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Electronic-structure and local-order study of Ge_xSe_{1-x} glasses

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X-ray photoelectron spectroscopy (XPS) and tight-binding calculations are used to study the electronic structure and the local order in Ge_xSe_{1-x} glasses ($0<x<0.42$). The shape of the valence electronic density of states in Ge-Se compounds is discussed in terms of (4:2)- or (3:3)-coordinated local structures and Ge—Se, Ge—Ge, and Se—Se bonds. It is shown that Ge 4*s* and Se 4*s* band shapes are very sensitive to the presence of Ge—Ge and Se—Se bonds, respectively. Se-rich glasses ($x<0.33$) can be described with 4:2 coordination and Ge—Se and Se—Se bonds whereas Ge-rich glasses ($x>0.33$) can be described with 4:2 and 3:3 coordinations and Ge—Se bonds.

I. INTRODUCTION

A great deal of experimental effort has been expended these last ten years to determine the nature of bonding in chalcogenide network glasses and in amorphous thin films such as Ge_xS_{1-x}, Ge_xSe_{1-x}, and Ge_xTe_{1-x}.[1–3] The Ge-Se system[4,5] is very attractive since it allows the formation of bulk glasses in a wide composition range ($0<x<0.42$) by quenching from the melt. For higher Ge concentrations, only amorphous thin films can be prepared by vapor quenching.

The short-range order of Ge_xSe_{1-x} glasses was studied using x-ray-diffraction measurements,[6] infrared and Raman spectroscopies,[4,7] and Mössbauer spectroscopy,[8] but there is still considerable controversy, especially for Ge-rich glasses ($x>0.33$). For $x<0.33$ there is some agreement on a model in which fourfold-coordinated Ge and twofold-coordinated Se form a random network with heteropolar Ge—Se bonds favored. In such a model no Ge—Ge bond exists and Se chains connect Ge tetrahedra. For Ge-rich glasses and amorphous films it is not clear whether the local structure is 4(Ge):2(Se) coordinated as in bulk $GeSe_2$ or 3(Ge):3(Se) coordinated as in crystalline GeSe.

It is now well established that valence and core electronic states measured by photoelectron spectroscopy can characterize the local atomic order in noncrystalline systems.[2] In ionic oxides like silicon oxides, large oxygen-induced core-level shifts exist. It is possible to distinguish fourfold-coordinated silicon atoms bonded to one, two three, and four oxygen atoms, respectively, in SiO_x films[9] and at the SiO_2-Si interface.[10] Ge_xSe_{1-x} glasses are much more covalent, which leads to much smaller chemical shifts, and core-level spectroscopy cannot be used in local-order studies. Valence-band spectra reflect the energy distribution of electronic states, which is a function of the local atomic order. Modifications in local order are thus associated to variations in shape and intensities of structures in photoemission spectra. This was already observed for amorphous Si, Ge, GaAs,[2] and glassy SiO_2,[11] when compared to crystalline materials. To distinguish between various structural models, photoemission spectra are usually compared to spectra of well-known compounds and to theoretical densities of states (DOS's) established for specific structural models.

Concerning noncrystalline chalcogenide compounds, valence-band spectra have already been used in the past to give some insight into the local order of Ge_xTe_{1-x} amorphous alloys[12] and of amorphous GeSe (Ref. 13) and GeTe (Ref. 14) films. Looking at amorphous GeTe, Schevchik *et al.*[14] found a peak at the top of the valence *p* band, which was not observed in crystalline (3:3)-coordinated GeTe; it was attributed to lone-pair orbitals of twofold-coordinated Te atoms. The data were used to suggest the presence of 4:2 coordination in amorphous GeTe. On the other hand, Robertson and O'Reilly[15] performed electronic-structure calculations on model (3:3)- and (4:2)-coordinated networks for amorphous GeSe and GeTe. They found that the valence *s* bands in the densities of states are very sensitive to changes in local order, particularly to the presence of homopolar bonds.

With this in mind, we have measured, using x-ray-photoelectron spectroscopy (XPS), the valence-band spectra of a series of Ge_xSe_{1-x} glasses in the composition range $0<x<0.42$. The data are compared to those of well-known standard compounds Se, Ge, GeSe, $GeSe_2$, GeS, and GeS_2. In order to examine the role of Ge—Ge bonds on the density of states of Ge_xSe_{1-x} compounds, we have calculated density of states for hypothetical (4:2)-coordinated Ge_xSe_{1-x} alloys with $0.33 \le x \le 1$. The results allowed us to discuss the local order in Ge-rich Ge_xSe_{1-x} glasses.

The compounds of the Ge-Se system and the experimental techniques are presented in Sec. II. The theoretical approach is described in Sec. III. Results are presented and discussed in Sec. IV.

II. EXPERIMENT

A. Ge-Se compounds

Details of preparation and characterization of Ge_xSe_{1-x} glasses are given in Refs. 4 and 5. The phase diagram of the Ge-Se system was discussed in Refs. 1, 4, and 5.

Bulk Ge_xSe_{1-x} glasses were obtained in the composition range $0<x<0.42$. They were prepared by cooling the quartz cell containing the homogenized liquid of proper composition at a suitable rate.

Crystalline Se, Ge, GeSe, and $GeSe_2$ were examined. The germanium monoselenide GeSe crystallizes in a distorted NaCl-type structure characterized by double layers normal to the c axis. Each selenide has three Ge neighbors and vice versa; the Ge—Se bond distance is equal to 2.56–2.59 Å. $GeSe_2$ has a layered structure with distorted $GeSe_4$ tetrahedra sharing common corners. This leads to a 4:2 coordination with an average Ge—Se distance of 2.36 Å. The layers are separated by 2.3 Å. Trigonal Se consists of helical chains which spiral around the axis parallel to the crystalline c axis. The Se—Se bond distance is equal to 2.32 Å.

Two polycrystalline Ge_xSe_{1-x} alloys were also measured; a sample with $x=0.42$ was prepared in a same way as $x=0.41$ glasses, but was not found to be amorphous. X-ray-diffraction studies indicated that it was made of GeSe crystallites probably embedded in a glassy matrix. A glass sample with $x=0.41$ was crystallized by annealing in air at 450 °C. X-ray-diffraction measurements showed that it was mostly made up of GeSe and $GeSe_2$ crystallites.

B. Experimental procedures

The XPS spectra were obtained with a Hewlett-Packard HP5950A photoelectron spectrometer which uses monochromatized Al $K\alpha$ radiation (1486.6 eV). The overall energy resolution was estimated to be ~ 0.7 eV. As we are interested in bulk properties, it is very important to prepare a clean surface in such way that the composition at the vicinity of the surface, in the first 50 Å probed by XPS, is representative of the bulk composition. We tried many surface-preparation procedures: ion sputtering, filing under vacuum, fracture under vacuum, and filing under a nitrogen flow. Ion sputtering induces chemical modifications and is not suitable for this kind of compound. The other procedures give similar results. We found that the easiest way to prepare the samples was to file them under a nitrogen flow. This method reduced surface contaminants (oxygen and carbon) to levels at which they do not noticeably affect the XPS valence-band structures.

We used Ge:Se atomic ratios, estimated from both $3p$ and $3d$ Ge and Se core-level intensities, to check the atomic composition in the surface region. It was always found to be very close to the bulk nominal composition.

As we studied metastable compounds, we checked for some possible irradiation effects. In fact, we did not detect any modification in spectra, as a function of the irradiation time, for most of the samples. Only Se and high-x Ge_xSe_{1-x} glasses showed some slight modifications after a few hours of irradiation. In the case of these last samples, we stopped measurements before modifications in spectra were significant. Most of the samples were insulators and exhibited charging effects in spectra. Charging was detected and compensated for by flooding low-energy electrons onto the sample. As we are mostly interested in the shape of valence-band spectra, we did not try to use a procedure to determine absolute binding energy referred to the Fermi level. The measured energies are referred to the top of the valence band.

III. THEORY

In this section we present theoretical calculations concerning the influence of eventual Ge—Ge bonds on the shape of the valence band. We proceed in two steps, first using an analytical model, then performing a more refined numerical treatment.

Let us discuss the analytical model. We consider the general situation where each Ge atom has n Se and $4-n$ Ge nearest neighbors. We use a nearest-neighbor tight-binding Hamiltonian with parameters derived from Ref. 22 and take Ge—Se—Ge angles equal to 90°. With such a configuration we can build on each Ge atom four sp^3 hybrids pointing towards its Ge or Se neighbors. On each twofold-coordinated Se we build two p_σ orbitals pointing towards the Ge neighbors and one perpendicular p_z lone-pair orbital (the "s" Se orbital, being lower in energy, is not considered here). From the sp^3 and p_σ orbitals engaged in the same bond, we build molecular bonding states of energies $E_{\text{Ge-Ge}}$ and $E_{\text{Ge-Se}}$ for Ge—Ge and Ge—Se bonds, respectively. We also allow broadening of these molecular bonding states into bands by incorporating the interactions between bonding states having a Ge atom in common. We call these $\Delta_{\text{Ge-Ge}}$ between two Ge—Ge bonds, $\Delta_{\text{Ge-Se}}$ between one Ge—Ge and one Ge—Se bond, and $\Delta_{\text{Se-Se}}$ between two Se—Se bonds. While this model is relatively crude, it incorporates the essential physical aspects in the simplest possible way.

We now write the wave function ψ as

$$\psi=\sum_{i,j}a_{ij}\varphi_{ij}+\sum_{i,\alpha}a_{i\alpha}\varphi_{i\alpha}\ , \tag{1}$$

where the φ are the bonding orbitals and where the Latin and Greek indices, respectively, correspond to Ge and Se atoms.

Introducing the quantities

$$S_i=\sum_{j}a_{ij}\ , \tag{2}$$

we can write the equations

$$(E - E_{\text{Ge-Ge}} + 2\Delta_{\text{Ge-Ge}})a_{ij} = \Delta_{\text{Ge-Ge}}(S_i + S_j) + \Delta_{\text{Ge-Se}}\left[\sum_{\alpha} a_{i\alpha} + \sum_{\beta} a_{j\beta}\right] , \quad (3a)$$

$$(E - E_{\text{Ge-Se}} + \Delta_{\text{Se-Se}})a_{i\alpha} = \Delta_{\text{Se-Se}} \sum_{\beta} a_{i\beta} + \Delta_{\text{Ge-Se}} S_i . \quad (3b)$$

We sum over α in (3b) to get

$$[E - E_{\text{Ge-Se}} - (n-1)\Delta_{\text{Se-Se}}] \sum_{\alpha} a_{i\alpha} = n\Delta_{\text{Ge-Se}} S_i , \quad (4)$$

and inject it into (3a) to obtain

$$(E - E_{\text{Ge-Ge}} + 2\Delta_{\text{Ge-Ge}})a_{ij} = \left[\Delta_{\text{Ge-Ge}} + \frac{n\Delta^2_{\text{Ge-Se}}}{E - E_{\text{Ge-Se}} - (n-1)\Delta_{\text{Se-Se}}}\right](S_i + S_j) . \quad (5)$$

If we sum Eq. (5) over j, we get a relation between S_i and the sum $\sum_j S_j$ over the nearest neighbors. As usual, this is analogous to an "s"-band tight-binding problem on the same Ge sublattice. If we call ε the eigenvalues of this problem (i.e., $\varepsilon S_i = \sum_j S_j$), we can write

$$(E - E_{\text{Ge-Ge}} + 2\Delta_{\text{Ge-Ge}}) = \left[\Delta_{\text{Ge-Ge}} + \frac{n\Delta^2_{\text{Ge-Se}}}{E - E_{\text{Ge-Se}} - (n-1)\Delta_{\text{Se-Se}}}\right](4 - n + \varepsilon) . \quad (6)$$

We also know that, for $n = 0,1,2$, we have $-(4-n) \le \varepsilon \le 4-n$, the other cases being more trivial: $n = 4$ is $GeSe_2$, $n = 0$ pure Ge, and $n = 3$ corresponds to diatomic Ge-Se units (we discuss this case later). The solutions of Eq. (6) lead to two broadbands, with $S_i \neq 0$, i.e., having "s"-like character. In addition, there are "p"-like solutions corresponding to $S_i = 0$ and leading to flat bands in our model. The first one is obtained from Eq. (5),

$$E = E_{\text{Ge-Ge}} - 2\Delta_{\text{Ge-Ge}} , \quad (7)$$

and the second one from (3b) as

$$E = E_{\text{Ge-Se}} - \Delta_{\text{Se-Se}} . \quad (8)$$

The corresponding results are schematically pictured in Fig. 1. They have been obtained from the parameters given in Ref. 16. They clearly show that, for Ge_xSe_{1-x} systems, there is a trend for a broadening of the "s"-like bonding band as x increases (from a δ function in $GeSe_2$ to a unique broadband in pure Ge).

The case $x = 0.4$ corresponding to $n = 3$ deserves special consideration since it is close to the upper experimental value of x, i.e., 0.413. In this case the system behaves as a collection of $Ge_2Se_{6/2}$ molecules. From the six Ge—Se bonds one can build four "p"-like combinations of energy equal to (8). One can also build one symmetrical combination on each Ge atom. Their difference is an eigenstate of energy equal to

$$E = E_{\text{Ge-Se}} + 2\Delta_{\text{Se-Se}} , \quad (9)$$

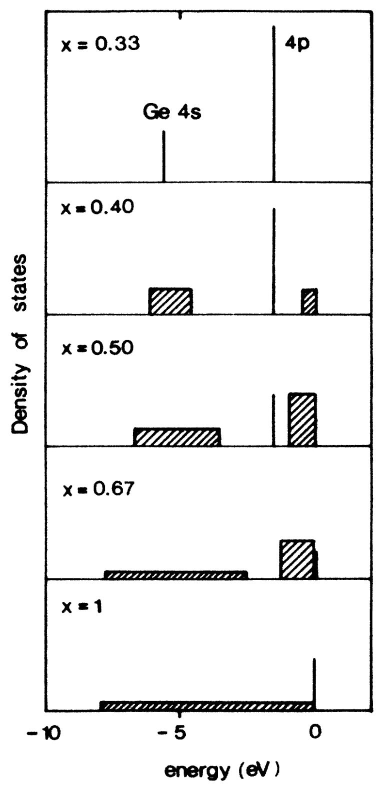

FIG. 1. Schematic band diagrams for Ge_xSe_{1-x} alloys showing the broadening of the "s" bonding states as x increases.

and their sum is coupled to the Ge—Ge bonding state. The solutions of the corresponding 2×2 matrix are

$$E = \frac{E_{\text{Ge-Ge}} + E_{\text{Ge-Se}} + 2\Delta_{\text{Se-Se}}}{2} \pm \left[\left[\frac{E_{\text{Ge-Se}} + 2\Delta_{\text{Se-Se}} - E_{\text{Ge-Ge}}}{2}\right]^2 + 6\Delta^2_{\text{Ge-Se}}\right]^{1/2} . \quad (10)$$

It is easy to show that the energy given by (9) is $|\Delta_{\text{Se-Se}}|$ above the "s"-like state of $GeSe_2$, with $|\Delta_{\text{Se-Se}}|$ of the order of 1 eV. One can prove that the lower state given by (10) is always lower than (9) and this by 1–2 eV for reasonable values of the parameters. This means that when going from $x = 0.33$ to 0.40, the "s"-like state of $GeSe_2$ tends to split into two components. This broadening effect should be observable and still increases at higher values of x.

As discussed above, this model is oversimplified. Inclusion of further interactions broadens the "s" and "p" molecular state into bands. This is also true for $x = 0.4$. However, for the reasons given above the width of the "s"-like bonding band should be significantly larger for $x = 0.4$ than for $x = 0.33$. This is confirmed by the numerical calculations in a more sophisticated tight-binding description using a cluster-Bethe-lattice approach. This method was already applied to SiO_2 (Refs. 17–19) and SiO_x (Ref. 20) systems.

TABLE I. Linear combination of atomic orbitals parameters (in eV) for both Ge-Ge and Ge-Se interactions in Ge_xSe_{1-x} alloys.

	E_s	E_p	β_{ss}	$\beta_{s\sigma}$	$\beta_{\sigma s}$	$\beta_{\sigma\sigma}$
Ge atom	−4.875	1.625				
Se atom	−10.875	−0.075				
Ge—Ge bond			−1.76	2.47	2.47	2.30
Ge—Se bond			−1.75	2.63	2.63	2.60

Briefly, the Green's-function method is applied to a small cluster (a $Ge\text{-}Ge_ySe_{4-y}$ tetrahedron) embedded in an effective medium. Only the cluster is treated exactly. The effective medium is treated as a Bethe lattice of the correct composition. In order to describe any composition, we used a mean-field approximation in which an approximate Bethe lattice is constructed on known probabilities and coordinations. We essentially used this method to predict densities of states for hypothetical (4:2)-coordinated Ge_xSe_{1-x} compounds with $0.33 < x < 1$. These systems can be described by tetrahedra of the form $Ge\text{-}Ge_ySe_{4-y}$ embedded in an effective medium where only Ge—Se and Ge—Ge bonds exist. We use a nearest-neighbor tight-binding Hamiltonian based on one *s* and three *p* orbitals for Ge and Se. We take Ge-Se-Ge angles equal to 110°. To obtain realistic densities of states, it was necessary, as shown previously,[17–19] to introduce first-neighbor overlap integrals for Ge—Se bonds.

According to the notation of Slater and Koster, five independent interaction parameters, β_{ss}, $\beta_{s\sigma}$, $\beta_{\sigma s}$, $\beta_{\sigma\sigma}$, and $\beta_{\pi\pi}$, and two orbital energy parameters, E_s and E_p, are defined. $\beta_{\pi\pi}$ is much smaller than the other four interaction parameters and can be neglected. It was shown that such an approach gives satisfactory results to describe the band structure of SiO_2.[18]

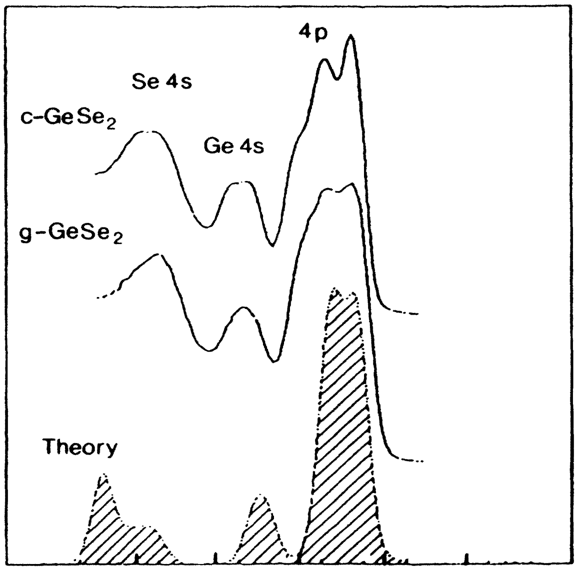

FIG. 2. XPS spectra for crystalline *c*-$GeSe_2$ and glassy *g*-$GeSe_2$ compared with calculated density of states for $GeSe_2$. For comparison, the density of states was broadened with a Gaussian of width 1 eV, and the photoionization cross sections are included.

The tight-binding parameters are given in Table I. β and E parameters were taken from work of O'Reilly *et al.*[21] They were established using a chemical pseudopotential method. Overlap integrals for Ge—Se bonds were estimated using Slater atomic wave functions.[22] The wave functions were concentrated by increasing the Slater exponents by 20% to give a more realistic gap.[18] The values of these integrals S_{ss}, $S_{s\sigma}$, $S_{\sigma s}$, and $S_{\sigma\sigma}$ are 0.08, −0.16, 0.19, and −0.28, respectively.

In Fig. 2 we compare the theoretical density of states for $GeSe_2$ obtained with this approach to XPS spectra for crystalline and glassy $GeSe_2$; good agreement is found. The same set of parameters was used to calculate densities of states for Ge_xSe_{1-x} alloys, as shown later in Fig. 7.

IV. RESULTS AND DISCUSSION

A. Electronic structure and chemical bonding in crystalline Ge-Se compounds

Let us start our discussion of the electronic structure of Ge-Se compounds with $GeSe_2$ as a reference model. In Fig. 2 three main structures are observed in the density of states. Partial densities of states presented in Fig. 3 allow us to identify the atomic character of the different structures. The states with the highest binding energy in the range 13–16 eV correspond to Se 4*s* levels. In a similar manner, the region at 7–10 eV is attributed to Ge 4*s* states. Bonding between Ge 4*p* orbitals and Se 4*p* orbitals gives rise to Ge—Se bonding states from 2 to 7 eV. The peak arising at the top of the valence band is related to the presence of pure Se π orbitals associated with twofold-coordinated Se atoms: the so called lone-pair orbitals.

In structural models describing Ge_xSe_{1-x}, glasses two main features have to be defined.

(i) The coordination type: 4:2 or 3:3.

(ii) The distribution of Ge—Se, Ge—Ge, and Se—Se bonds.

We will now examine if the shape of the DOS can be used to identify these features.

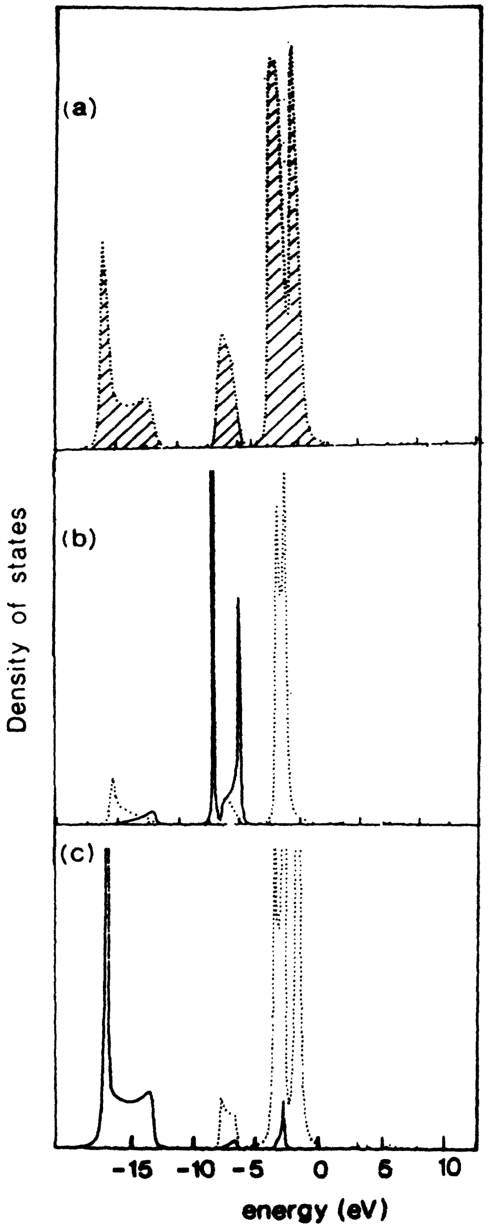

FIG. 3. Calculated densities of states for (4:2)-coordinated $GeSe_2$. (a) Total density of states broadened by 0.6 eV (photoionization cross sections included), (b) partial Ge 4s (——) and Ge 4p (· · ·) densities of states, and (c) partial Se 4s (——) and Se 4p (· · ·) densities of states.

1. 3:3 versus 4:2 coordination

Lone-pair orbitals are characteristic of 4:2 coordinations,[16] whereas in (3:3)-coordinated compounds such as GeSe, Ge p and Se p orbitals are strongly mixed.[23] This can be checked experimentally when valence-band spectra for $GeSe_2$ and GeSe are compared to that of analogous compounds GeS_2 and GeS, which have similar electronic and structural properties, respectively. XPS spectra can be considered the sum of partial densities of states weighted by atomic photoemission cross sections.[24] Therefore, differences in XPS valence-band intensities

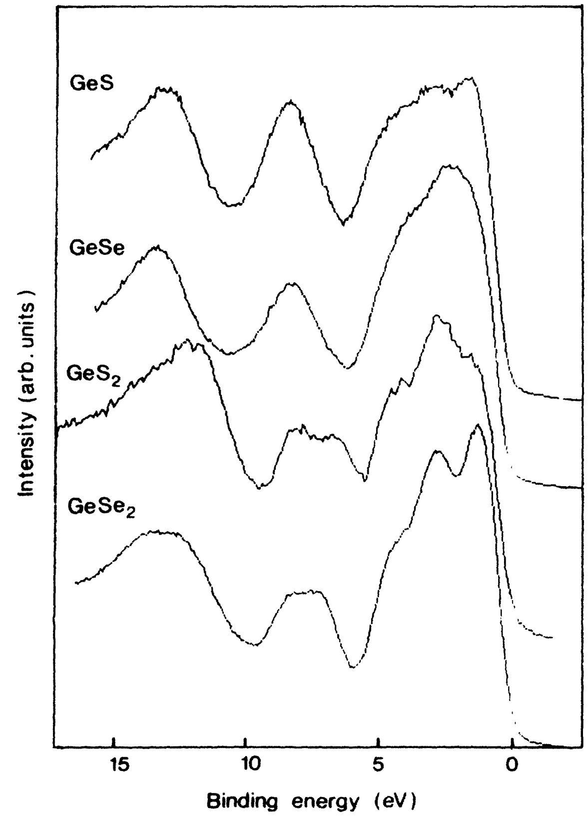

FIG. 4. XPS valence-band spectra for GeS, GeSe, GeS_2, and $GeSe_2$.

from $GeSe_2$ to GeS_2 or GeSe to GeS are mostly related to variations in cross section. According to Scofield calculations,[25] we found $\sigma(\text{Se } 4p)/\sigma(\text{Ge } 4p)=3.75$ and $\sigma(\text{S } 3p)/\sigma(\text{Ge } 4p)=0.66$ for XPS atomic cross-section ratios. This means that pure Se states appear much stronger than S states in Ge-X (X = S or Se) XPS spectra. This is exactly what can be observed in Fig. 4. The Se lone-pair peak is stronger for $GeSe_2$ than for GeS_2, whereas GeSe and GeS have similar p bands. It is then clearly established that the existence of pure Se states at the top of the valence band is an indication of 4:2 coordination. However, a strong peak of the type detected in crystalline $GeSe_2$ should not be expected since it does not appear in glassy $GeSe_2$ (which is described as a 4:2 material[1,4]), probably because the lone-pair band is broader in glasses than in crystals. Moreover, GeSe and glassy $GeSe_2$ have similar XPS p bands. These findings are in agreement with those of Robertson et al.,[15] who found multiple-peaked p bands in theoretical DOS's for both (3:3)- and (4:2)-coordinated GeSe. They are at variance with those of Schevchik et al.,[14,2] who used the presence of a peak at the top of the valence band to identify amorphous GeTe as a (4:2)-coordinated compound.

A last attempt to find a "fingerprint" of 4:2 and 3:3 coordinates was done by studying the crystallized Ge_xSe_{1-x} alloys with $x=0.41$ and 0.42. Figure 5 shows that the crystallized sample with $x=0.42$, made of GeSe crystallites embedded in a glassy matrix, and the glass

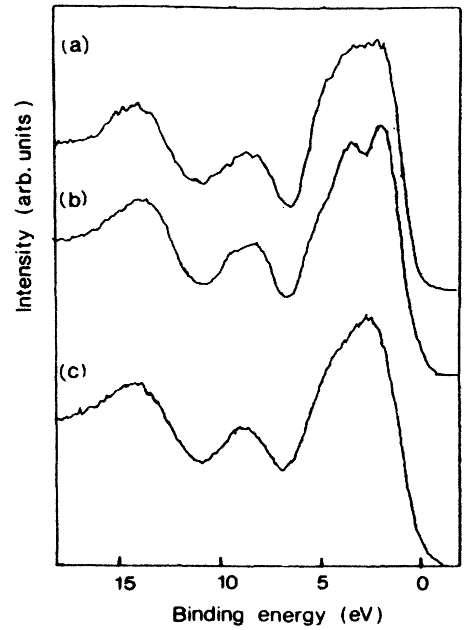

FIG. 5. Comparison of XPS valence-band spectra for Ge_xSe_{1-x} compounds. (a) A glass sample with $x=0.41$, (b) the same sample after crystallization (c-$GeSe_2$+c-GeSe), and (c) a crystallized sample (c-GeSe+glassy matrix) with $x=0.42$ prepared in the same way as sample (a).

sample with $x=0.41$ have similar spectra. By contrast, the crystallized sample with $x=0.41$ made up of $GeSe_2$ and GeSe crystallites is characterized by a spectrum with features reminiscent of crystalline $GeSe_2$. This allows us to conclude that, from the shape of the XPS valence-p-band spectra, we cannot distinguish between 3:3 and 4:2 coordinations in glasses, but we can detect crystalline 4:2 regions.

2. Ge—Ge and Se—Se homopolar bonds

XPS valence-band spectra for crystalline Ge, GeSe, $GeSe_2$, and Se are presented in Fig. 6. GeSe and $GeSe_2$ have only Ge—Se heteropolar bonds and their spectra are characterized by narrow, almost corelike, Ge 4s and Se 4s bands. However, we note that in crystalline $GeSe_2$ (as in crystalline GeS_2) these bands are split. As we do not observe such phenomenon for glassy $GeSe_2$, and in theoretical spectra we attribute this effect to the particular layered structure of $GeSe_2$ and GeS_2. It is probably due to electronic interactions between layers.

The Se spectra shown in Fig. 6 are representative of trigonal Se, but according to Takahashi *et al.*[26] the overall structure of the DOS remains unaltered when crystalline and amorphous Se are compared. Joannopoulos *et al.*[27] studied theoretically the density of states of various allotropic forms of selenium. Three regions can be identified which correspond in order of decreasing binding energy to s states, bonding p states, and nonbonding or lone-pair p states. The rectangular shape of the s band is characteristic of one-dimensional chains. The two singularities at the s-band edges correspond to bonding and antibonding states. Takahashi *et al.*[26] showed that the width of the s band varies from one structure to another. This was attributed to different kinds of Se rings.

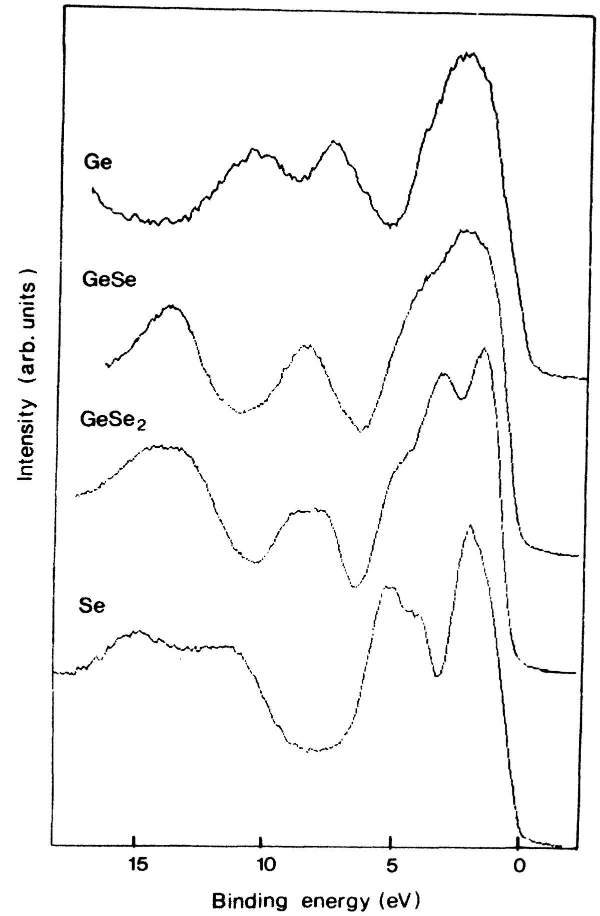

FIG. 6. XPS valence-band spectra for crystalline Ge, GeSe, $GeSe_2$, and Se.

Lannoo and Bensoussan,[16] using the tight-binding approximation, studied the electronic structure of Ge_xSe_{1-x} compounds in the range $0<x<0.33$. They predicted a narrow Se s band for $GeSe_2$ and increasing width of the Se s band for increasing x, when the length of —Se—Se— chains increases.

In a similar manner, we can expect analogous trends in the Ge 4s band when Ge—Ge bonds exist. The only existing model compound with Ge—Ge bonds is crystalline or amorphous Ge, which display a wide s-p band. Using the theoretical approach described in Sec. III, we have investigated the effect of existing Ge—Ge bonds in the density of states. Figure 1 and 7 present calculations for hypothetical 4:2 compounds with Ge atoms bonded to 0, 1, 2, 3, and 4 Se atoms, which correspond to the x concentrations 1, 0.67, 0.50, 0.40, and 0.33, respectively. In both cases it is clearly observed that the width of the Ge s band increases when the number of Ge—Ge bonds per Ge atom increases. This conclusion is in agreement with the calculations of Robertson *et al.*[15] They found a much broader Ge s bond in (4:2)-coordinated GeSe (Ge—Se and Ge—Ge bonds) than in (3:3)-coordinated GeSe (only Ge—Se bonds).

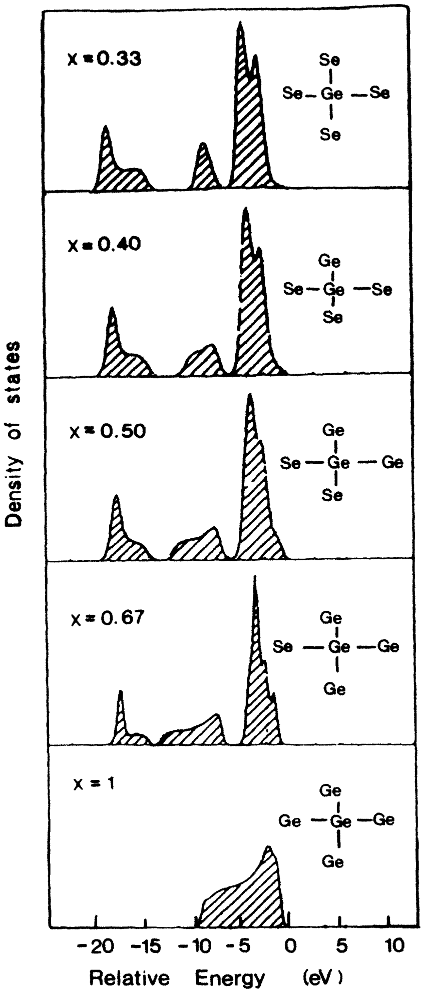

FIG. 7. Calculated occupied densities of states for (4:2)-coordinated Ge_xSe_{1-x} alloys with $x = 0.33$, 0.40, 0.50, 0.67, and 1. The DOS's were broadened by 1 eV. The reference energy is the top of the valence bands.

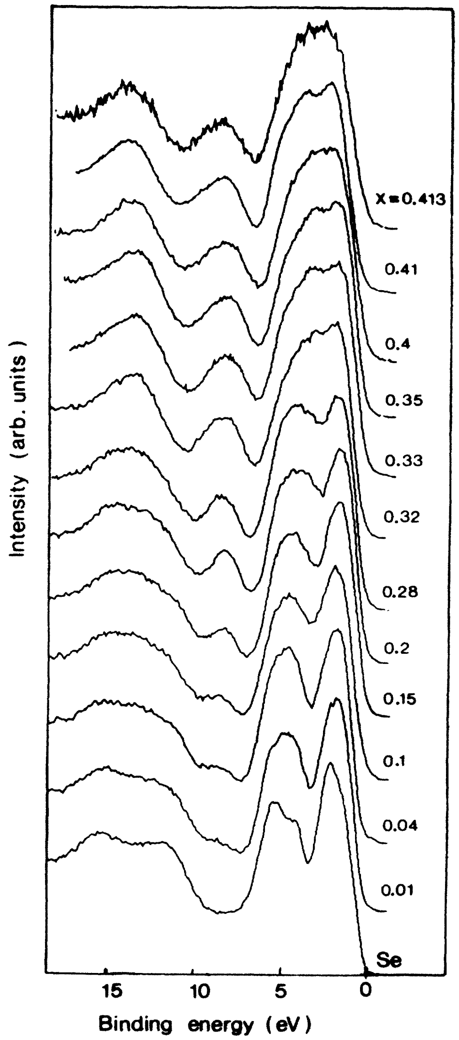

FIG. 8. Experimental XPS valence-band spectra for *c*-Se and Ge_xSe_{1-x} glasses with $0 < x < 0.42$.

B. Electronic structure and local order in Ge_xSe_{1-x} glasses

Our main results are presented in Fig. 8. We will first discuss the case of Se-rich compounds ($x < 0.33$). There is some agreement in the literature[1,3–5] on structural models which describe the local order in this composition range. It is assumed that Ge atoms are fourfold coordinated and Se atoms twofold coordinated. In addition, there is a tendency to a maximum dilution of Ge atoms in Se. No Ge—Ge bond exists and the number of Se—Se sequences decreases when x increases and vanishes for $x = \frac{1}{3}$. It is clear that the behavior observed in Fig. 8 is in agreement with such models. Starting from pure selenium, insertion of a Ge atom induces s and p states located, respectively, between s and p bonding states of Se, and between p bonding and p nonbonding states of Se. When x increases the intensity of the Ge s band increases, but this band remains narrow, indicating that these states arise from Ge—Se bonds and that no Ge—Ge bond exists. On the other hand, the width of the Se bond remains constant, which is consistent with the existence of Se chains, but its shape varies. The dip between the two edges is filled and a density-of-states maximum develops. This is due to the formation of $GeSe_2$-like states. The shapes and the width of the Se 4s band varies dramatically in the range $0.26 < x < 0.33$ to reach the symmetrical peak form of $GeSe_2$. This is attributed to the disappearance of Se chains and the existence of only Se—Se sequences. For the composition $x = 0.33$ we do not detect any feature which could support models which include Se-Se and Ge-Ge dimers. Note, however, that these kinds of dimers should be numerous enough to be seen in XPS spectra.

Let us now discuss the Ge-rich domain. According to Tronc *et al.*,[5] the coordination would still be of the 4:2 type and one Ge—Ge bond per Ge atom appears. From the calculations shown in Fig. 7, such Ge—Ge bonds should induce—for $x = 0.40$—a strong modification in both shape and width of the Ge 4s band. As an example, the width of the theoretical Ge 4s band for $x = 0.40$ is almost twice that estimated for $x=0.33$. From Fig. 8 it appears clearly that when x increases to 0.41 the shapes of the experimental Se 4s and Ge 4s bands remain unchanged. This allows us to reject models which favor 4:2 coordination and Ge—Ge bonds. Consequently, we have to admit the apparition of a (3:3)-coordinated GeSe-like local order for $x>0.33$.

Our results support models based on 4:2 and 3:3 coordinations with Ge—Se bonds in the majority. Our approach (photoemission spectra and parametric calculations) is not sensitive enough to go further in the description of the local order of Ge-rich glasses; the distribution of 4:2 and 3:3 sites, the nature of second neighbors, etc. remain matters of speculation. Only the crystallization behavior[5] of Ge_xSe_{1-x} glasses gives some hint at a precise structural model. It appears that GeSe crystallites exist only for $x>0.4$. This seems to indicate that 3:3 units are highly dispersed in the range $0.33<x<0.41$ and that, consequently, intermediate local order could exist to connect 3:3 and 4:2 units. It would be interesting to reevaluate Raman spectra in view of these new findings.

V. CONCLUSION

We have shown that the shapes of the valence Ge 4s and Se 4s bands in Ge_xSe_{1-x} alloys are sensitive to the presence of Ge—Ge and Se—Se bonds, respectively. On the contrary, no "fingerprinting" of 4:2 and 3:3 coordination in Ge_xSe_{1-x} glasses is found. Se-rich glasses ($x<0.33$) can be described with (4:2)-coordinated local structures and Ge—Se and Se—Se bonds, whereas Ge-rich glasses ($x>0.33$) are discussed with both (4:2)- and (3:3)-coordinated local structures and Ge—Se bonds.

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