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X-Ray Photoelectron Emission Studies of Mixed Selenides $AgGaSe_2$ and Ag_9GaSe_6

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Auger and direct electron specta from crystalline $AgGaSe_2$ and Ag_9GaSe_6 have been studied with X-ray photoelectron spectroscopy. It is shown that the $AgM_5N_{4,5}N_{4,5}$ and $M_4N_{4,5}N_{4,5}$ Auger spectra are more sensitive to the chemical environment than the Ag 3*d* direct photoelectron spectra. Furthermore the Auger parameter as defined by Wagner is used in order to characterize the chemical state of these compounds. Last, the *XPS* spectra of the valence-band region are investigated and chalcogen *s* and *p* and noble-metal *d* bands are clearly identified. The electronic structure of these two selenides does not seem to be determined predominantly by the crystal structure. As a whole, the spectral features are discussed in connection with the character of the chemical bonding and the physical properties of these compounds.

Introduction

Ternary semiconducting compounds of I_B–III–VI_2 type are of promising technological interest, in view of their potential for optoelectronic and nonlinear optical devices (*1*, *2*). $AgGaSe_2$ belongs to this large family. Its crystal structure is that of the tetragonal chalcopyrite lattice in which each Ag or Ga atom occupies a slightly distorted tetrahedral site of Se anions and each Se is coordinated by two Ag and two Ga atoms. As shown recently from electroreflectance and adsorption edge studies the electronic energy-band structure of such compounds exhibits some anomalies with respect to that of their isoelectronic II–IV binary analogs (*3*–*5*). Such changes include downshifts of the energy gaps and reduction of the spin–orbit splittings. More or less strong hybridization of the anion *p* orbitals with the noble-metal *d* orbitals is believed to be responsible for these changes. In order to obtain direct information on the electronic states of $AgGaSe_2$, X-ray-induced photoelectron studies have been performed. Measurements concern both core levels and the valence band. In addition, *XPS* data are also reported for Ag_9GaSe_6, which is a new compound in the Ag–Ga–Se system (*6*). Last, spectra from pure Ag and Ga elements have been recorded for the purpose of comparison.

Experimental

The ternary selenides are prepared by a direct combination of high-purity elements. The stoichiometric mixtures are sealed in evacuated quartz tubes, melted at high tem-

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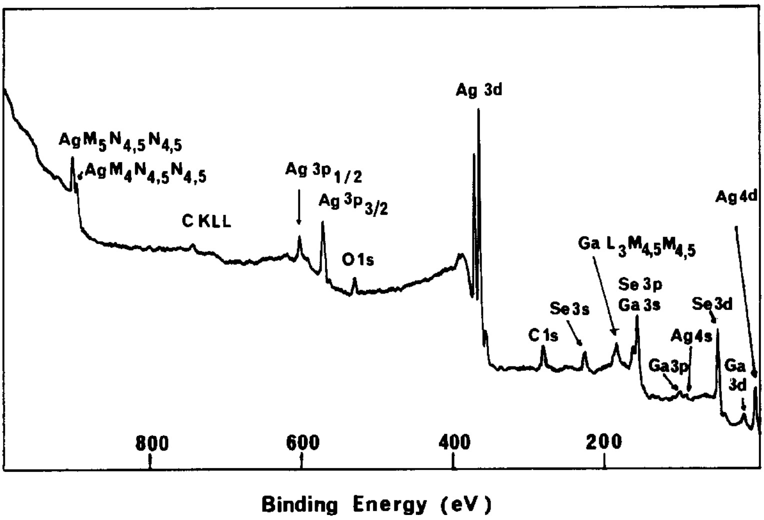

FIG. 1. Wide-scan *XPS* spectrum for Ag_9GaSe_6.

perature (900–1000°C) and cooled progressively. The selenides are characterized by powder X-ray diffraction (Cu$K\alpha$ radiation; Guinier–Nonius Camera).

All photoelectron measurements were made on a Vacuum Generators ESCA 3 spectrometer using the nonmonochromatized Mg$K\alpha$ (1253.6 eV) X radiation as the photon source. The gold-decorated technique (Au $4f_{7/2}$ at 84.0 eV) is used for calibration and binding energies are given with respect to the Fermi level. Selenides are ground and mounted onto the sample rod as compressed pellets. Just prior to their insertion into the spectrometer their surfaces are mechanically scratched. This procedure is shown to be efficient for removing quite significantly the surface contamination of the compounds investigated here. As seen from the wide-scan electron spectrum of Ag_9GaSe_6 (Fig. 1) only small 1*s* signals of oxygen and carbon may be observed. However, by taking into account the low known O 2*p*/O 1*s* and C 2*p*/C 1*s* ratios the contribution of the adsorbed oxygenated and

TABLE I

CORE AND VALENCE ORBITALS OF Ag, Ga, AND Se IN PURE ELEMENTS AND MIXED SELENIDES $AgGaSe_2$ AND Ag_9GaSe_6[a]

Orbital	Ag	Ga	$AgGaSe_2$	Ag_9GaSe_6
Ag $4d_{3/2,5/2}$	5.0		5.8	5.4
Ag $3d_{5/2}$	368.4		368.4	368.2
Ag $3p_{3/2}$	573.0		573.95	573.4
Ga $3d_{3/2,5/2}$		18.9	20.1	18.9
Ga $3p_{3/2}$		104.3	105.5	104.8
Ga $2p_{3/2}$		1117.1	1118.7	1117.7
Se 3*d*			54.7	54.6

[a] Binding energies are given in electronvolts with respect to the Fermi level.

carbonaceous contaminants to the valence-band structure is estimated to be negligible in this work.

Results and Discussion

Table I lists the binding energies of various core and valence orbitals. The shifts of the Ag and Ga inner levels provide evidence of a redistribution of electrons between the corresponding atoms and the Se atoms. Noticeable chemical shifts are seen except for the Ag $3d_{5/2}$ level. Ag $3p_{3/2}$ and Ga core levels are shifted toward higher binding energies as compared with pure metals. These results point to a drift of electron density from both the Ag and Ga atoms to Se atoms. However, gallium exhibits shifts significantly larger than those measured for silver, an observation which has similarly been noted for $AgGaS_2$ (*7*). It is noteworthy that it is contrary to what could be expected only from ionicity considerations. For instance, in $AgGaSe_2$ the fractional ionicities f_i of the individual bonds Ga–Se and Ag–Se are equal to 0.561 and 0.852, respectively (*8*). The explanation seems rather to be due to the particular *XPS* behavior of the silver compounds with respect to the pure metal (see below) while data concerning silver oxide, sulfide, and selenide are between them in excellent agreement with the ionicity scale (*9*, *10*). A further noteworthy point is that the Ag $3d_{5/2}$ photolines are found to be unshifted for $AgGaSe_2$ and slightly shifted toward lower energies (−0.2 eV) for Ag_9GaSe_6 relative to pure metal. Actually this unusual trend is not surprising in so far as negative chemical shifts have been reported previously for the binary silver chalcogenides Ag_2S and Ag_2Se (*9*, *10*) and more generally for some copper and silver compounds (*11*, *12*). As the Ag Auger shifts are frequently larger than photoelectron shifts (*11*, *12*) the $AgM_5N_{4,5}N_{4,5}$ and $M_4N_{4,5}N_{4,5}$ Auger spectra are also reported (Fig. 2). With respect to pure Ag, −0.7- and −1.4-eV negative chemical shifts in kinetic energies are determined for Ag_9GaSe_6 and $AgGaSe_2$, respectively. By using the Auger parameter defined by Wagner (*13*) the chemical shifts of this parameter are then −0.9 and −1.4 eV, respectively. On the basis that differences in the Auger parameter are only explainable by changes in polarization of the media (*14*), and in view of other results dealing with Ag_2O, Ag_2S, and Ag_2Se (*9*, *10*), it seems plausible that a higher degree of delocalization of the Ag 4*d* electrons exists in Ag_9GaSe_6 relative to $AgGaSe_2$. At the room temperature in which these experiments are performed, a quasi-metallic behavior of Ag_9GaSe_6 could be possible.

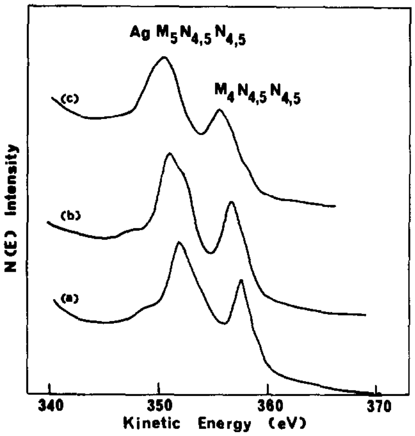

FIG. 2. Auger spectra of (a) Ag, (b) $AgGaSe_2$, (c) Ag_9GaSe_6.

The spin–orbit components Ag $3d_{5/2}$ and Ag $3d_{3/2}$ from the mixed selenides show quite symmetric peaks with low full-width at half-maximum: 1.4 eV for Ag_9GaSe_6 and 1.6 eV for $AgGaSe_2$, while the corresponding value for silver metal is 1.4 eV. In addition, the spin–orbit splitting Ag $3d_{3/2}$–Ag $3d_{5/2}$ is equal to 6.0 eV in both Ag and the selenides. These spectral features are characteristic of diamagnetic Ag(I) compounds. Indeed the 3*d* photolines of paramagnetic silver(II) species are markedly broader, the corresponding effects being partly related to multiplet-splitting processes. These experimental data again support a noticeable degree of delocalization of the valence Ag 4*d* electrons

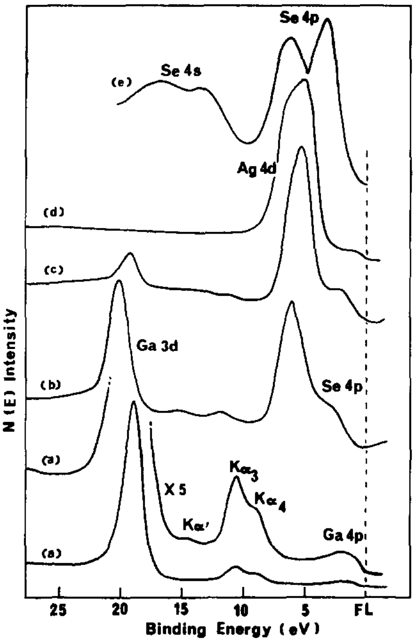

FIG. 3. *XPS* spectra in the valence band region of (a) Ga, (b) $AgGaSe_2$, (c) Ag_9GaSe_6, (d) Ag, (e) Se. This latter spectrum for amorphous Se is taken from Shevchik *et al.* (*15*).

in the two mixed selenides. It also seems likely that Ag_9GaSe_6 contains only one kind of Ag site.

Figure 3 exhibits the valence-band structures of the mixed selenides. The corresponding spectral features of Ag and Ga are shown for comparison. In addition the raw X-ray ($h\nu = 1486.6$ eV) photoemission curve for the amorphous form of selenium is given. This spectrum is taken from Schevchik *et al.*'s investigation (*15*). The peak centered around 13 eV below the top of the valence band may be associated primarily with the Se 4*s* states while the peaks at 5 and 2 eV are associated with the bonding *p* band and the lone-pair orbitals, respectively. Now let us again consider $AgGaSe_2$ and Ag_9GaSe_6. The most striking result is the great similarity of their spectra in so far as intensities are not taken into account. In each case the main feature located 5 eV or so below the top of the valence band arises from the noble-metal 4*d* orbitals. In both $AgGaSe_2$ and Ag_9GaSe_6 the uppermost valence bands are derived from a combination of the 4*p* orbitals of selenium with the Ag 4*d* and Ga 4*p* orbitals.

First, it is noteworthy that the Ga 3*d* peak intensity ratio for $AgGaSe_2$ and Ag_9GaSe_6 agrees well with the Ga content ratio. Furthermore, it is gratifying to see that in going from $AgGaSe_2$ to Ag_9GaSe_6 the Ag 4*d*/Ga 3*d* intensity ratio varies to a first approximation, as does the Ag/Ga atomic ratio. Although the intensity of the Ag 4*d* type of band partly depends on the degree to which it mixes with the Se 4*p* states, these observations lend much support to the confidence we have concerning the samples under study.

We turn next to the valence-band structures. Regarding $AgGaSe_2$ at least, the tetrahedral crystal field of the chalcopyrite lattice splits the fivefold degenerate *d* levels into a threefold Γ_{15} and a twofold Γ_{12} level. Moreover the spin–orbit coupling splits both the *d*-like Γ_{15} and the *p*-like Γ_{15} states. The uppermost valence band of this compound is dominated by these latter states. Let us note, however, that the aforementioned splittings are too small (0.2–0.3 eV) to be shown with these X-ray photoelectron measurements.

In $AgGaSe_2$ the separation between *d*- and *p*-like bands is about 3.1 eV. This value is larger than that (2.3 eV) reported by Luciano and Vesely (*7*) for the analog sulfide $AgGaS_2$. This implies a smaller *p*–*d* admixture in $AgGaSe_2$. This should be supported by electroreflectance measurements (*16*), which indicate a fractional *d*-like character of the uppermost valence bands equal to 16 and 20% for $AgGaSe_2$ and $AgGaS_2$, respectively. In addition, these results pertaining to $AgGaSe_2$ confirm that the *p*–*d* hybridization is less significant in Ag than in Cu compounds (*7*, *8*, *17*–*19*), as one would expect from the binding energies of the Cu 3*d* and Ag 4*d* levels in the pure elements.

The shape of the density of states of Ag_9GaSe_6 appears very similar to that of $AgGaSe_2$ previously described. This could be explained by the absence of drastic changes in the local order of atomic arrangements. Unfortunately, suitable cristallographic data concerning Ag_9GaSe_6 are not currently available. Moreover, it seems more plausible that the electronic structure of these two selenides is not determined predominantly by the crystal structure. Indeed, strong analogies are seen between the density of states of these ternary compounds and those of the binary silver oxide and chalcogenides Ag_2O, Ag_2S, and Ag_2Se (*9*, *10*).

$AgGaSe_2$ has a photoemission threshold approximately 0.7 eV below the Fermi energy. As this compound exhibits a direct gap of 1.8eV, the energy of the top of the valence band is less than the magnitude of this gap. This suggests that the Fermi level is located in the middle of the forbidden gap and confirms the semiconducting character of $AgGaSe_2$. Conversely the valence-band spectrum of Ag_9GaSe_6 shows that its photoemission threshold coincides with the Fermi energy within the limits of experimental error (<0.2 eV). Given that the Se $4p$ band is expected to have some metal character, these photoemission investigations are unable to predict whether Ag_9GaSe_6 is a semimetallic, a narrow-gap intrinsic semiconducting, or a p-type semiconducting material. In addition it should be noted that the overall width of the valence band in Ag_9GaSe_6 is about 0.2 eV wider than that of $AgGaSe_2$. This slight broadening also supports a moderate increase of the covalent character of the bonding in progressing from $AgGaSe_2$ to Ag_9GaSe_6.

Last, let us note that the excitation of the Ga $3d$ core levels is observed at 20.1 and 18.9 eV below the Fermi level for $AgGaSe_2$ and Ag_9GaSe_6, respectively. Additional structures occur at lower binding energies. The relevant peaks must first be attributed to the excitation of the Ga $3d$ levels by the Mg $K\alpha_{3,4}$ satellites. The energies of these peaks are 8.5 and 10.1 eV less than that of the Ga $3d$ photoline. These satellite structures as seen from the Ga valence-band spectrum are well illustrated for compounds with a high Ga content. This latter spectrum also emphasizes the presence of another structure at 5 eV below the energy of the Ga $3d$ peak. This corresponds to the excitation of the Ga $3d$ levels by the Mg$K\alpha'$ satellites. Great care must be then taken in assigning subbands in the valence-band region whether sufficiently intense photolines are stimulated by unmonochromatized Mg or Al$K\alpha$ radiations. Under such conditions the precise location of the chalcogen s band in Ga compounds may be quite inaccurate. For instance, the photoemission spectrum of $AgGaS_2$ (*7*) includes an S $3s$-like band at a binding energy which corresponds approximately to the location of the Ga $3d$ (α_3) satellites. In the same way, a photoline of GaSe (*20*) around 13 eV below the top of the valence band is interpreted as arising from the excitation of the Se $4s$ electrons. In our opinion this peak is partly attributable to the $K\alpha'$ satellite from the Ga $3d$ inner levels. This would contribute to the observed broadening of the Se $4s$ band. In view of these remarks, the Se $4s$ band in $AgGaSe_2$ should be located around 15 eV below the Fermi level. For practical purposes let us note, however, that the Ga $3d$ (α', α_3, α_4) spectral contribution may be subtracted from the apparent valence-band envelope by considering the influence of these satellites near the intense Ga $2p_{3/2}$ core levels (*21*).

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