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Authors

Kowalczyk, S.P.

Ley, L.

McFeely, F.R.

et al.

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A HIGH-RESOLUTION X-RAY PHOTOEMISSION STUDY OF THE
TOTAL VALENCE-BAND DENSITIES OF STATES OF GaSe and BiI₃ *

S. P. Kowalczyk, L. Ley,^{†‡} F. R. McFeely, and D. A. Shirley

Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT: The total valence band density of states spectra for the semiconducting layered compounds GaSe and BiI₃ were obtained by x-ray photoemission spectroscopy. The results for GaSe were used to test recent band structure calculations and are compared with earlier photoemission results. The BiI₃ data are the first experimental determination of the total valence band density of states for this compound. Since no calculations exist for BiI₃, tentative assignments were made.

Layered compounds have been the subject of much experimental and theoretical activity because of their interesting anisotropic properties and possible application in switching and memory devices.¹ In this communication we report a high-resolution x-ray photoemission spectroscopy (XPS) investigation of the total valence band density of states (VB DOS) for the semiconducting layered compounds GaSe and BiI₃. It has been demonstrated previously that XPS can yield rather direct and detailed information on the total occupied density of states for semiconductors,² in particular allowing narrow limits to be placed on the positions of the valence bands.

The optical properties of both GaSe and BiI₃ have been studied previously, mainly near threshold.³⁻¹⁰ These measurements yield transition energies between the top of valence band and the bottom of the conduction band. Low-energy UPS data,^{11,12} as well as low-resolution XPS data¹³ are available for GaSe. To our knowledge, BiI₃ has not been studied experimentally by any total valence-band probe.

The XPS measurements were performed with a Hewlett-Packard HP-5950A electron spectrometer, which has been modified for ultra-high vacuum studies. Monochromatized AlK α x-rays (1486.6 eV) were employed as the excitation source. The total resolution of this system has been determined to be 0.55 eV from the broadening of the Fermi level of several metals.¹⁴ The samples were crystals, which were cleaved in a sample-introduction chamber filled with dry nitrogen. The samples were "cleaved" by the standard method for layer structures: removal of adhesive tape. The sample-

introduction chamber was then immediately evacuated, and within several minutes the freshly-cleaved surfaces were inserted into the main spectrometer chamber. These measurements were done at a relatively poor vacuum of 5×10^{-9} torr. The samples were analyzed *in situ* for contamination by scanning 20 eV regions around the oxygen and carbon 1s peaks and by taking a 1280 eV overall scan. For the samples from which the spectra reported here were obtained, no oxygen or carbon could be detected. The BiI₃ analysis indicated the presence of some reduced Bi. After the valence band and outer d-core regions were scanned (approximately 6 hrs accumulation time), another *in situ* analysis was performed on each sample to insure that no contamination had occurred.

Figure 1 shows our XPS spectrum, to be interpreted in terms of the VBDOS for GaSe. The energies of the characteristic features, along with pertinent UPS results, are given in Table I. Band-structure calculations have been carried out by Kamimura and Nakao¹⁵ (tight-binding, π bands only), Bassani and Parravicini¹⁶ (tight-binding, two-dimensional), denoted hereafter as BP, and Schlüter¹⁷ (empirical pseudopotential method, EPM, three-dimensional). Schlüter's EPM results possessed some qualitative similarities for the valence bands to the BP calculations. This is not surprising because of the weak interaction between the layers, the largely two-dimensional character of the charge density, and the fact that tight-binding calculations do fairly well for valence bands. A very useful feature of Schlüter's work is the calculation of charge densities, which gives insight to the origin of structure in the density of states and information about the bonding in GaSe. The EPM calculation puts the

lowest set of 4 bands in the 12.4 - 13.6 eV region relative to the top of the valence bands. Bassani and Parravicini obtained a somewhat wider distribution in the two lowest bands from 12.5 to 14.7 eV. (There are twice as many bands in the three-dimensional EPM calculation as in the two-dimensional structure used by BP.) These lowest bands correspond to selenium 4s nonbonding states. Our measurements yield a peak (G) of width 3.8 eV, centered at 14.15 eV. Thus both calculations give bands which are too flat, provided that the experimental width is equivalent to the true band width (i.e., ignoring relaxation broadening). It is well known that EPM calculations must include a non-local potential to obtain agreement with the lowest bands.^{19,20} Pure Se has a broad (~ 9 eV wide) 4s peak centered at ~ 13 eV.²¹ This peak falls at 11.6 eV in ZnSe,² 12.9 in PbSe,²² and 13.4 in ZrSe₂.²³

Next BP found two bands extending from 4.2 to 7.5 eV. The EPM calculation yielded two sets of two bands each, at 6.1 to 6.7 and 3.4 to 5.0, respectively, with a distinct gap between them. The XPS spectrum shows a peak (E) at 7.23 which extends from (D') 6.0 to (F) 8.99 eV. There is no evidence for a gap though peak E may in fact be two peaks, with a splitting of approximately 0.5 eV. These bands derive respectively from Ga-Ga bonding states (lower bands) and Ga-Ga anti-bonding plus some Ga-Se bonding states (higher bands).

Next BP have two sets of bands at the top of the valence band, one (consisting of 4 bands) from 2.5 to 3.8 eV and the other (consisting of one band) from 1.0 to 2.0 eV. For this region, the EPM calculations yield ten bands from 0 to 2.3 eV, with peaks at 0.8 and 2.1 eV. The XPS spectra show an intense peak (B) at 2.89 eV, a well-separated shoulder

(C) at 4.38 and a possible shoulder (A) at 1.56 eV. None of these features could be resolved in the earlier low resolution measurements.¹³ Feature C is presumably due in large measure to contributions to the VB DOS from 4 valence electrons involved in the Ga-Ga bond, mixed with some Se pz orbitals (π bands). There are 16 remaining electrons which, according to the EPM charge densities^{17,18} results, form GaSe bonds (σ bands). These contribute to features B and A. In summary, both the EPM and BP calculations show qualitative agreement with our XPS results but both still leave much to be desired. Part of the problem may be that the position of the atoms are not known very accurately and better agreement may be expected with improvement of atomic distances within the unit cell.²⁴ Also the EPM calculation may overestimate inter-layer coupling.

Table I shows qualitative agreement with the earlier XPS¹³ results, the present results allow structure in the top valence band to be resolved. This clears up some confusion which resulted from the low-energy UPS measurements. Earlier low-energy UPS^{11a,11b} attributed two peaks at 0.8 and 2.1 eV and separated by a gap to the density of states and concluded that it supported the BP calculations. More recent UPS work at higher (although still low) photon energies yield a somewhat different spectrum. These XPS results establish criteria that future calculations will have to meet.

One interesting result of the charge densities obtained by Schlüter^{17,18} is that, while they show GaSe to be covalently-bonded, there is an ionic component in the GaSe bond. An upper limit to the effective charge on Se of 0.4e was derived.^{17,18} Infrared measurements²⁵

have led to an estimate of 0.74e and x-ray absorption discontinuities²⁶ to 0.5e as the effective charge on Se. It would be interesting to apply the XPS scale of ionicity proposed by Kowalczyk *et al.*²⁷ to derive an ionicity for GaSe. The formulation of ref. 27, is not readily applicable to GaSe because of its anisotropic nature and the existence of Ga-Ga bonding states. Using a weighted average of the nearest-neighbor distances to derive the covalent splitting contribution,²⁷ an ionicity of $\sim .60$ was obtained for GaSe. This puts GaSe between the ionicities of GaAs and ZnSe as obtained by Kowalczyk *et al.*²⁷ This seems reasonable, considering that the electronegativity of Se is greater than that of As. However, before this approach can be applied with confidence to this class of compounds, measurements on more layered compounds must be made.

We turn briefly to BiI_3 , for which there exists to our knowledge, neither band-structure calculations nor any measurements of the total VB DOS (XPS, UPS, x-ray emission, etc.). Thus we shall simply describe our results and offer a preliminary interpretation.

Figure 2 shows the XPS valence band spectrum, which consists of a three peak structure and Table II lists the energies of the characteristic features. First there is a broad peak (D) centered at 12.1(3) eV. As in the case of GaSe, this should be the anion s-state. Iodine 5s states were observed in NaI at 11.21 eV and in KI at 10.82 eV.²⁸ An EPM calculation²⁹ for the layered compound PbI_2 yielded two very flat bands corresponding to nonbonding iodine 5s states at about 11.5 eV. The XPS spectrum next exhibits a gap (C - C') of about 3 eV. The top of the valence band is a broad doublet (A,B). Feature B is most likely derived from states possessing some bismuth "s-like" character, while feature A corresponds to I 5p levels. In NaI and KI, this feature occurs at 1.67

and 1.48 eV, respectively.²⁸ There is evidence of a slight shoulder A'. The A - A' separation is about 0.4 eV. It may be the origin of the 0.38 eV splitting in absorption measurements that has been attributed to transitions from spin-orbit split iodine 5p valence band to an $n = 1$ exciton level.⁸ As discussed for the alkali halides,²⁸ this uppermost band is probably dominated by band-structure effects rather than spin-orbit splitting. Absorption data for PbI_2 and BiI_3 are similar,⁹ which indicates that their upper most valence bands are similar. Thus the upper valence band we obtained for BiI_3 is very similar to the PbI_2 results of Ishii et al.³⁰ The EPM calculations for PbI_2 ²⁹ have several bands in the region 1.8 to 4.5 eV, which yield peaks at approximately 2.5 and 3.1 eV. There is also a gap and a narrow peak at 0.8 eV. The broad peak derives from anion p states with bonding between Pb and I. The uppermost narrow peak is a lead "s-like" state. Except for this upper most feature, the calculation is in qualitative agreement with our BiI_3 spectrum. Again, the calculated bands are too flat. One special problem in the PbI_2 case is that the calculations were done with no previous knowledge of the iodine form factors.²⁹ Using the XPS ionicity scale with an anion-size correction which proved necessary for the alkali halides,²⁷ an ionicity value of .68 is obtained, making BiI_3 more ionic than GaSe and just over the ionic side of the dividing line between "covalent" and "ionic" compounds.²⁷ As mentioned above, it is not clear whether this model is valid for these anisotropic compounds.

In conclusion we have used XPS to obtain the total valence band density of states spectrum for GaSe and BiI_3 and to test theoretical studies on layered materials. The calculations were shown to require further refinements if they are to reproduce the experimental results.

FOOTNOTES AND REFERENCES

* Work performed under the auspices of the U.S. Energy Research and Development Administration.

† Present address: Max Planck Institut für Festkörperforschung, Stuttgart, West Germany.

‡ IBM Fellow.

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FIGURE CAPTIONS

Fig. 1. Valence-band XPS spectrum of GaSe.

Fig. 2. Valence-band XPS spectrum of BiI_3 .

TABLE I. Comparison of energies (eV) of characteristic features in the valence band spectra from XPS, UPS, and EPM calculation for GaSe.

Feature	XPS ^a	UPS b c		XPS ^d	Theory ^e
A	1.56(10)	--	~ 1	--	(~ 0.5)
B	2.89(10)	3.0	2.2	2.5	0.8
C	4.38(10)	4.6	4.3	--	2.1
D	5.0 (3)	--	--	--	2.3
D'	6.0 (3)	--	--	--	~ 3.0
E	7.23(10)	6.8	7.2	7	6.4
F	9.0 (2)	8.5	--	--	6.7
G	14.15(15)	--	--	13	~ 13.0
H	16.0 (4)	--	--	--	13.6
Ga3d _{3/2,5/2} ^f	19.39(10)	--	--	18.7	--
Se 3d _{5/2} ^f	54.19(10)	--	--	--	--
Se 3d _{3/2} ^f	54.82(10)	--	--	54	--

^aThis work (Relative to the top of the valence band).

^bRef. 12,

^cRef. 12, HeI

^dRef. 13.

^eRef. 17.

^fThis peak exhibits characteristic energy losses at 7.2(3) and 16.0(2)eV.

TABLE II. Energies (eV) of characteristic features in the XPS valence band spectrum of BiI_3

Feature	Energy ^a
A	1.68(8)
A'	2.07(8)
B	3.97(14)
C	5.63(8)
C'	8.64(8)
D	12.11(30)
E	14.12(40)
Bi 5d _{5/2} ^b	24.99(8)
Bi 5d _{3/2} ^b	28.09(8)
I 4d _{5/2} ^b	48.43(8)
I 4d _{3/2} ^b	50.11(8)

^aThis work (Relative to the top of the valence band).

^bThis peak exhibits characteristic energy losses at 6.0(2) and 15.6(2)eV.

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Fig. 1

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Fig. 2

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