

though the relative intensities vary. The pronounced structure predicted by theory is not observable, which only in part may be due to the low resolution in the experimental work (approximately 2 eV). The largest difference between the theoretical and experimental maxima occurs at the lowest maximum which, predicted at about − 10 eV, seems to be located at about − 11.5 eV according to the present work.

Additionally the 2p state of Si was measured. We found it to be 100.5 eV below the top of the valence band. The calculated value is − 101.1 eV. Measurements of the 2s state are in progress. The calculated value for Si2s is − 143.7 eV below the top of the conduction band.

In GaP and ZnS the onset of the valence band has not been as clearly recognizable as in Si. Therefore the experimental values reported for ZnS and GaP will relate the Fermi level as the zero energy. The calculated values refer to the top of the valence band as zero energy. The difference between energy maxima is still a good quantity to be compared; the absolute values, however, are off by the energy difference between the top of the valence band and the Fermi level. Unfortunately it was not possible to determine whether or how much it deviated from its ideal position at the center of the band gap.

Figure 2 shows the experimental result for the Ga 3d level in GaP. The dashed lines, the separation between which is equal to the band gap, indicate the limits for the theoretically determined peak. The lower energy line corresponds to the case where the Fermi level would coincide with the top of the valence band and the upper dashed line corresponds to the case where the Fermi level coincides with the bottom of the conduction band. Unless the Fermi level is well within the conduction band one would have to conclude that the calculations have resulted in Ga 3d levels which are about 2 eV low.

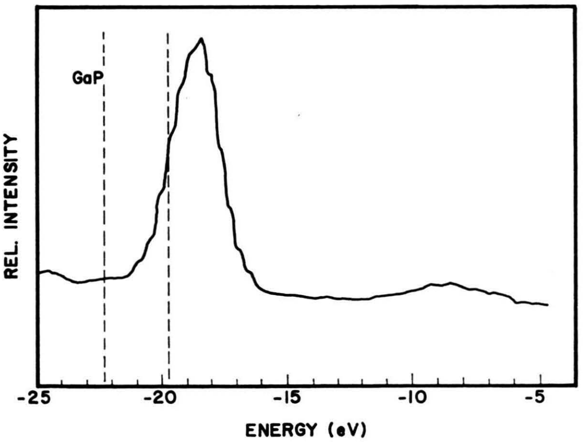

Fig. 2. Electron distribution near te Ga 3d level in GaP. Zero energy refers to the Fermi level of the sample. The dashed lines indicate the limits of the calculated position for Ga 3d in GaP bands.

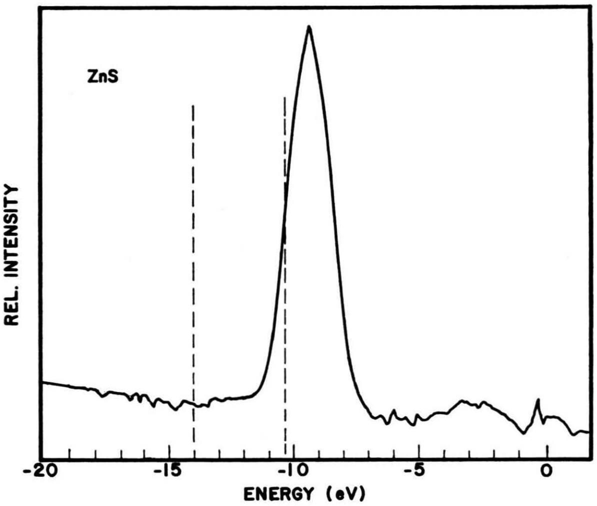

Fig. 3. Electron distribution near the Zn 3d level in ZnS. Zero energy refers to the Fermi level of the sample. The dashed lines indicate the limits of the calculated position for Zn 3d in ZnS.

Other core levels in GaP have been measured and calculated as follows (energies in eV):

	P		Ga			
	2s	2p	2p	$3p_{1/2}$	$3p_{3/2}$	3d
Experiment	− 185.9	−128.4	− 1115.4	− 107	− 104	− 18.6
Theory	− 180.4	− 132.8	− 1118.8	− 101.9		− 22.3
Difference	− 5.5	4.4	3.4	≈ − 3.1		5.7

Figure 3 shows a measurement of the Zn 3d band in ZnS. Dashed lines are the limits of the theoretical band maximum analogous to Fig. 2. The valence band structure extends probably between − 1 eV and − 5 eV. The top of the valence band however is again not clearly recognizable. Other values for ZnS are as follows (energy in eV):

	S			Zn					
	2s	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	3s	$3p_{1/2}$	$3p_{3/2}$	3d
Experiment	− 225.9		− 160.5	− 1043	− 1020.3	− 138.5	− 90.5	− 87.6	− 9.9
Theory	− 220.7	− 168		− 1025.0		− 130.4	− 87.7		− 14.25
Difference	− 5.2	≈ 8.0		≈ − 2.9		− 8.1	≈ − 0.9		4.35

Though a common small (positive) difference could be accounted for by the fact that the Fermi energy certainly is not at the top of the valence band (as one can see by comparing the theoretical values with the experimental ones) the differences between theoretical and experimental values are larger than permissable on the basis of these arguments. They even vary in sign and thus point to a genuine discrepancy of some eV between theory and experiments.

It is hoped that this extention of experimentally determined core levels will help to inspire further refinements of the theoretical approaches.

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