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X-ray photoemission spectroscopy of alkali-metal antimonide photocathodes: Valence-band spectra

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Na_2KSb, $Na_3Sb(Cs)$, $Na_2KSb(Cs)$, and Cs_3Sb photocathodes were prepared in ultrahigh vacuum and studied by x-ray photoemission spectroscopy. These measurements for the first time give sufficient experimental data on the entire valence band of these compounds for comparison with the spectra of related compounds. The spectra obtained show that alkali-metal antimonides are of the essentially-ionic-bond type, in agreement with chemical-shift measurements. The structure of the valence band evolves systematically with increasing ionicity and anion-anion distance. We perform a tight-binding calculation and give an interpretation of the experimental valence-band spectra. Previously published calculations are not in agreement with experimental spectra.

I. INTRODUCTION

The alkali-metal (Na, K, Rb, Cs) antimonide photocathodes have been extensively used in technological applications ever since their discovery in the 1950s. Alkali-metal antimonides form a class of solids whose particular properties are not very well understood. However, these simple compounds have the highest known photoemission sensitivities for visible light; only complex devices, such as negative-electron-affinity III-V photocathodes, can improve on their performance. (See Refs. 1–3 for a review.) Alkali-metal antimonide photocathodes are semiconductive polycrystalline films about 250–1000 Å thick. Many alkali-metal antimonides are known to exist. For example, Cs_3Sb_7, $CsSb_2$, CsSb, Cs_5Sb_4, Cs_5Sb_3, Cs_2Sb, Cs_5Sb_2, and Cs_3Sb have been identified in the Cs-Sb system.[4] However, if sufficient alkali metal is available, only the alkali-metal-saturated antimonides of the type $A_2A'Sb$ (A, A' different or the same alkali metal) are stable and these are the only ones present in high-sensitivity photocathodes, as shown by extensive investigations.[2,4–7]

The spectral photoemission response has proved to be extremely sensitive to composition and crystal structure, and of great help in characterization. Alkali-metal-saturated antimonides crystallize either in the Cu_3Al cubic DO_3 structure, such as Cs_3Sb, K_3Sb, K_2CsSb, Na_2KSb, or in the Na_3As hexagonal DO_{18} structure, for example K_3Sb, NaK_2Sb, Na_3Sb. These structures appear to be easily understood in terms of the Na^+, K^+, Cs^+, and Sb^{3-} ionic radii and typical ionic coordinations. These considerations also seem to explain why the Na_2CsSb phase does not exist.[2,8] Some researchers[9,10] who considered the crystal structures of alkali-metal antimonides, have however proposed models involving both ionic and covalent bonds. In cubic $A_2A'Sb$, $(A_2Sb)^-$ was assumed to form a tetrahedrally bonded covalent structure through the formation of shared-electron-pair bonds or sp^3 hybridized orbitals. This was suggested because of the similarity with the zinc-blende structure. The A'^+ cations were assumed to be in the octahedral holes of the $(A_2Sb)^-$ structure. However, the high ionic conduction of alkali-metal antimonides has been known since very early in experimental work on these photocathodes.[1,11,12] Also, the ionic character of other alkali-metal compounds, such as CsAu, is well known.[1,13] Kansky concluded from his thermodynamic studies[4] that alkali-metal antimonides were ionic compounds. Their heats of formation are about -2×10^5 J/mol.

Alkali-metal antimonides have band gaps varying from about 1 eV in Na_3Sb to about 1.6 eV in Cs_3Sb. They have been determined from the long-wavelength threshold of optical absorption and photoconductivity.[1] These small band gaps resemble those of some covalent semiconductors. The optical, electrical, and photoelectrical properties of the alkali-metal antimonides were consequently studied by means of covalent-semiconductor models. However, the nondirect character of the optical transitions in the alkali-metal antimonides, determined by ultraviolet photoemission spectroscopy (UPS) studies, has shown no conservation of the k crystal momentum, due to the strong localization of the valence-band hole.[14–16] Correspondingly, very small values of the hole mobility about 2 to 10 $cm^2/V\,s$, have been measured in these compounds.[17,18] The refractive index at low energies varies between 1.8 for Cs_3Sb and 2.2 for Na_2KSb.[1,3,19] The absorption constant is about 5×10^5 cm^{-1} at 3 eV.[1] The optical constants of K_3Sb, Na_3Sb, and Na_2KSb have also been determined.[19,20] The $\epsilon_2(w)$ curves of Na_3Sb and Na_2KSb strongly resemble those of Mg_2Si, Mg_2Ge, and Mg_2Sn (Ref. 21). These compounds have the antifluorite structure, very similar to that of cubic alkali-metal antimonides; their strong ionic character is well known.[22]

Alkali-metal antimonide photoemitters, Cs_3Sb, $Na_3Sb(Cs)$, Na_2KSb and $Na_2KSb(Cs)$, have been studied by x-ray photoelectron spectroscopy (XPS).[2,8,23] The results pertaining to the valence-band spectra are presented and discussed in the following sections. These spectra represent the first experimental data on the complete valence-band structure since only some information on the top bands of Cs_3Sb was obtained from previous UPS measurements[24] and no relevant information at all on $Na_2KSb(Cs)$ (Ref. 20). Determination of valence-band structure in those UPS studies was incomplete due to the low energy of the exciting radiation, and obscured by a large background due to inelastic electron scattering. The analysis of core-level binding energies and Auger electron energies in XPS (Refs. 2 and 23) by the localized-hole point-ion model, as it has been applied to other essentially ionic compounds,[13,25] made it possible to estimate a charge transfer of about 0.8 electrons from each alkali metal to the antimony. Also, extra-atomic relaxation energies due to electronic polarization about 2 eV ($\sim 50\%$) higher at the cation sites than at the anion site, showed both the strong localization of valence electrons at the anions and the high polarizability of these Sb^{3-} ions. The hypothesis of a predominantly ionic bond proved to be very successful in explaining and correlating many properties, among them crystal structure, relative stability, and nonstoichiometry, and their relation to photoelectronic properties and preparation processes.[2,8,23]

II. EXPERIMENT

The equipment and measurement techniques have been described previously.[2,23] The alkali-metal antimonide photoemitters Cs_3Sb, Na_2KSb, $Na_2KSb(Cs)$, and $Na_3Sb(Cs)$ were processed in ultraclean conditions over quartz substrates in a preparation chamber attached to the XPS spectrometer. The base pressure of this chamber was in the 10^{-10} torr range. The pressure in the spectrometer was in the 10^{-11} torr range and mostly of nonreactive gases. No oxygen or carbon contamination was ever detected. It must be stressed that the great chemical reactivity of alkali-metal antimonides imposes very rigorous requirements on the experimental apparatus and might have held up surface analysis research on these photocathodes.

The alkali-metal antimonide photoemitters were prepared by a coevaporation method[2,26] at relatively high temperatures under conditions as similar to the conventional commercial tube processing as practicable. This method produces reproducible films nearly at equilibrium and well characterized. The photoemitting surfaces were characterized by their spectral photoemission response and by quantitative XPS.[2,8] The samples studied here had high photoemission responses, comparable to commercial ones (S-20, etc.).

To avoid deterioration of the photoemission response the x-ray source had to be operated at low power. Consequently the low signal-to-noise ratio and the use of nonmonochromatic Al $K\alpha$ radiation caused problems in the study of the valence-band region. Only Cs_3Sb, the simplest alkali-metal antimonide to prepare, has been studied in a monochromatic spectrometer, ESCA HP5950A.[23] Furthermore, the spectra were recorded in the rate-meter mode, i.e., exponential or time-constant smoothing, on an X-Y recorder. Thus, in order to obtain spectra comparable to those of monochromatic spectrometers (a) spectra were accurately digitized, (b) five to fifteen runs were summed to obtain each spectrum, thus restoring part of the high-frequency noise and improving signal-to-noise ratio, and (c) the Al $K\alpha$ satellites were numerically deconvoluted. The resulting signal-to-noise ratio and the resolution are adequate for the physical interpretation to be discussed in this paper.

III. RESULTS AND DISCUSSION

In Fig. 1 we show general overviews of the valence band (VB) and outer-core levels of the alkali-metal antimonide photocathodes studied. Only that of Cs_3Sb, Fig. 1(b), was obtained with a monochromatic spectrometer. The Sb $4d_{3/2,5/2}$, Cs $5p_{1/2,3/2}$, and K $3p$ lines are clearly corelike with very little broadening apart from spin-orbit doublet and instrument resolution. The Na $2p$ line is just under the Sb $4d_{5/2}$ peak. The VB (Sb $5p$) appears to be quite flat and separated from the Sb $5s$ levels and the less-bound alkali-metal p levels at 10–30 eV below it. The Cs $5p$ levels are comparable to that in the Cs halides showing no interaction with the Sb levels. The atomic Cs $6s$, K $4s$, and Na $3s$ levels would be at 4 eV above the VB and should form the conduction band. It should be noticed that the intense narrow triangular VB (Sb $5p$) resembles that of strongly ionic solids. These spectra should be compared with those of alkali-metal iodides[27] on one hand and with those of Ga, In, and Al antimonides[28] on the other hand.

Further detailed analysis and comparison with published XPS VB's of related compounds would require better spectra. Numerically monochromatized spectra with improved signal-to-noise ratio revealed structure in the VB. From these monochromatized XPS spectra the XPS density of states (DOS) of the VB can be obtained, correcting for the background.[29] This was done assuming that any signal produces a typical background formed by extrinsic and intrinsic plasmon energy losses plus a smooth background (true secondary electron production, etc.).[30] The energies and magnitudes of these contributions were adjusted to the background at the low-kinetic-energy side of the Sb $4d$ peaks. The only physically significant assumption involved is that the energy loss processes for the VB region of the spectrum and for the core levels are the same.[28,30] Also, the Cs $5p_{1/2,3/2}$ peaks were substracted from the VB spectra. Accordingly, energies, line shapes, and relative intensities of Cs $5p_{1/2,3/2}$ and $4d_{3/2,5/2}$ were accurately measured for CsI. Thus from the Cs $4d$ peaks in the alkali-metal antimonide spectra we could calculate and substract the Cs $5p$ peaks.

The resulting XPS VB DOS spectra are shown in Fig. 2. The $Na_3Sb(Cs)$ is not really a photocathode. It was

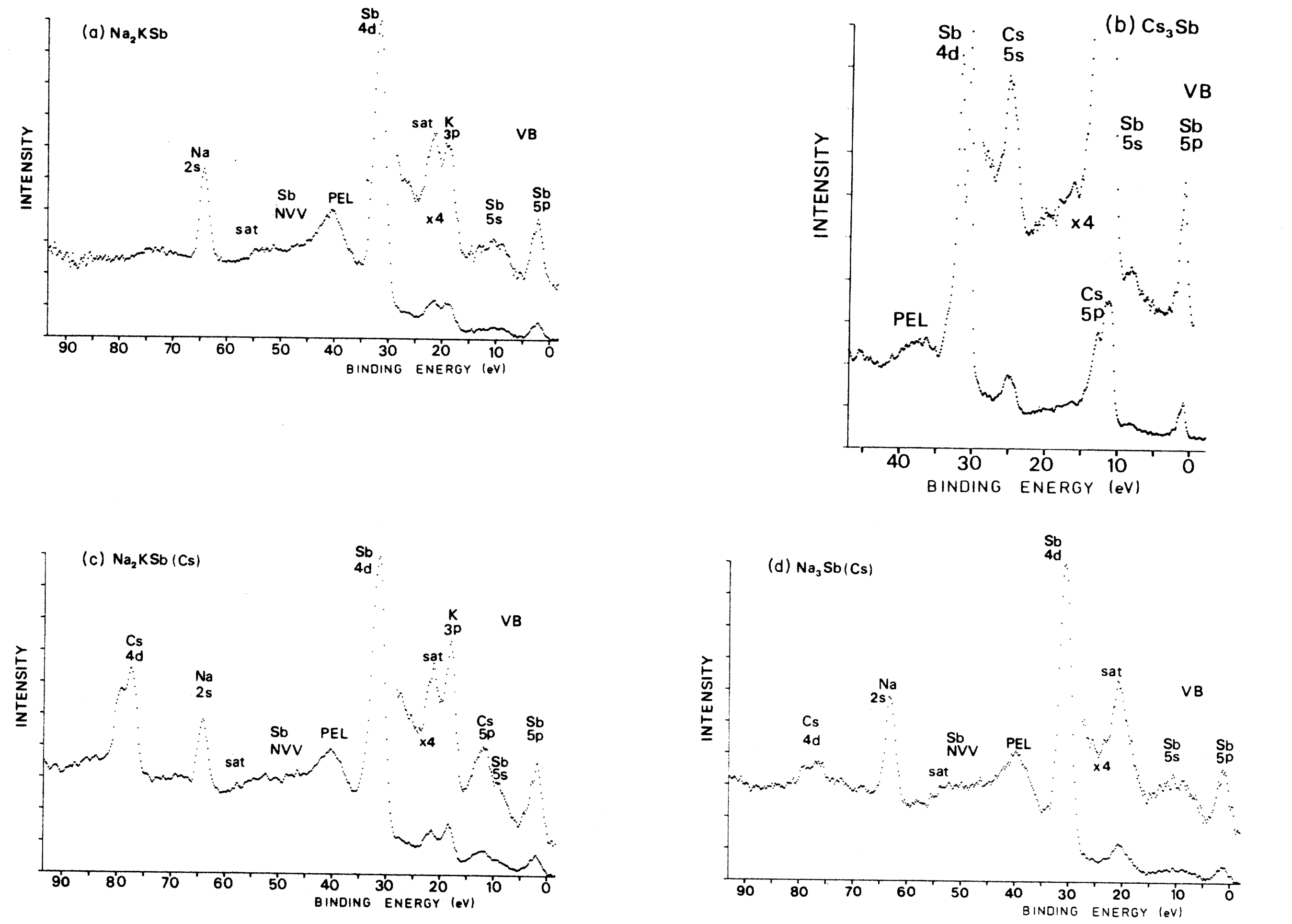

FIG. 1. Al $K\alpha$ XPS of (a) Na$_2$KSb, (b) Cs$_3$Sb, (c) Na$_2$KSb(Cs), (d) Na$_3$Sb(Cs) photocathodes. Only that of Cs$_3$Sb is monochromatic. sat: Al $K\alpha_{3,4}$ satellite. PEL: plasmon energy loss. *NVV*: Auger transition.

only prepared to investigate the unlikely existence of the compound Na$_2$CsSb. Quantitative XPS proved that this latter compound is not formed, but only Na$_3$Sb with a Cs surface monolayer.[2,8] Also Cs$_3$Sb and Na$_2$KSb photoemitters consist of the corresponding compounds in the bulk and an alkali-metal surface monolayer of Cs or K. In the case of Na$_2$KSb there is the possibility of NaK$_2$Sb formation at the surface as a consequence of excess K.[2,6–8] For the multialkali-metal Na$_2$KSb(Cs) or S-20 type photocathodes the situation is more complex. The bulk is Na$_2$KSb and three phases, Na$_2$KSb, NaK$_2$Sb and K$_2$CsSb, may coexist with a Cs surface monolayer.[2,6–8] The relative amounts of these phases in a more or less thick surface layer depend on the processing conditions. For the Na$_2$KSb(Cs) photocathode of Fig. 2(c), K$_2$CsSb and Na$_2$KSb appear to be present in a 20-Å-thick surface layer.

Therefore, we feel that the XPS VB DOS's of Figs. 2(a), 2(b), and 2(d) are representative of the Na$_2$KSb, Cs$_3$Sb, and Na$_3$Sb phases, respectively, since the contribution to the spectra of the alkali-metal surface monolayer should be practically negligible for the resolution and signal-to-noise ratio of these spectra. For the Na$_2$KSb(Cs) photocathode we expect the spectrum shown in Fig. 2(c) to be the overlapping of Na$_2$KSb and K$_2$CsSb ones, with a possible contribution of NaK$_2$Sb.

The structures distinguished in the VB's of Fig. 2 are labeled according to the corresponding ones in XPS VB's of other A_nB_{8-n} compounds.[27–29,31] As is general in these compounds, the main structure is formed by three bands, I, II, and III, expected to be due to p, $p(s)$, and s-like states, respectively. It is clear that the small banding and splitting ($\Delta E_p^{\mathrm{XPS}}$) of the p-like peaks (I,II) correspond to ionic compounds. One would expect correspondingly a narrow s-like peak (III) with a more or less clear ionic gap between peaks III and II. However, peak III appears to be a wide structured band extending close to the p-like bands. This type of band is quite different from that found in most A_nB_{8-n} compounds[27–29,31] but it is quite similar to that of Mg$_2$Sn, Mg$_2$Ge, and Mg$_2$Si (Ref. 22).

In Table I we show the energies of these structures of the VB of alkali-metal antimonides, together with other isoelectronic related compounds, antimonides, Zintl phases, and alkali-metal iodides. The decrease of the p splitting $\Delta E_p^{\mathrm{XPS}}$ together with the increase of the s split-

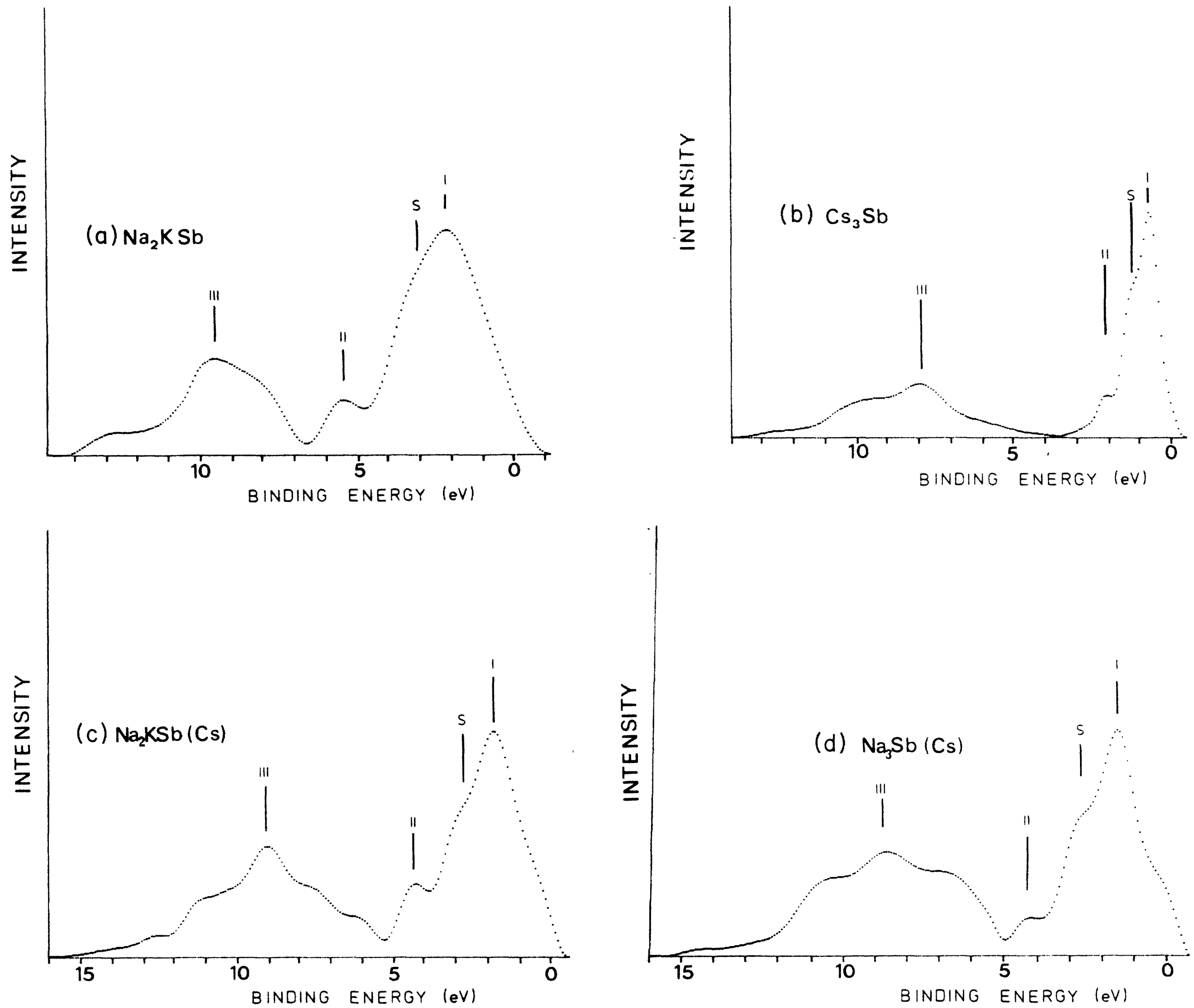

FIG. 2. XPS valence-band DOS of the following. (a) Na_2KSb; sensitivity 50 μA/lm; threshold, 1.9 eV; maximum yield, 16%. (b) Cs_3Sb; sensitivity, 30 μA/lm; threshold, 2 eV; maximum yield, 10%. (c) $Na_2KSb(Cs)$; sensitivity, 230 μA/lm; threshold, 1.4 eV; maximum yield, 30%; (d) $Na_3Sb(Cs)$; sensitivity, 10 μA/lm; threshold, 1.6 eV; maximum yield, 1.4%. For labels I, *S*, II, and III see text.

ting ΔE_s^{XPS} with increasing ionicity is clearly thrown. It should be pointed out that for Na_2KSb and $Na_2KSb(Cs)$ photocathodes the higher values (lower ionicity) correspond to higher sensitivity (μA/lm).

In Table I, the ionicities F_i^{XSP} calculated from XPS VB energies are also shown.[29,32] The covalent contribution to the *s* splitting ΔE_s^{XSP} is obtained from the nearest-neighbor distance following the empirical correlation found in covalent elements. It appears that this ionicity scale needs corrections to take into account both the anion size and the cation-anion coordination. The ionicity of alkali-metal antimonides could be overestimated due to the extremely large Sb^{3-} radius, 2.5 Å, and the high coordination number, 12. Nevertheless, a clear ionic character of these compounds can be inferred from Table I. For comparison with F_i^{XPS}, we also include ionicities F_i^{DT} based on the dielectric theory of Phillips and van Vechten.[33] Although this theory is developed for binary tetrahedrally-coordinated compounds, the calculated values follow the general trends of the XPS ionicity scale.

Band structure of some cubic alkali-metal antimonides (Na_2KSb, K_2CsSb, K_3Sb) has been calculated by the empirical pseudopotential methods.[34,35] These calculations clearly underestimate the bandwidth of the *s* and *p* levels and give too high binding energies for the anion *s* levels. This is similar to the case of alkali-metal halides.[27] The experimental spectra of Fig. 2 reveal strong banding effect due to anion-anion interactions that is not reproduced by these theoretical band structures. We have performed a tight-binding calculation in order to elucidate the magnitude and character of the anion-anion interactions as well as to give a more realistic band description of Cs_3Sb and Na_2KSb. We have

TABLE I. Valence-band energies and ionicities from XPS. Binding energies relative to the top of the valence band in units of eV. d is the nearest-neighbor distance. I,S,II,III, see Fig. 2. $\Delta E_p^{\mathrm{XPS}}=E_{\mathrm{II}}-E_{\mathrm{I}}$, $\Delta E_s^{\mathrm{XPS}}=E_{\mathrm{III}}-E_{\mathrm{I}}$, F_i^{XPS} is XPS ionicity and F_i^{DT} is dielectric theory ionicity.

	Structure	d (Å)	Binding energies I	S	II	III	$\Delta E_p^{\mathrm{XPS}}$	$\Delta E_s^{\mathrm{XPS}}$	F_i^{XPS}	F_i^{DT}
Sb[a]	A_7	2.87	2.2		8.8	10.5	6.6	1.68	0	0
GaSb[b]	Zinc blende	2.65	2.1	3.8	6.4	10.0	4.3	3.6	0.39	0.26
InSb[b]	Zinc blende	2.81	2.3	3.2	5.9	10.0	3.6	4.1	0.56	0.32
Mg_2Sn[c]	Antifluorite	2.93	1.37		4.08	8.12	2.71	4.08	0.61	0.56
Na_2KSb	DO_3	3.35	2.13	2.9	5.41	9.6	3.28	4.2	0.85	0.90
			1.94	2.46	5.03	9.1	3.09	4.1		
Na_3Sb(Cs)	DO_{18}	3.17	1.67	2.7	4.45	9.0	2.78	4.5	0.78	0.90
Na_2KSb(Cs)	d	d	1.80	2.65	4.30	9.0	2.50	4.7	d	
			1.49	2.25	3.79	8.2	2.30	4.4		
Cs_3Sb	DO_3	3.96	0.49	0.97	2.00	7.9	1.51	5.9	1	0.94
NaI[e]	Rock salt	3.24	1.67		3.15	11.21	1.48	8.1	0.89	0.93
KI[e]	Rock salt	3.53	1.48		2.56	10.82	1.08	8.3	0.97	0.95

[a] Reference 28.
[b] Reference 27.
[c] Reference 22.
[d] Phases of Na_2KSb, K_2CsSb, and NaK_2Sb possibly are present, see text.
[e] Reference 26.

chosen these compounds because they have the two extreme anion-anion distances and are most important compounds in alkali-metal antimonide photocathodes.

Both materials crystallize in the cubic DO_3 structure with four molecules per unit cell. The anion-cation coordination is of the ionic type. The anions form a fcc lattice and the cations are placed in a rock-salt (K) and antifluorite (Na_2) structure. A strong ionic character is expected in these compounds.

In order to obtain a good description of the valence-band structure we can consider these compounds as purely ionic, with the three electrons of the cations transferred to the Sb atoms. Thus a minimal basis set containing only 5s and 5p Sb orbitals has been used in our calculations.[36] An augmented basis set including the cation s functions was also considered, but did not give a significantly better agreement with the XPS spectra. Another reason for considering only anion-anion interactions is that the experimental splitting of the p-like bands ($\Delta E_p^{\mathrm{XPS}}$) decreases (3.19, and 2.78 eV) with the anion-anion distance (5.47 and 5.52 Å) and not with the anion-cation distance (3.35 and 3.17 Å) in Na_2KSb and Na_3Sb, respectively.

We have taken into account all possible nearest-neighbor anion-anion interactions. The difference between s- and p-orbital self-energies $E_p - E_s$ is fixed by the energy difference of s and p experimental peaks. The $ss\sigma$ interaction gives rise to the s band broadening and the $pp\sigma$ and $pp\pi$ interactions produce the banding of the p states. In order to avoid an excessive number of adjustable parameters we have fixed $pp\pi$ equal to $\frac{1}{8}$ of $pp\sigma$ interaction as has been found in other similar ionic compounds.[22,33] The importance of the $sp\sigma$ interaction in reproducing the band structure of Mg_2X (X=Si,Ge,Sn)

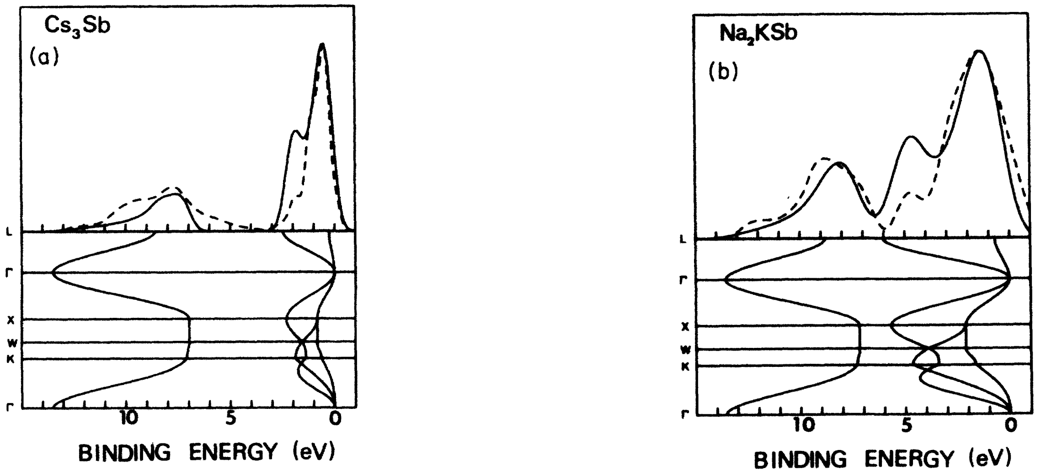

FIG. 3. Calculated valence-band structure (lower figure) and DOS (upper figure, solid line) compared with experimental XPS valence band (dashed line) for (a) Cs_3Sb and (b) Na_2KSb.

TABLE II. Best-fit interaction parameters (eV) for Cs_3Sb and Na_2KSb. Definitions similar to the those given in Ref. 35 have been used.

	Cs_3Sb	Na_2KSb
E_s	-9.1	-8.8
E_p	-1.5	-2.5
$ss\sigma$	-0.41	-0.40
$pp\sigma$	-0.33	-0.80
$pp\pi$	-0.04	-0.09

semiconductors has been pointed out.[22] The main effect of this interaction is to mix s- and p-like states. However, we have found that this interaction produces only very small variations in width and shape of the bands and does not reproduce the anomalous s bands observed in alkali-metal antimonides and Mg_2Sn, . . . , contrary to other investigators.[22] Since there is no experimental data to elucidate the magnitude of the s-p mixing, we have set $sp\sigma$ interaction to zero in our final parameters.

In order to compare with the XPS spectra we have calculated the corresponding electronic density of states. The Gilat-Raubenheimer method[37] has been used, with a sampling of 5950 points in the irreducible Brillouin zone. The results for Cs_3Sb and Na_2KSb are shown in Figs. 3(a) and 3(b). The overall shape of the XPS spectrum is well reproduced. However the experimental peak labeled S in Fig. 2 does not appear in our calculation. This feature has been assigned[38] to the spin-orbit splitting for Cs_3Sb, which has not been included in our calculations. However, Table I shows that this shoulder appears in all the antimonides and approximately follows the banding of the p levels, so it could be due to band structure. Our calculation does not reproduce the small relative intensity of peak II, even including $sp\sigma$ interaction. Probably different cross sections for states of peaks I and II must be taken into account. This apparent smaller cross section for peak-II states in heavier anions can be observed also in the series Mg_2Si, Mg_2Ge, and Mg_2Sn (Ref. 22); InP, InAs, and InSb; GaP, GaAs, and GaSb (Ref. 28).

Two main features can be observed in band structure. (i) The strong s and p banding effect due to high-energy anion-anion interactions. (ii) The top of the valence band is very flat, resulting in a k-independent photoemission. The p valence band shown in Fig. 3 is very similar to those obtained for Mg_2X (X=Si,Ge,Sn) (Ref. 22). This is in accordance with the great similitude of the experimental $\epsilon_2(w)$ spectra of these compounds.[19–21]

In Table II we show the best fit parameters for Cs_3Sb and Na_2KSb. It can be seen that, although the interaction parameters involving p states increase with smaller lattice constant a, they do not scale satisfactorily with $1/a^2$. This fact could be related to the different cation size and its effect on the crystalline potential. Strong deformation of the anion charge density should be expected due to the strong polarizability of the Sb^{3-} anion. On the other hand, $ss\sigma$ interaction is the same for both systems.

IV. CONCLUSIONS

The valence band of alkali-metal antimonides is formed by the $5p$ and $5s$ levels of Sb that appear clearly separated in XPS spectra. The p-level bands show structure that can be correctly interpreted by the tight-binding method with only anion-anion interactions, i.e., an essentially ionic model. The banding of the p levels due to anion-anion interaction increases greatly from Cs_3Sb to Na_2KSb, and is clearly related to the anion-anion distance. However, this banding does not scale satisfactorily with the inverse square of the lattice constant. On the other hand, the s-level band appears very broad and with structure that cannot be properly explained by this tight-binding model. Also, the expected ionic gap between s and p levels does not appear, the s-band tail extending close to the p bands. The shape and width of the s band does not vary with lattice constant. This is similar to the valence bands observed in Mg_2Sn, Mg_2Ge, . . . , compounds with definite ionic character and related crystal structure.

Another result of our calculation is that the experimental shape of the s band can be explained neither in the alkali-metal antimonides nor in the Mg_2X compounds (X=Si,Ge,Sn) contrary to previous evidence. Thus there appears to be no satisfactory explanation for this type of s band.

The contribution of the alkali-metal levels to the valence band seems negligible, since the less bound alkali-metal p levels appear in XPS very well separated from the VB and clearly corelike. Also we have found that the inclusion of the cation s levels into the calculation does not improve the agreement between the calculated and experimental DOS. This apparent lack of admixture of alkali-metal levels into the valence band would require the transfer of almost one electron from each alkali metal to Sb, in agreement with chemical-shift measurements, thus showing the essentially ionic type of chemical bond in the alkali-metal antimonides. This should be expected from their crystal structure and cation-anion electronegativity difference.

We have found that alkali-metal antimonides show a broad range of ionicities. From this point of view the most efficient alkali-metal antimonide photocathode, S-20, is formed by the less ionic antimonide in the bulk and the most ionic ones at the surface. This structure is thus somehow similar to that of the III-V negative-electron-affinity photocathodes.

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