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## Theoretical Densities of States of $\alpha$ -Si<sub>1-x</sub>Ge<sub>x</sub>:H Alloys. Comparison with X-Ray Spectra.

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**Abstract.** – A model of hydrogenated amorphous silicon based on the tight-binding coherent-potential approximation method is used to calculate the densities of states and the X-ray spectra of  $\alpha$ -Si<sub>1-x</sub>Ge<sub>x</sub>:H alloys. For the first time a quantitative comparison between calculated and measured X-ray spectra is made which reveals good agreement.

*Introduction.* – In recent years, a model for hydrogenated amorphous silicon has been proposed [1] that, despite neglecting topological disorder, gives a very good account of the electronic and transport properties of  $\alpha$ -Si:H. The model describes  $\alpha$ -Si:H by an effective lattice which is randomly occupied by Si atoms, vacancies, and vacancies whose dangling bonds are saturated by H atoms. An extensive set of calculations based on this model and the computational machinery of the tight-binding coherent-potential approximation (TB-CPA) method produced results that gave very good agreement with experiment. Specifically, the CPA densities of states identified the main features of the UPS and XPS measurements in the valence band and demonstrated the restoration and widening of the band gap upon hydrogenation. In addition, excellent agreement was found between optical absorption measurements and first principles evaluation of the a.c.-conductivity. Furthermore, use of the potential-well analogy (PWA) theory [2] resulted in reasonable estimates of the mean free path, the mobility edge and the d.c.-conductivity by including localization correction in  $\alpha$ -Si:H.

Finally, preliminary results of an extension [3] of this TB-CPA theory to  $\alpha$ -Si<sub>1-x</sub>Ge<sub>x</sub>:H alloys gave a variation of the band gap with Ge concentration in good agreement with optical data. In this letter we present for the first time a calculation of both the emission and absorption X-ray spectra in these alloys and compare them with the measurements. Our calculated spectra are in good agreement with the experiments, further justifying that the TB-CPA provides a reliable model for studying amorphous semiconductors.

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*Method of calculation.* – The calculations were performed by the TB-CPA method in a form that treats only diagonal disorder. The off-diagonal disorder was incorporated by taking geometrical averages between the Si, Ge, Si-H and Ge-H matrix elements [3]. The basic equation to be solved in the CPA is the condition that the scattering from each site is, on the average, equal to zero. In our case, this equation contains four terms representing the four different sites that we are considering, *i.e.* Si atoms, Ge atoms, 4H clusters in the vicinity of Si and 4H clusters in the vicinity of Ge. Thus the CPA condition has the following forms:

$$x \bar{t}_{\text{Si}} + y \bar{t}_{\text{Ge}} + c \frac{x}{x+y} \bar{t}_{\text{HSi}} + c \frac{y}{x+y} \bar{t}_{\text{HGe}} = 0 \quad (1)$$

with

$$x + y + c = 1, \quad (2)$$

where  $x$  and  $y$  are the Si and Ge concentrations, respectively, and  $4c$  is the amount of H.

The matrix  $\bar{t}_A$  has the following form:

$$\bar{t}_A = (\bar{\varepsilon}_A - \bar{\Sigma})[1 - (\bar{\varepsilon}_A - \bar{\Sigma})\bar{G}]^{-1}, \quad (3)$$

where  $\bar{\varepsilon}_A$  and  $\bar{\Sigma}$  are diagonal matrices representing the on-site Slater-Koster (SK) parameters and CPA self-energy, respectively. The Green's function  $G$  is determined by the following integral over the irreducible wedge of the Brillouin zone:

$$\bar{G}(z, \Sigma) = \int_{\text{Bz}} \frac{d^3 k}{z - H(\varepsilon, k)}, \quad (4)$$

where  $z$  is the complex energy and  $H$  the  $8 \times 8$  periodic Hamiltonian (involving  $s$  and  $p$  orbitals for two atoms) with the on-site SK parameters replaced by the self-energies  $\Sigma_s$  and  $\Sigma_p$ .

Equations (1) and (4) are solved simultaneously by iteration to determine  $\bar{\Sigma}$  and hence  $\bar{G}$ . The diagonal elements of the Green's function matrix  $G$  are then used to calculate the densities of states (DOS)  $N_s(E)$  and  $N_p(E)$ .

*Results.* – In our calculations we have used 505  $k$ -points to perform the integrals of eq. (4). We have performed five independent calculations with the hydrogen composition fixed at 0.1 and varying the Ge content with respect to Si equal to 0.0, 0.2, 0.3, 0.4 and 1.0. In the case of Ge two calculations with H content equal to 0.1 and 0.4 have also been performed.

*Hydrogenated Si-Ge alloys.* Our resulting DOS for the Si-Ge alloys are plotted in fig. 1. The origin of the energy scale is the top of the valence band. The DOS show three peaks in the valence band and one peak in the conduction band; only small changes occur as a function of Ge content. The energy gap decreases from a value of about 1.3 eV for  $\text{SiH}_{0.1}$  to about 1.0 eV for  $\text{GeH}_{0.1}$ .

Due to electric-dipole selection rules, the X-ray emission and absorption spectra correspond, respectively, to the occupied and unoccupied  $l \pm 1$  DOS broadened by the lifetime of the  $nlj$  core level. As the matrix element is a slow varying function of the energy, it can be considered as a constant over the energy range of the spectra. Consequently Si  $K$  X-ray emission and absorption spectral distributions for the alloys are calculated by applying to our  $p$ -DOS a 0.6 eV wide Lorentzian broadening accounting for both the inner Si  $1s$  level distribution and the instrumental function. The resulting curves are plotted in fig. 2a) and b).

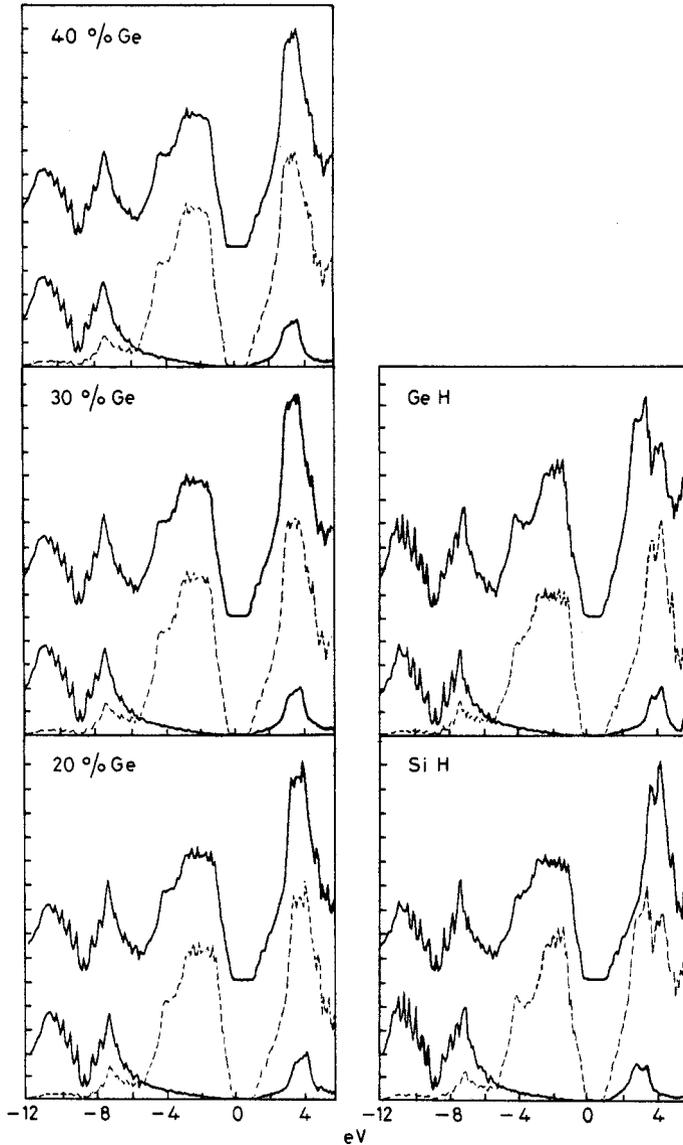


Fig. 1. - Calculated DOS for pure hydrogenated Si and Ge and  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  alloys. On each figure: upper curve: — total DOS; lower curves: —  $s$  DOS; ---  $p$  DOS.

In these figures, we report comparatively the experimental Si  $K\beta$  emission ( $\text{VB} \rightarrow 1s$ ) and Si  $K$  absorption ( $1s \rightarrow \text{CB}$ ) spectra for  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  alloys, prepared by glow discharge decomposition of  $\text{SiH}_4 + \text{GeH}_4$  gases, with  $\text{GeH}_4$  concentration in the mixture 0.2, 0.3 and 0.4 [4]. The experimental curves are referenced to the Fermi level as discussed in ref. [4].

In order to adjust the theoretical curves to the experimental data, we have located  $E_F$  on the calculated curves. For  $a\text{-Si:H}$ , we have superposed the low-binding energy edges of the curves. For the alloys, we have taken into account the progressive decrease of the distance between  $E_F$  and the top of the valence band with  $X_{\text{Ge}}$  increasing, as observed experimentally [4].

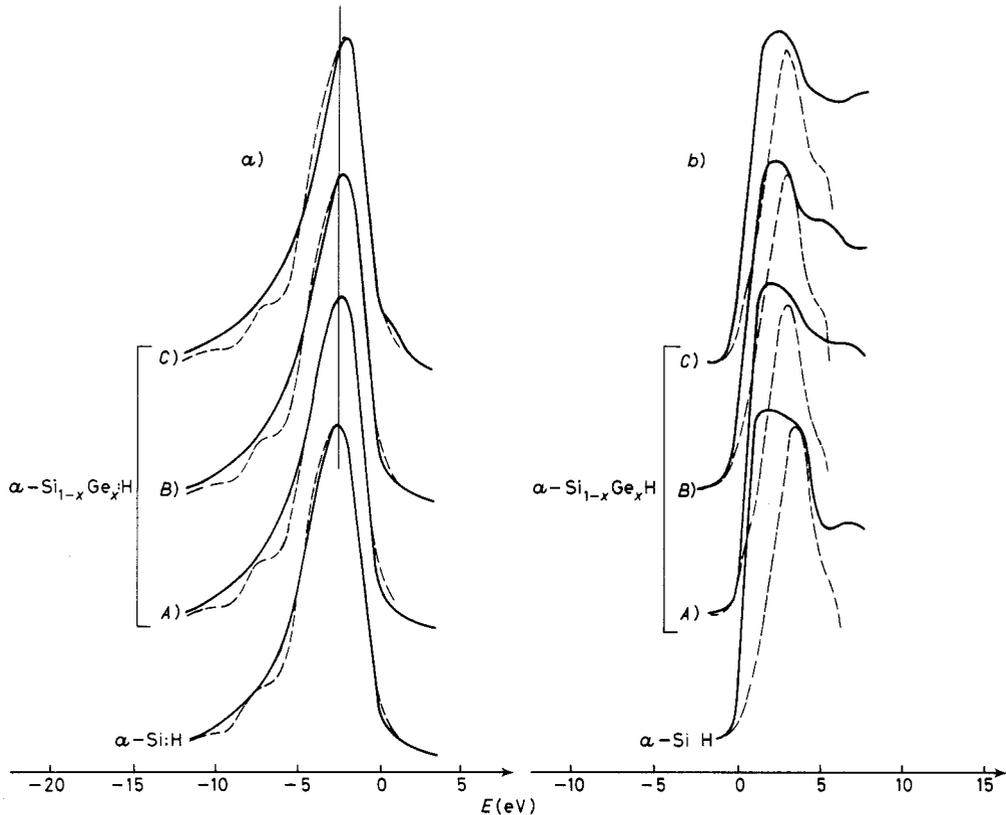


Fig. 2. - Calculated  $K$  X-ray spectra (---) compared to experimental data (—). a)  $K\beta$  emission, b)  $K$  absorption. A, B and C correspond, respectively, to  $\text{GeH}_4$  concentration 0.2, 0.3 and 0.4.

Figure 2a) shows that there is a very good agreement between theoretical and experimental data for the  $p$ -like valence band spectra: for each alloy, the maximum is located at the same energy and the low-binding energy edges are quite superposed; the widths at half-maximum are very close. A difference between the shapes of the curves is found on the high-binding energy side. The experimental curve is smooth while the calculations predict the presence of two structures at about  $E_F = -7.4$  eV and  $E_F = -10.2$  eV. Previous theoretical works concerning the DOS of amorphous silicon have shown that the presence of odd-membered rings of bonds involve a merging of the high-energy peaks [5]. The presence of these two peaks at the bottom of the calculated valence band DOS may be due to the fact that topological disorder of the network is not effectively introduced in the calculation; in particular, odd-membered rings of bonds are not taken into account.

The good agreement found between the calculated and experimental spectral densities for each Ge content emphasizes the strong covalent character of Si-Ge bonding in the alloys. Indeed, the  $p$ -DOS involved in the Si  $K\beta$  spectra concern only states around Si atoms, while the calculation refers to all  $\alpha\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  states. Such a conclusion has already been deduced from comparison between X-ray spectra and XPS valence band spectra obtained for the same alloys [4].

For the conduction band, the calculation predicts that  $p$  states are predominant at the bottom of the band. The corresponding absorption peak is narrower on the calculated curve than observed. Due to an approximation made in the construction of the TB Hamiltonian [6],

the conduction band is described by  $s$  and  $p$  orbitals without the inclusion of  $d$  orbitals which may be nonnegligible in this part of the conduction band: the presence of hybridized  $p$ - $d$  states could explain the differences observed.

The shape of the edge observed experimentally (fig. 2b)) is sharper than that predicted theoretically; this effect becomes less pronounced as Ge is incorporated since the experimental edge becomes less abrupt. We had suggested [4] that the effect observed experimentally could be related to differences in topological disorder and H incorporation as  $x_{\text{Ge}}$  varies. These parameters are not accounted for in the theoretical model, which can explain the differences observed on the edge shape.

*Hydrogenated amorphous germanium.* Calculations for hydrogenated germanium have been performed for two hydrogen contents: 10% ( $a\text{-Ge:H}_{0.1}$ ) and 40% ( $a\text{-Ge:H}_{0.4}$ ). Due to the CPA model, some degree of disorder is involved in the DOS calculations. Disorder increases with hydrogen content and is not possible to estimate rigorously; this leads to a self-broadening that smoothes out the DOS features much more for  $a\text{-Ge:H}_{0.4}$  than for  $a\text{-Ge:H}_{0.1}$ . So, we will compare the Ge  $L_3$  absorption spectra to the DOS as obtained directly from the calculation which concerns 6 eV beyond the top of the valence band.

On fig. 3a) and b), we show the  $s$  and  $p$  partial DOS for  $a\text{-Ge:H}_{0.4}$  and  $a\text{-Ge:H}_{0.1}$ , respectively. The  $s$ -DOS intensities given by the calculation have been multiplied by a factor 5 in fig. 3a) and by a factor 10 in fig. 3b) relatively to  $p$ -DOS, for clarity. We display also on these figures experimental Ge  $L_3$  absorption spectra as a function of the X-ray transition energies. Figure 3a) refers to a sample containing about 50% hydrogen, as obtained from the reaction of  $\text{H}_2\text{O}$  on GeCa [7]. Figure 3b) concerns a sample heated at 470 K in which small H content remains due to H exodiffusion during the heating procedure [7].

Within the experimental uncertainties, about 0.2 eV, the feature  $m$  is at the same energy position on the experimental absorption spectra of both samples; it is clearly a minimum in the case of  $a\text{-Ge}$  with 50% H and corresponds to a change in the slope of the curve related to low hydrogenated  $a\text{-Ge}$ . We have adjusted the experimental curves to the  $s$ -DOS theoretical ones by aligning  $m$  to the minima of the calculated  $s$ -DOS curves. The adjustment with  $p$ -DOS is deduced directly from the calculations.

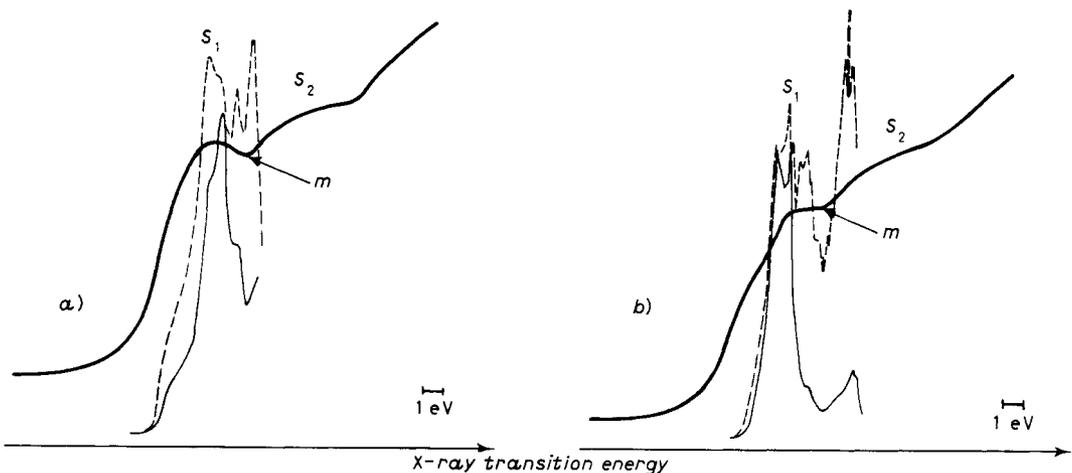


Fig. 3. - Calculated  $s$  (—) and  $p$  (---) DOS compared to Ge  $L_3$  absorption (—); a) high hydrogen content; b) low hydrogen content.

For  $a\text{-Ge:H}_{0.1}$ , from the overlap between  $s$  and  $p$  curves (fig. 3b)), it arises that the states at the bottom of the conduction band are slightly  $sp$  hybridized. Feature  $S_1$ , between the edge and  $m$ , corresponds to the barycentre of the  $s$ -DOS distribution, situated at about  $-(1.2 \pm 0.2)$  eV from  $m$ . For  $a\text{-Ge:H}_{0.4}$  (fig. 3a)) the maximum of feature  $S_1$  and the barycentre of the  $s$  states distribution are also in coincidence, at about  $-(0.9 \pm 0.2)$  eV from  $m$ , in agreement with the slight shift towards high energies observable for  $S_1$  with increasing H content. The  $s$  states are thus pushed towards high energies, while  $p$  states remain in the same range making  $sp$  hybridization different from that of  $a\text{-Ge:H}_{0.1}$ . Both  $s$  and  $p$  states distributions are affected by the increase in H content, in particular, for  $a\text{-Ge:H}_{0.4}$  with respect to  $a\text{-Ge:H}_{0.1}$  at half-maximum, the  $s$  states distribution is broader and shows one peak instead of a two-peaked line.

Then, a rather good agreement is observed between the calculated  $s$ -DOS distributions and the experimental results. However, transitions towards  $s$ - $d$  empty states can be involved beyond the Ge  $L_3$  edge; such transitions are not accounted for in the calculation.

*Conclusion.* – The comparison of calculated  $K$  X-ray emission spectra deduced from occupied DOS with experimental data is in very good agreement for pure  $a\text{-Si:H}$  as well as for  $a\text{-Si}_{1-x}\text{Ge}_x\text{:H}$  alloys. Both the general shape and the energy shifts of the curves with increasing Ge content are well predicted by the calculation.

For the unoccupied states an overall agreement is observed between theoretical predictions and experimental results, nevertheless slight discrepancies remain. In particular, the calculation does not account totally for the states located at the bottom of the conduction band. This could be explained by the fact that the theoretical model does not involve topological disorder of the network and does not include  $d$  orbitals in the Hamiltonian.

In summary, our experimental results give further support to the validity of the hypothesis brought forward in forming the theoretical model.

\* \* \*

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