Submitted to Physical
Review Letters

LBL-1204
Preprint

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July 1972

AEC Contract No. W-7405-eng-48

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X-RAY PHOTOEMISSION VALENCE BAND SPECTRA AND THEORETICAL VALENCE BAND DENSITIES OF STATES FOR Ge, GaAs, AND ZnSe*

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Abstract:

We report the first high resolution valence band x-ray photoemission spectra for the isoelectronic series Ge, GaAs, and ZnSe. The results are compared with a theoretical valence-band density-of-states calculation using the empirical pseudopotential method. The agreement between the experimental and theoretical results are quite good, particularly for Ge and GaAs. For ZnSe the x-ray photoemission spectrum shows the Zn 3d-states to be higher in energy than the lowest valence-band s-state. In order to obtain this ordering of states in the theoretical calculation, a pseudopotential with an explicit energy dependence is required.

Much theoretical and experimental effort has been devoted to the study of the band structures of tetrahedrally coordinated semiconductors because of their numerous applications. Most earlier measurements (optical spectroscopy, transport properties, etc.) have been useful in yielding information concerning electronic properties near the Fermi energy. Only recently have there been any experimental data (e.g. soft x-ray spectroscopy) which yield information about the density of states in regions near the bottom of the valence band.

We report here the first high resolution XPS (X-ray Photoemission Spectroscopy) spectra for all valence bands in the isoelectronic series Ge, GaAs, and ZnSe. These experimental results are compared with theoretical valence band density-of-states calculations using the EPM[1] (Empirical Pseudopotential Method). Since the lattice constants and ion cores are essentially constant for the series, the band spacings are used to obtain information about the increasing ionicity from purely covalent Ge to the more ionic ZnSe. The experimental results also yield information about the asymmetric part of the pseudopotential.

High-purity single crystals were cleaved in a dry nitrogen atmosphere immediately before insertion into the spectrometer vacuum ($\sim 8 \times 10^{-9}$ Torr). The spectra were obtained on an HP 5950A electron spectrometer using monochromatized Al K_α x-rays (1486.6 eV). The possibility of using this method to study the valence band density of states in semiconductors has recently been demonstrated by L. Ley et al.[2] and the experimental resolution of the HP 5950A has been discussed by R. Pollak et al.[3] The spectra were referenced to the Fermi level E_F of a thin layer of Au evaporated onto the semiconductor surfaces after the valence band measurement. The Au 4f lines were used as a secondary standard by assuming that their binding energies are the same relative to E_F in the evaporated film and in bulk gold.

In Fig. 1 are shown the experimental and theoretical densities of states for Ge, GaAs, and ZnSe, and the corresponding theoretical band structures. The theoretical valence-band densities of states were obtained from band-structure calculations for Ge,[4] GaAs,[5] and ZnSe[6] using the EPM. A broadened theortical density of states is also provided to facilitate comparison with experiment. The experimental curves have not been corrected for energy losses. This tends to exaggerate the intensities of the peaks at the bottom of the valence-band. In Table I we list the energies of the various peaks from the theoretical density of states and from the XPS spectra.

For Ge there is good agreement between theory and experiment in regard to the energy positioning and the widths of the peaks, as was reported earlier.[2] In the XPS spectrum the 3d states of Ge fall at 29.0 eV, 18.7 eV lower than the first peak shown in Fig. 1. In GaAs we again find good agreement between theory and experiment. The first peak on the left in the XPS spectrum (Fig. 1) comes from the 3d states of Ga. The lowest s-like valence band has shifted to a lower energy and has become dissociated from the next peak. This shift to a lower energy occurs because of the localization of electrons in the first band around the strong As potential, and can be related to the antisymmetric form factors. The "antisymmetric gap" (between the lowest s-like valence band and the second valence band) may provide some measure of the ionicities of these compounds. It is surprising that the EPM agrees so well with experiment for this lowest valence band. This band does not make any contribution to optical transitions in the 2.8 to 6 eV range, which were used to determine[5] the pseudopotential form factors. Furthermore these states are far from E_F and the energy dependence of the pseudopotential has not been taken explicitly into account.

The largest differences between the experimental and theoretical spectra are found in ZnSe. Here the XPS spectrum shows that the Zn 3d-states lie higher in energy than the s-like states at the bottom of the valence band, and the "antisymmetric gap" has become larger. The agreement between theory and experiment is less satisfying than for Ge and GaAs. The widths of the theoretical peaks are smaller than the corresponding experimental widths and the theoretical energy gap between the first two valence bands is larger than the experimental energy gap. It appears that the explicit energy dependence of the pseudopotential form factors cannot be neglected for ZnSe. It is interesting to note that the introduction of an explicit energy dependence[7] to lowest order, by using an effective mass, gives better agreement with experiment for the two peaks at the top of the valence band but leaves the antisymmetric gap almost unchanged. OPW calculations[8] for several II-VI compounds give band structures and density of states curves very similar to EPM results.

The 3d-states can be included in the EPM by using a non-local d-potential in addition to the usual pseudopotential form factors in the EPM calculation. Band structure calculations using the KKR method for hexagonal II-VI compounds have been carried out by Rössler,[9] who found d-states close in energy to valence bands for some of these compounds. We expect the KKR to give similar results for the II-VI zincblende structure.

This research illustrates the way in which XPS and band-structure calculations can be used together. The EPM calculations provided a framework within which to interpret the XPS spectra. The spectra in turn gave empirical valence-band energies with which to calibrate the EPM results. We are confident that further research combining the two methods will continue to provide valuable information about the electronic structure of crystalline and amorphous semiconductors.

We thank Prof. G. Somorjai for a single crystal of GaAs and Prof. Y. Pertroff for a single crystal of ZnSe. One of us (L.L.) greatly appreciates a grant from the Max-Kade Foundation.

FOOTNOTES AND REFERENCES

*Work performed under the auspices of the U. S. Atomic Energy Commission.

†In partial fulfillment of Ph.D.

††On leave from University of Bonn.

‡Supported in part by the National Science Foundation Grant GP 13632.

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Table I. Energies of characteristic features in the valence band spectra of Ge, GaAs, and ZnSe. The theoretical entries are taken from the density of states calculations after appropriate broadening

	Ge		GaAs		ZnSe	
	Expt.†	Theory††	Expt.†	Theory††	Expt.†	Theory††
X_4	2.4 eV	2.4 eV	2.4 eV	2.4 eV	3.0 eV	3.0 eV
W_2	3.6	3.5	3.9	3.4	--	--
V^*	4.9	4.5	5.1	4.6	5.2	4.6
L_1	7.2	7.0	6.8	6.5	6.3	5.3
W_1	8.6	8.6	8.9	--	--	--
L_2'	10.3	9.8	11.5	11.2	13.8	15.6
Γ_1	13.0	12.5	13.8	12.9	14.5	16.4

†Positions relative to gold Fermi level.

††The positions are normalized to the experimental values of X_4.

*The valley between W_2 and L_1 is arbitrarily called V.

FIGURE CAPTION

Fig. 1. XPS-spectra, band structures and densities of states for Ge, GaAs, and ZnSe. The top row I(E) shows the uncorrected experimental spectra. At the bottom the corresponding band structures E(k) and densities of states $\rho(E)$ as derived from EPM calculations are shown. The broadened theoretical densities of states $\rho'(E)$ in the second row facilitate comparison with experiment.

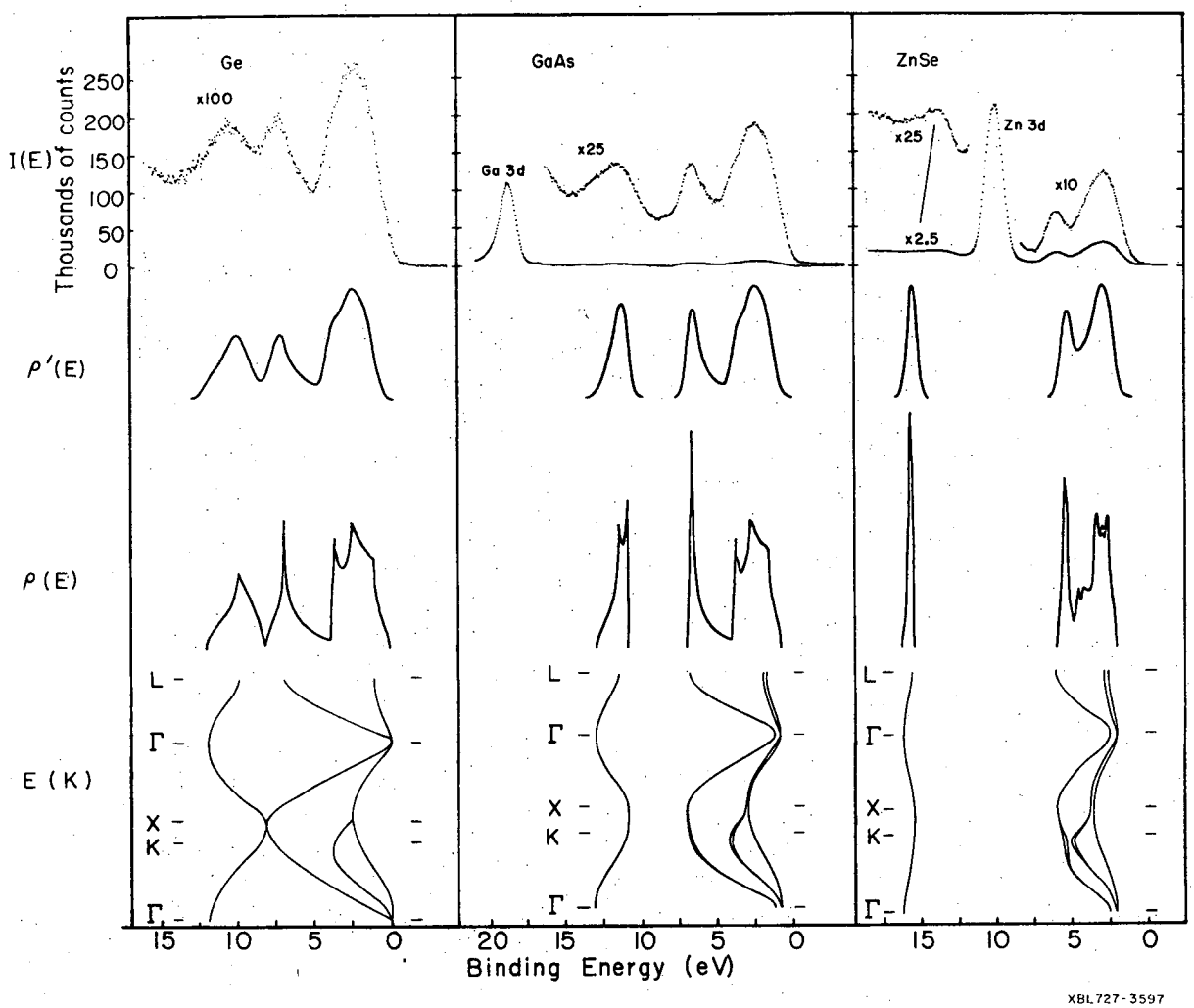
Ge
x100
GaAs
Ga 3d
x25
ZnSe
x25
Zn 3d
x10
x2.5
I(E) Thousands of counts
250
200
150
100
50
0
ρ'(E)
ρ(E)
E(K)
L
Γ
X
K
Γ
15
10
5
0
20
15
10
5
0
15
10
5
0
Binding Energy (eV)
XBL727-3597

Fig. 1

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