

Valence-band density of states and chemical bonding for several non-transition-metal layer compounds: SnSe_2 , PbI_2 , BiI_3 , and GaSe

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(Received 9 February 1976)

A theoretical description of the valence-band structure and chemical bonding for a series of non-transition-metal layer compounds is developed which is consistent with calculated charge densities, densities of states, and with the experimental crystal-structure data and photoemission measurements.

I. INTRODUCTION

In recent years, compounds crystallizing in layer structures have been the objects of many studies.¹ Even though the nature of the chemical bonding in these compounds has been investigated for some time,² quantitative results about the electronic structure of some of these compounds became available³⁻⁸ only recently. With the advent of ultraviolet (UPS) and x-ray (XPS) photoemission measurements of several layer compounds,⁹⁻¹² direct experimental information is now also available about the valence-band structure of these materials. It is therefore of interest to reopen the discussion concerning the chemical bonding in these materials, by comparing calculated densities of states based on the band-structure calculations of Refs. 3-8 with the experimental photoemission data. Simultaneously this comparison acts as a check on the quality of the empirical band-structure calculations.

II. DISCUSSION AND RESULTS

The following non-transition-metal layer compounds are studied: SnSe_2 , PbI_2 , BiI_3 , and GaSe . The compounds crystallize in layered structures in which the atoms are tightly bound in two-dimensionally extended sandwiches which are only several atomic layers thick. These sandwiches are stacked on top of each other and held together by relatively weak interactions. It is thus mainly the bonding and the atomic arrangement and coordination *within* the sandwiches which determines the valence-band structure of these compounds. Interlayer interactions may essentially be considered as perturbations on the isolated sandwich system. This is particularly true for mechanical properties which depend on the electronic screening of the entire ensemble of valence electrons. However this approximation may be poor for the detailed structure of individual electronic states. As an example one may cite the band structure of GaSe

in the vicinity of the (2 eV) fundamental gap; this gap is partly influenced by interlayer interactions of the order of 1 eV.³ Even though these interlayer interactions are generally weak, they can have considerable influence on the details of the optical¹³ and electrical¹⁴ properties. In the present discussion, however, only the strong covalent or ionic bonding inside the sandwiches shall be considered and be compared to the photoemission data which do not in general resolve interlayer effects.

The layer compounds to be discussed show different atomic arrangements within the sandwiches. In Fig. 1 perspective views of the different structures are given. SnSe_2 and PbI_2 , both crystallize in the same structure. The cations forming the middle layer are octahedrally surrounded by six anions, which form top and bottom layers of the sandwiches. Each anion is thus bound to three cations within the sandwich in addition to a weak bonding to the adjacent sandwich. In BiI_3 the cations are also octahedrally coordinated, but occupy only $\frac{2}{3}$ of their regular (PbI_2 -type) lattice sites. This creates cation voids and leaves the anions, which form the outer atomic layers, bound only to *two* cations within the sandwich. In GaSe the atomic arrangement is trigonal prismatic, rather than octahedral. In addition, the middle cation sheet is doubled. Thus each cation is bound to three anions and one other cation, whereas each anion is bound to three cations within the sandwiches. The peculiarity of this structure is the diatomic cation molecule with the "like-atom" bond in the middle of each sandwich, which has been found to determine the optical properties of the material^{13,8,13} and which also, as we shall see is directly reflected in the photoemission data.

The main structural characteristic of this group of compounds, the layer arrangement, results from the particular bonding properties of the constituents. We shall show that the structures are compatible with the types of chemical bonds that are formed and the degree of filling of the bond

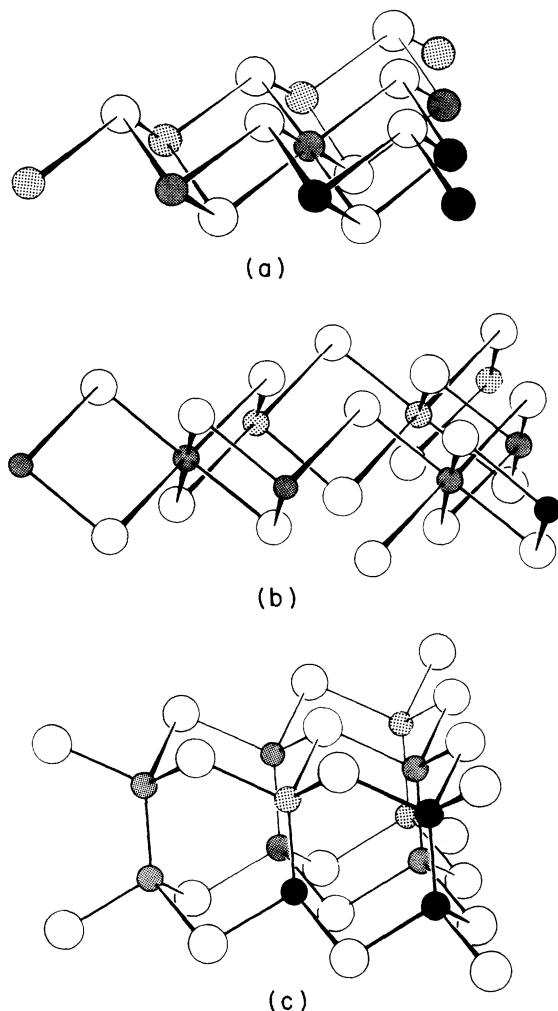


FIG. 1. Perspective view of the one-sandwich atomic arrangement of some layer compounds. (a) SnS_2 , SnSe_2 , PbI_2 , (b) BiI_3 , (c) GaSe .

orbitals by valence electrons. The four different compounds shall now be discussed separately in some detail.

A. SnSe_2

SnSe_2 and SnS_2 are semiconductors with the CdI_2 structure. With 16 electrons per unit cell the lowest eight bands are filled. According to the general principles of crystal chemistry, i.e., the filling of the anion valence shells, the eight occupied bands in SnSe_2 are expected to originate from anion s and p orbitals. This has essentially been confirmed by charge-density calculations based on the empirical pseudopotential (EPM) band-structure calculations of Ref. 4. Figure 2 shows a contour plot of the total valence charge of SnSe_2 as discussed in Ref. 7. It can be seen from this figure that most of the charge is located around the

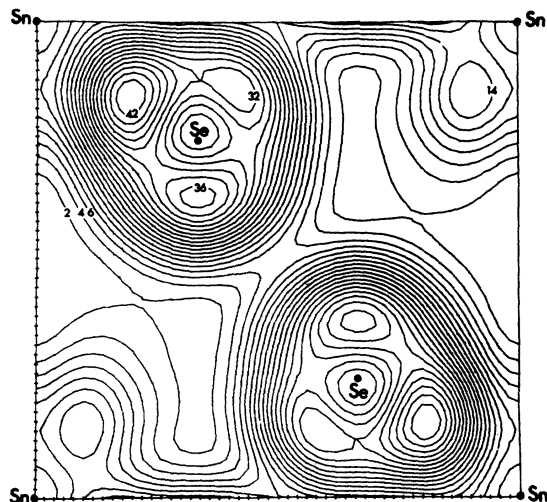


FIG. 2. Charge-density contour plot of the total valence charge of SnSe_2 displayed in a (110) plane extending over two half-layers and containing anion-cation bonds. The contours are given in units of electrons per unit cell (after Ref. 7).

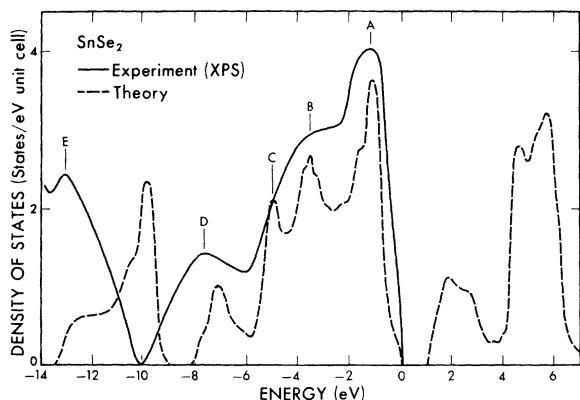
anion sites. A comparison of the experimental interatomic distance which is 2.57 Å for SnS_2 and 2.67 Å for SnSe_2 , respectively, with the sums of covalent or ionic radii² also favors an ionic picture (see Table I). The total charge in Fig. 2 is however not exactly centered around the atomic positions, thus indicating that the anion valence shell is not completely filled. In fact, total filling of the anion valence shells would ionize the tin atoms completely to Sn^{4+} which also is not consistent with Fig. 2. Moreover, photoemission studies¹⁰ combined with a calculated density-of-states curve, as presented in Fig. 3, indicate the presence of some filling of cation s states. A detailed analysis of the valence band density of states in Fig. 3 (broken curve) shows, that the upper three peaks, labelled A, B, and C correspond essentially to anion p states whereas the experimentally well-resolved structure around -8 eV (D) originates predominantly from cation s states. Some cation character, including d -like character is in fact found extended over the whole upper part of the spectrum. The low-lying peak, labelled E, theoretically extending from -14 to -9 eV corresponds mostly to anion s states with some slight p admixture. Experimentally, this peak has been observed at somewhat lower energy, but its position is somewhat unclear due to the excitation of Sn 4d electrons by the Al $K_{\alpha 3\alpha 4}$ satellite in the XPS experiment.¹⁰ The positions of the structure in the UPS or XPS data and the corresponding calculated densities of states are summarized in Table II. The favorable comparison between XPS data and

TABLE I. Lattice parameters and experimental bond lengths for various bonds. The sums of covalent and ionic radii and an estimated electronegativity difference are indicated.

a	c^a	Bond	$d_{\text{expt.}}$	d_{cov}^b	d_{ion}^b	Configuration	ΔX^b
3.64	5.87	Sn-S	2.57	2.43	2.55	(Sn ⁴⁺ , S ²⁻)	0.8
3.81	6.14	Sn-Se	2.67	2.57	2.69	(Sn ⁴⁺ , Se ²⁻)	0.7
4.56	6.98	Pb-I	3.15	2.80	3.36	(Pb ²⁺ , I ⁻)	0.9
7.50 ^c	6.90	Bi-I	3.04	2.79	$\sim 3.20^d$	(Bi ³⁺ , I ⁻)	$\sim 0.9^d$
3.76	7.97	Ga-Se	2.46	2.42	$\sim 2.85^e$	(Ga ²⁺ , Se ²⁻)	$\sim 0.9^e$
3.76	7.97	Ga-Ga	2.46	2.52	$\sim 1.94^e$	(Ga ²⁺ , Se ²⁻)	$\sim 0.9^e$

^a These c dimensions extend over one layer.^b From Ref. 2.^c The BiI₃ structure has a $\sqrt{3}$ times larger a dimension.^d These values have been obtained by interpolation.^e These values are obtained by assuming an ionic configuration which is certainly not present in GaSe (see text).

the calculated valence density of states helps to establish a picture of the nature of chemical bonding in SnSe₂. The asymmetry of the total charge around the anions (Fig. 2) and the strong charge buildup between neighboring atoms indicate covalent contribution to the bonding in SnSe₂. As already pointed out earlier^{2,7} the bonding of the octahedrally coordinated cations can be viewed as resonating sp^3d^2 -like bonds rather than p^3d^3 -like bonds. The bonding of the threefold coordinated anions is achieved by incomplete sp^3 hybridization with possibly some small d admixture. On the other hand, the ionic contribution to the bonding is significant, as indicated by the calculated charge distribution (the cation p states are mainly found as empty conduction states in the band-structure calculation) and as also suggested by the value of the sum of the ionic radii of cation and anion (Table I).

FIG. 3. Calculated density of states for SnSe₂, based on the EPM calculations of Ref. 4 and experimental photoemission data from Ref. 10.B. PbI₂

The electronegativity difference $\Delta X = 0.9$ between divalent Pb and I is appreciable and PbI₂ should therefore be considerably more ionic than SnSe₂. This general trend is confirmed by the calculated total valence charge density, displayed in Fig. 4. It can be seen that there is only a very small covalent charge buildup between neighboring Pb and I atoms, both of them being surrounded by nearly spherical charge clouds. Since iodine has seven valence electrons two p -like electrons are transferred from lead to the two iodine atoms. As indicated in Table I the experimental interatomic distance of 3.15 Å compares more favorably with the sum of the ionic radii of the configuration (Pb²⁺, I⁻) than to the sum of the covalent radii. The transfer of two electrons leaves the lead 6s states occupied and one would expect them to exist as nonbonding or lone-pair levels. This tendency of the heavier group-IV elements to maintain a nonbonding pair of s electrons has already been pointed out earlier by Mooser and Pearson.² The existence of occupied cation s states is well illustrated by the charge density plot of Fig. 4. It is of interest to determine the position in energy of these s -like states. An inspection of the calculated density-of-states curve of Fig. 5 and the corresponding charge distributions (as given in Ref. 7) shows the result that the lead 6s states combine to some extent with the valence orbitals of iodine to produce a pair of bonding-antibonding bands. The corresponding structures are located at -0.5 and -5.5 eV below the valence-band edge in the calculated density of states of Fig. 5. Since both bands are occupied their net effect on the cohesive energy of PbI₂ is negligible and in this sense these electrons can be viewed as nonbonding. This effect of hybridizing "nonbonding" states with orbitals of the other atom in a bonding and antibonding

TABLE II. Energy location of some main structure in the calculated density-of-states curves and the experimental XPS and UPS data.

Compound Structure	Expt. ^a	SnSe ₂ Theor. ^b	Nature	Expt. ^c	PbI ₂ Theor. ^d	Nature	Expt. ^e	BiI ₃ Theor. ^f	Nature	Expt. ^e	GaSe ⁱ Theor. ^g	Nature
A	-1.0	-1.0	} Se(<i>p</i>)	...	-0.5	Pb(<i>s</i>) + I(<i>sp</i> ³)	...	-0.5	Bi(<i>s</i>) + I(<i>sp</i> ³)	-0.8	-0.9	Ga-Ga(<i>p</i> _z)
B	-3.6	-3.6		-1.5	-2.5	} I(<i>p</i>)	-2.2	-2.4	} I(<i>p</i>)	-2.0	-1.9	} Se(<i>p</i>)
C	...	-5.0		-3.0	-3.5		-4.2	-4.0		-3.6	-2.9	
D	-7.7	-7.1	Sn(<i>s</i>)	-8.0	-5.5	Pb(<i>s</i>) + I(<i>sp</i> ³)	~-10.0	-7.5	Bi(<i>s</i>) + I(<i>sp</i> ³)	-5.6	-5.6	Ga-Ga(<i>s</i>)(<i>pb</i>)
E	-13.0 ^h	-12.6	Se(<i>s</i>)	-12.2	-11.5	I(<i>s</i>)	-12.2	-11.0	I(<i>s</i>)	-6.5	-6.5	Ga-Ga(<i>s</i>)(<i>b</i>)
F		-12.8	-12.1	Se(<i>s</i>)

^a Reference 10 (XPS, UPS).^b Reference 4.^c Reference 12 (XPS).^d Reference 5.^e Reference 9 (XPS).^f Reference 6.^g References 3 and 8.^h The Sn 4*d* states overlap due to the Al K_{α3}α₄ satellite in the XPS experiment of Ref. 10.ⁱ Theory and experiment are lined up to give best agreement for the valence bands. If the Ga 3*d* state emission (not shown) is shifted to -18.6 eV, [the value obtained for various other Ga compounds (GaP, GaAs, GaSb)] all experimental energies should be shifted by -0.6 eV.

fashion has also been found in the other iodine compound⁶ BiI₃ and for the cation pair in GaSe,^{3,7} but has *not* been obtained for Se or⁷ Te which also retain lone-pair electrons. The experimental XPS spectrum shown in Fig. 5, however, differs somewhat from the calculated curve in its quantitative aspects. In fact, this curve seems to favor the existence of nonbonding Pb *s* electrons at -8 eV (structure *D*) only without any of the aforementioned hybridization effects. This conclusion, however, may be misleading as the results on BiI₃ show (Fig. 7), where theoretically similar hybridization effects as in PbI₂ are found, coupled to a very *asymmetric* density of states, just as experimentally observed in PbI₂. Thus the quantitative disagreement between theory⁵ and experiment¹² for the energetic position of some bands in PbI₂ does not seem to rule out the calculated hybridization effects of the cation-*s*-lone-pair electrons. One reason for the occurrence of these effects may be the unusually large size of the ions in PbI₂ and BiI₃. In fact, as seen from Table I the sum of the respective ionic radii exceeds the actual interatomic distance by some (5-10)%, whereas in the tin-dichalcogenides the two distances nearly agree.

C. BiI₃

The structure of BiI₃ resembles that of PbI₂, with the exception that only $\frac{2}{3}$ of the cation sites are occupied. (See Fig. 1.) This still leaves the cations in an octahedral coordination, whereas the anions are only *twofold* coordinated. Filling of the anion valence shells can be achieved by the three *p* electrons of the cations. Similar to Pb²⁺ in PbI₂, Bi³⁺ in BiI₃ thus retains only its *s* electrons. The calculated,⁶ total charge density for BiI₃ is shown in Fig. 6. The contours are displayed in a (100) plane which contains an anion-cation bond. As compared to PbI₂ the charge distribution around the anions is less spherically symmetric, indicating the presence of more covalent character in the bonding. Inspecting the charge distributions one may place BiI₃ on an ionicity scale between SnS₂, SnSe₂, and PbI₂. The relationship between the experimental bond length and the sum of ionic radii on the other hand resembles strongly that of PbI₂ (Table I). As mentioned in the discussion of PbI₂, the 6*s* electrons of Bi³⁺ also combine with iodine orbitals to form a pair of bonding and antibonding bands which are both occupied. In Fig. 7, where the calculated density of states⁶ is compared to recent XPS results,⁹ the two hybridized *s*-like bands are labelled *A* and *D*. They are located in a rather asymmetric fashion with respect to the main peak of the anion *p* states thus showing some tendency towards the nonbonding arrangement. The

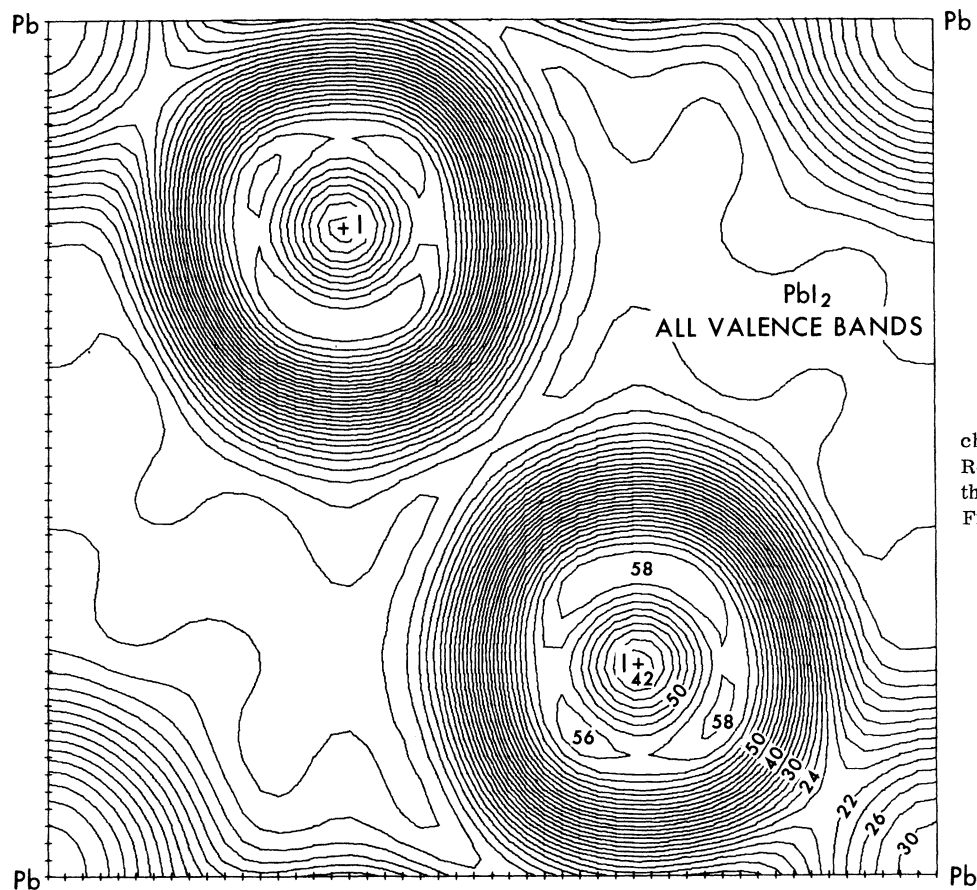


FIG. 4. Total valence charge density of PbI_2 from Ref. 7; characteristics of the plot are the same as in Fig. 2.

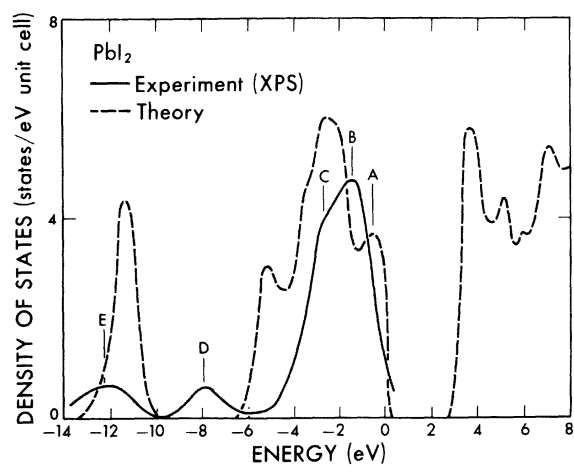


FIG. 5. Calculated density of states for PbI_2 based on the EPM calculation of Ref. 5 and experimental photoemission data from Ref. 12.

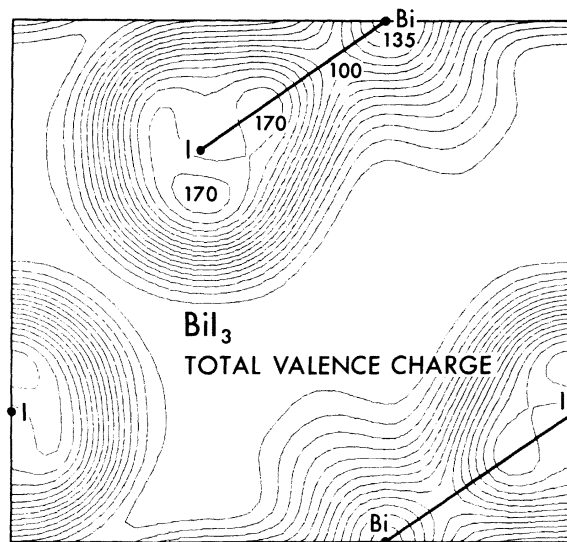


FIG. 6. Total valence charge density of BiI_3 from Ref. 6. The charge is displayed in a (100) plane of the BiI_3 structure, which corresponds to the usual (110) plane of the PbI_2 structure (Figs. 2 and 4).

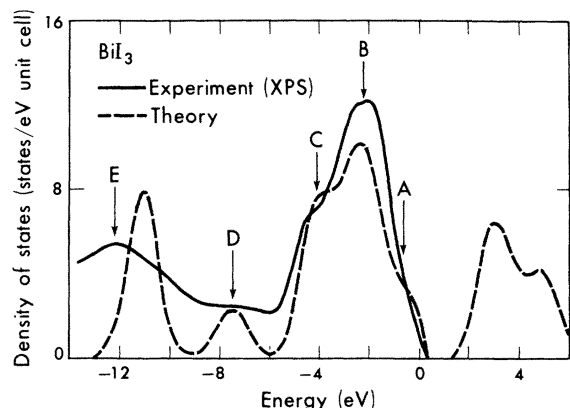


FIG. 7. Calculated density of states for BiI_3 , based on the EPM calculation of Ref. 6 and experimental photoemission data from Ref. 9.

agreement with experiment is only fair as in PbI_2 ; peak D and peak E merge in the experimental curve. Table II shows a quantitative comparison between the structure observed in XPS and calculated by EPM. In both iodine compounds (PbI_2 and BiI_3) the cation s states are found too high in energy in the calculations. The reasons for this behavior are not completely clear yet and further studies are necessary.

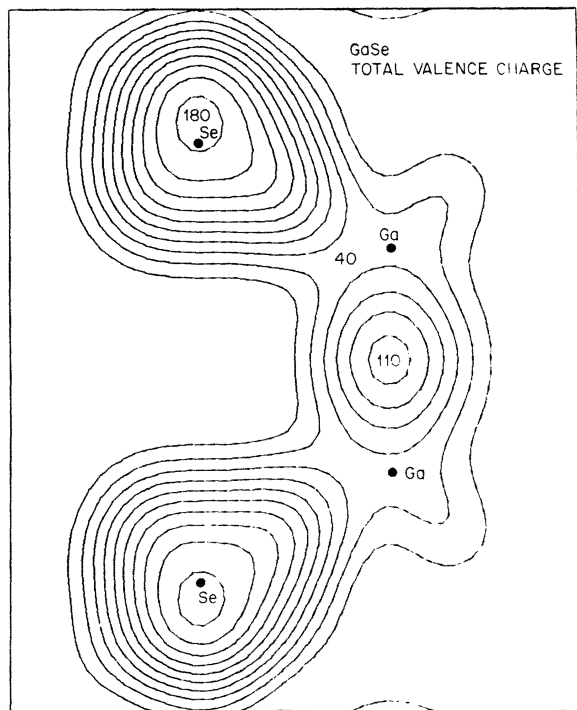


FIG. 8. Total valence charge density of GaSe from Refs. 7 and 8. The charge is displayed in a (110) plane extending over one layer and containing anion-cation as well as cation-cation bonds.

D. GaSe

The nature of chemical bonding in GaSe has already been discussed in great detail.^{3,7} The new information we present here is a highly resolved density-of-states calculation based on a slightly modified band-structure calculation of Ref. 3, which leads to good results for the optical properties of $\text{GaS}_x\text{Se}_{1-x}$ mixed crystals.⁸ The calculated density of states compares quite favorably with recent XPS measurements.⁹ It thus confirms the established view of the nature of chemical bonding in GaSe, which we shall briefly review here. Similar to PbI_2 and BiI_3 , in GaSe the cations possess more electrons than necessary for the saturation of the anion valencies. These excess electrons in GaSe also occupy an antibonding rather than a non-bonding band. The situation in GaSe, however, differs from the previous examples by the presence of a pair of neighboring cations in the middle of each sandwich (see Fig. 1). The corresponding covalent bond can be seen in the total valence charge distribution in Fig. 8 and has been found to be responsible for a large part of the optical and galvanomagnetic properties of GaSe.^{8,14} Figure 8 also shows the strongly asymmetric charge distribution around the anions, indicating the presence of covalent character in the anion-cation bond. In fact, a strong ionic configuration, like the straightforward ($\text{Ga}^{2+}, \text{Se}^{2-}$) configuration listed for comparison in Table I is very unlikely to exist, since the resulting $\text{Ga}^{2+}-\text{Ga}^{2+}$ Coulombic repulsion would not allow a stable structure with direct cation contacts. Another indication for the presence of more covalent and little ionic character in the cation-anion bond can be obtained from Table I. In fact, an imaginary ($\text{Ga}^{2+}, \text{Se}^{2-}$) configuration results in a sum of ionic radii, which is about 15% larger than the experimental bond length which on the other hand corresponds very well to the sum of covalent radii. From the total charge density an effective charge on the anion of about 0.4 electrons has been calculated.³ In Fig. 9 the calculated density of states is compared to XPS data. Due to the existence of two neighboring cations the spectrum shows more structure than the previous spectra of SnSe_2 , PbI_2 , or BiI_3 . The lowest peak (F) at about -12.1 eV corresponds as usual to the anion s states. They are obviously nonbonding and charge-density calculations⁷ show that the electrons occupying them behave like core electrons. The next higher structure between -8 and -5 eV can clearly be resolved into two peaks. The two peaks, labelled E and D correspond mainly to the cation s electrons. These states hybridize somewhat (by adding cation p_z character) and form a pair of bonding, antibonding bands of the Ga-Ga

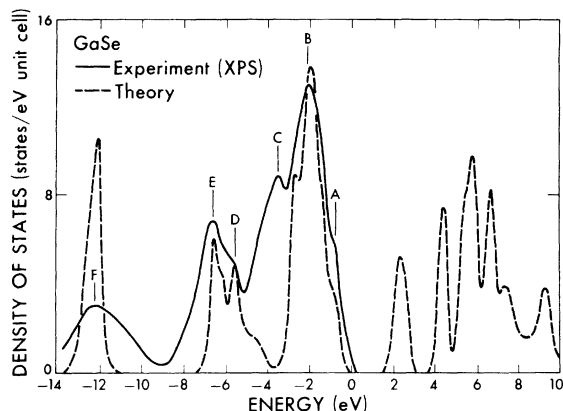


FIG. 9. Calculated density of states for GaSe, based on the EPM calculation of Ref. 8 and experimental photoemission data from Ref. 9.

bond in the middle of the sandwiches. Since both bands are occupied, their net effect on the cohesive energy of GaSe is negligible similar to the situation met in the iodine compounds. The separation of the two peaks *E* and *D* is very sensitive to the Ga-Ga bond length. Earlier bandstructure calculations³ and approximate density of states curves derived from them¹⁵ were based on a Ga-Ga bond length which was too small. This resulted in unsatisfactory agreement with photoemission results. The theoretical results presented in Fig. 9 are based on an assumed Ga-Ga distance of twice the covalent radius of Ga.⁸ Only recently, precise x-ray diffraction measurements¹⁶ were able to determine the Ga-Ga bond length to be 2.46 Å which is about 3% smaller than the sum of covalent radii and which corresponds almost exactly to the interatomic distance in Ga metal.

The next higher two peaks (*C*) and (*B*) in the XPS spectrum of GaSe correspond mainly to anion *p* states, with some cation *p* admixture. These states are responsible for the (mostly covalent) Ga-Se bond. About 0.7-eV disagreement is found for peak *C* between theory and experiment. The shoulder (*A*) corresponds to an-

other bonding band of the Ga-Ga bond involving mainly Ga *p_x* orbitals (with some *s* admixture). The corresponding antibonding band is unoccupied and gives rise to the isolated peak at +2 eV in the calculated density-of-states spectrum of the conduction bands. On the basis of these results one is therefore tempted to describe the total Ga-Ga interaction as the result of a superposition of σ_s bonding, σ_s^* antibonding, and σ_{p_z} bonding states. The paradox of this description illustrates the difficulties encountered by attempting to correlate the chemist's bond picture too narrowly to the physicist's band picture.

III. CONCLUSIONS

A consistent picture of the valence-electron structure and the chemical bonding has been developed for a series of non-transition-metal layer compounds: SnSe₂, PbI₂, BiI₃, and GaSe. Theoretical EPM band-structure calculations provide information like density-of-states curves and charge-density distribution plots for the valence electrons; whereas x-ray and ultraviolet-photoemission measurements and crystal-structure data provide the experimental input. With the exception of SnSe₂, the cations in all compounds possess excess electrons which do not contribute effectively to the bonding. It has been found, however, theoretically and experimentally, that these excess (cation) *s* electrons do not occupy simple lone-pair states, but rather hybridize to form antibonding bands. Combined with the corresponding bonding bands no net contribution to the cohesive energy of the crystals is produced by these hybridization effects.

ACKNOWLEDGMENTS

Part of this work was done under the auspices of the U. S. Energy Research and Development Administration. We thank Dr. G. Mason for communicating to us the PbI₂ photoemission results prior to publication.

[†] Work supported in part by the NSF grant No. DMR 72-03206-A02.

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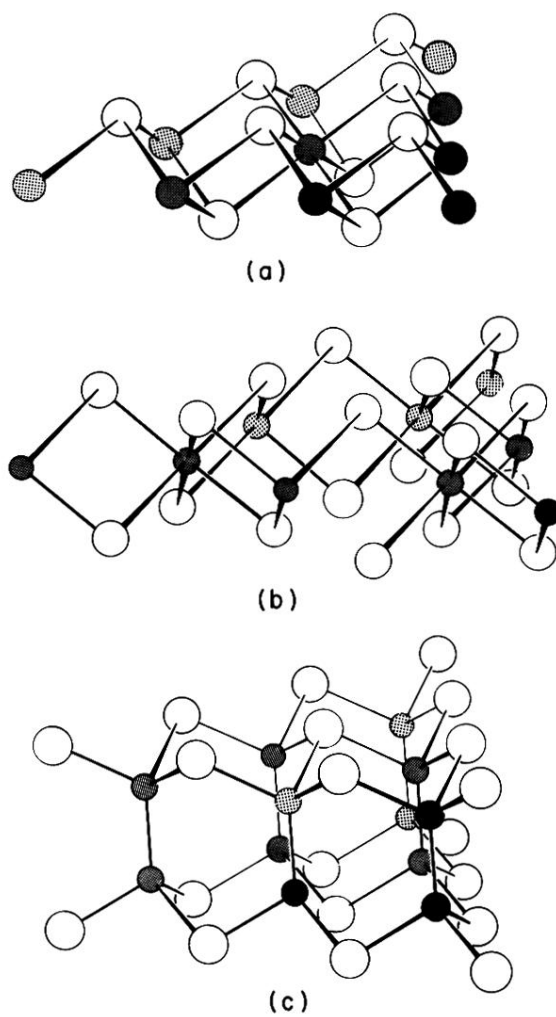


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