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# K AND L X-RAY THRESHOLDS IN III-VI LAYER SEMICONDUCTORS.

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The absorption spectra at the Ga K-edges in GaS and GaSe, and the In L-edges in InSe have been measured as a function of the polarization with respect to the crystal $\underset{\sim}{c}$ axis using synchrotron radiation. The transitions associated with the lowest energy structure in the Ga K spectra were found to be allowed only for $\underset{\sim}{\varepsilon} \perp \underset{\sim}{c}$, and were attributed to final Ga $4p_x p_y$ high--lying conduction bands. Transitions to the lowest $p_z$-like conduction bands were not observed in both polarizations in the Ga K spectra, but they were in the In L spectra. Since structures near X-ray thresholds reproduce the conduction band density of states, weighted by the atomic-like symmetry of the crystal wavefunction at the absorbing atom, these experimental results allowed to identify the atomic character of the lowest conduction bands. In support to recent calculations, we found that the lowest conduction band states are formed by Ga 4s (In 5s) states and not by Ga $4p_z$ (In $5p_z$) orbitals. The second group of conduction bands derive from chalcogen orbitals and the third group from Ga $4p_x p_y$ (In $5p_x p_y$), and in part from empty s orbitals.

## 1. - INTRODUCTION.

In the last years, the dispersion curves of the valence bands of the III-VI layer compounds were measured directly by means of angle resolved photoemission[1]. The symmetry of the highest valence band wavefunctions was probed also by photoemission using the polarization of synchrotron radiation[2]. These facts have stimulated more refined and accurate energy band calculations and recently a very good agreement between theory and experiment was achieved[3]. These calculations yield also the conduction bands, but the intrinsic approximations of the method make them somewhat questionable. Thus, tests as stringent as those used for the valence bands are necessary. Photoemission does not have direct access to the lowest conduction bands below the vacuum level. Optical transitions from the valence bands probe the joint density of states. Only transitions from core states yield the conduction bands density of states in the one-electron model and assuming constant transition matrix elements. As a matter of fact, the calculated density of states of the lowest conduction bands reproduces well the structures near the thresholds of the Ga 3d and In 4d transitions in the Ga and In III-VI compounds respectively[4]. However, the observed large excitonic effects mask or modify the one-electron density of states[4]. Moreover, the d spectra give little information on the symmetry of the final states.

We report here on measurements performed at the Ga K-edge in GaS and GaSe, and In L-edges in InSe. The structures near X-ray thresholds can be related to a weighted conduction band density of states - in a way that we shall define later -, so that, by using different initial core levels and changing the polarization vector $\underset{\sim}{\varepsilon}$ with respect to the crystal $\underset{\sim}{c}$ axis, it is possible to asses the atomic-like wavefunctions that form the lowest empty states. In agreement with the most recent band calculations[5], we find that the first group of conduction bands originates mostly from s-like metal orbitals, and that the third group of conduction bands are formed mostly by the metal $p_x p_y$ orbitals.

## 2. - EXPERIMENTAL SET-UP AND RESULTS.

The measurements have been performed at the PULS synchrotron radiation facility at the Laboratori Nazionali di Frascati. 1 mrad of X-rays emitted from the 1.5 GeV electrons orbiting in the Adone storage ring are collected through a 70 $\mu$m Be window that separates the ultra high vacuum pipe ($10^{-7}$ Pa) from the monochromator and the sample chamber. The monochromator uses a (220) channel-cut Si crystal diffracting in the vertical plane. The intensity of the radiation incident on the sample and that transmitted are detected by two ionization chambers. The entire set-up is controlled by a PDP 11/03 computer, which is also used for storing and processing the data.

Thin slabs of GaS, GaSe and InSe were peeled to the proper thickness of a few $\mu$m and attached on Cu masks, so to leave the most uniform portion of the sample exposed to the radiation. The samples were mounted on a vertical shaft inside the sample chamber. A rotation of the shaft allowed to perform transmission measurements at different angles of incidence, $\theta$,

with p-polarized radiation. Another type of mounting, with a fixed 45° angle, was used for measurements in s-polarization.

The spectra of the optical density OD at the K-edges of GaS and GaSe are shown in Figs. 1a and 1b respectively for several θ's, p-polarization. A smooth background, originating from both the pre-edge absorption due to the less bound shells, and geometrical effects, has been subtracted, so that the bare Ga K absorption is shown. Far from the edge, the absorption should be atomic-like (neglecting the extended fine structure), and should depend on neither the compound nor the polarization of the radiation. Thus, all the spectra have been normalized about 20 eV above the edge to the GaS spectrum for $\theta = 0^{\circ}$. Since at oblique incidence, $OD(\theta) = OD(0)/\cos\theta$, the normalization gave the nominal value of θ within $\pm 1^{\circ}$.

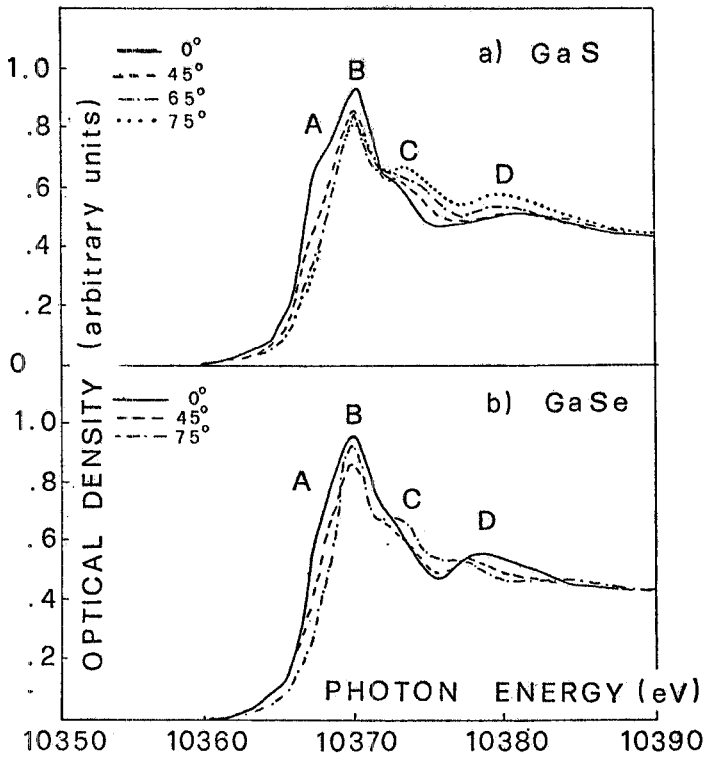


FIG. 1 - Optical densities measured around the Ga K absorption edges in GaS (a) and GaSe (b) at several angles of incidence, p-polarization.

The spectra of the Ga K-edge in GaS and GaSe are very similar to each other and are characterized by a strong peak at 10370 eV (labelled B), that does not depend on the polarization. Weaker structures are observed as well, that depend on the polarization. The low energy feature (labelled A) almost disappears for $\underset{\sim}{\varepsilon} // \underset{\sim}{c}$, while the high energy one (labelled C) increases and shifts to higher energies for increasing θ's. The 1.2 eV half-width-at-half-maximum (HWHM) found for all the structures is caused by both the intrinsic lifetime broadening of the Ga 1s level (0.8 eV) and the monochromator resolution (0.8 eV at about 10 keV). Since the setting of the initial diffraction angle at the beginning of each scan is accurate within 3", corresponding to 0.5 eV in this energy range, all the energy scales have been shifted so to align peak B of each spectrum at the same energy of 10370 eV. We measured also the absorption of GaS at $\theta = 45^{\circ}$ s-polarization in order to check if the differences of the spectra at different θ's p-polarization could be due to trivial measurement effects[6]. No variation from the $\theta = 0^{\circ}$ spectrum was observed.

In Fig. 2 we show the In $L_3$ spectrum in InSe. The $L_2$ spectrum beginning at about 3862 eV, reproduces the $L_3$ spectrum, but for the intensity that is reduced by the spin-orbit $j = 1/2 - 3/2$ statistical ratio of 0.5. Beyond the first two weak structures at threshold, the absorption rises smoothly, possibly with minor features superimposed. The In $L_1$ spectrum is similar

to the Ga K spectra in the Ga compounds, but it is somewhat broader.

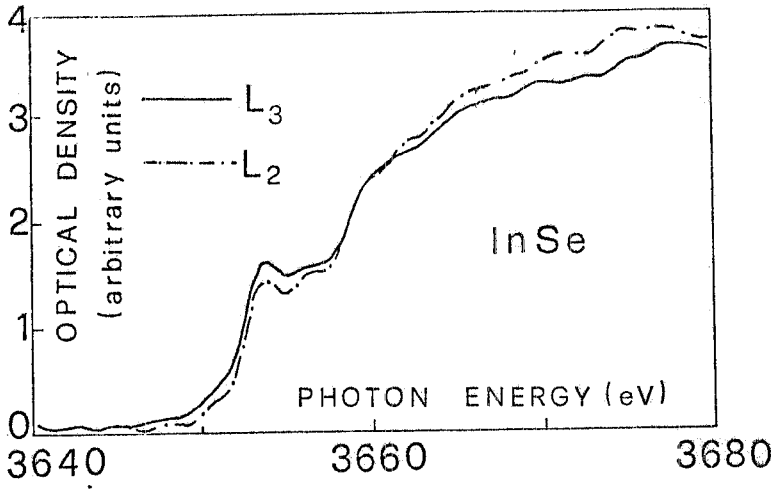


FIG. 2 - Optical densities measured around the In $L_2$ - $L_3$ edges in InSe. Both ordinate and abscissa scales refer to the $L_3$ spectrum. The $L_2$ spectrum has been shifted to lower energies by the $L_2$-$L_3$ spin-orbit splitting of 211.3 eV, and its intensity has been multiplied by 2.

## 3. - DISCUSSION.

In many materials the structures around the X-ray absorption thresholds are understood presently in terms of the one-electron density of empty states of the unrelaxed crystal. Effects due to the presence of the deep core hole and to relaxation seem to give minor contributions[7]. Thus we shall discuss our spectra within the one-electron approximation.

The bonding combination of the Ga 4s and $4p_z$ orbitals and of the Se $4p_z$ orbitals generates the highest valence band, the strong $p_z$ character of which has been demonstrated experimentally[2]. Some hybridization with the Se $4p_xp_y$ states occurs near the Brillouin zone boundary. The first conduction band is formed mostly by the antibonding combination of the above orbitals, so a large $p_z$ character is expected for it too. The second group of bands is formed by empty chalcogen s orbitals; bonding and antibonding combinations of the Ga $4p_xp_y$ empty orbitals generates the third group of conduction bands[5]. This description of the conduction bands, made for GaSe, holds also for GaS and InSe, provided that the right principal quantum numbers for the S and In states are used instead of those of Se and Ga, respectively.

From the above description of the conduction bands of the III-VI layer semiconductors, one should expect that transitions to the first conduction band are allowed only for $\underset{\sim}{\varepsilon} // \underset{\sim}{c}$ and those to the third group of $p_xp_y$ bands for $\underset{\sim}{\varepsilon} \perp \underset{\sim}{c}$. The spectra of Fig. 1 clearly show that the first structure A is allowed for $\underset{\sim}{\varepsilon} \perp \underset{\sim}{c}$ only. We associate the structure A with transitions to the Ga $4p_xp_y$ conduction bands. We stress that polarization-dependent measurements are crucial for such an identification. In fact, the similarity of the density of states of GaS with the

GaS optical density measured at $\theta = 0^o$, shown in Fig. 3, would have suggested to associate the structure A to the lowest $p_z$-like conduction band, and the structure B to the Ga $4p_xp_y$ bands.

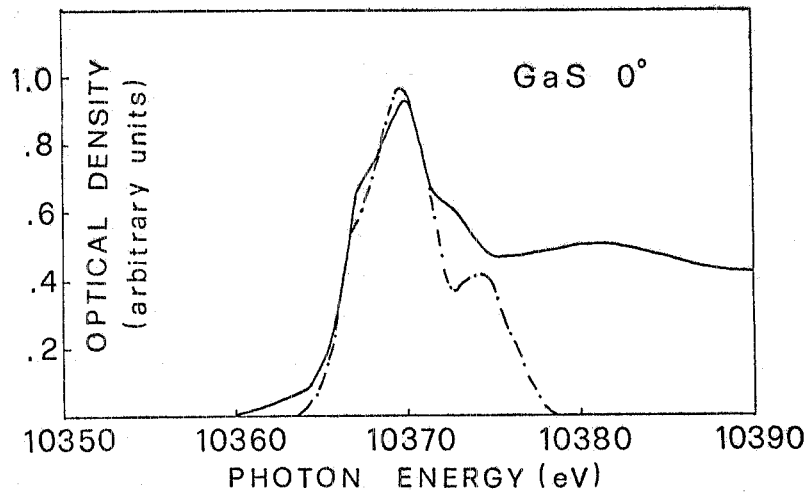


FIG. 3 - Ga K-edge in GaS measured at $\theta = 0^o$ (continuous line), compared with the conduction bands density of states (dash-dotted line) (after ref. (3)), convoluted with a Lorentzian function of 1.2 eV HWHM.

In the spectrum corresponding to $\underset{\sim}{\varepsilon} // \underset{\sim}{c}$, the feature A is still present even if very weak. This may be due to the following reasons : first, synchrotron radiation actually is elliptically polarized, with a degree of linear polarization of about 0.9 at 10 keV. Thus, even at very large angles of incidence, a small component of $\underset{\sim}{\varepsilon}$ perpendicular to $\underset{\sim}{c}$ is still present. Second, the bands are actually not purely $p_xp_y$, but some hybridization with other atomic orbitals may occur, thus relaxing the selection rules.

At large angles of incidence a structure corresponding to the first $p_z$-like conduction band should appear below A, but we did not have evidence for it. We note that, in the case of BN, another hexagonal layer semiconductor, the expected feature has been found at the boron K-edge[8].

In the tight-binding approximation, the leading term of the absorption coefficient at the Ga K-edge is given by[9] :

$$\mu(\hbar\omega) \propto \left| P_{1s \to \nu} \right|^2 \sum_{\underset{\sim}{k}} \left| A_{\nu, c}(\underset{\sim}{k}) \right|^2 \delta(E_c(\underset{\sim}{k}) - E_{1s} - \hbar\omega) \qquad (1)$$

where $P_{1s \to \nu} = \int \Phi_{1s}^*(\underset{\sim}{r})\, \underset{\sim}{\varepsilon} \cdot \underset{\sim}{r}\, \Phi_\nu(\underset{\sim}{r}) d^3\underset{\sim}{r}$ is the atomic dipole transition matrix element between states centered around the absorbing atom. $\Phi_{1s}$ is the Ga 1s orbital and $\Phi_\nu$ is either the Ga $4p_xp_y$ or the Ga $4p_z$ orbital, according to whether $\underset{\sim}{\varepsilon} \perp \underset{\sim}{c}$ or $\underset{\sim}{\varepsilon} // \underset{\sim}{c}$. $A_{\nu, c}(\underset{\sim}{k})$ is the coefficient corresponding to the orbital $\nu$ of the expansion of the crystal state $\underset{\sim}{k}$ of band c into atomic wavefunctions centered around all atoms of the crystal. For example, $A_{\nu, c} = 0$ if

$\nu = 4p_x p_y$ for the lowest group of conduction bands at $\Gamma$. Eq. (1) has a very simple meaning. The absorption coefficient is given by the atomic transition probability (for $\underset{\sim}{\varepsilon} // \underset{\sim}{c}$ $P_{1s \to 4p_z}$ is allowed, while for $\underset{\sim}{\varepsilon} \perp \underset{\sim}{c}$ $P_{1s \to 4p_x p_y}$ is allowed), times the density of states, each state being weighted by the presence in it of the proper Ga empty p orbital (weighted density of states). According to ref. (5), the lowest conduction band of GaSe, as an average, is formed by the Se $4p_z$ and $4p_x p_y$ orbitals, hybridized mainly with the Ga 4s states. The Ga $4p_z$ orbitals contribute only for a very small fraction[5]. Thus, $A_{4p_z}$, averaged over the whole band, is very small, while $P_{1s \to 4s} = 0$. For this reason we think that the transitions to the lowest conduction band (and also to bands generated by Se orbitals) are not seen. The situation is different in the case of BN, where the lowest conduction band is formed mostly by boron $p_z$ orbitals. The third group of bands in the III-VI compounds do have a strong Ga $p_x p_y$ character[5] and transitions to them depend on the polarization.

The higher bands have different contributions at the various $\underset{\sim}{k}$'s from more excited Ga p orbitals, but with a poorer defined character. In addition, they are wider than the experimental band-width. Rather than observing an average of Eq. (1) over the whole band, as in the case of the lowest bands, we can discriminate in part the different portions of the band. The absorption structures, such as C, change in energy and strength with polarization in a way that present available calculations do not allow to predict.

The In $L_3$ edge is characterized by a smooth rise due to the 2p-to-d delayed transition matrix element. Of particular interest are the first two structures at threshold. According to Eq. (1), that is quite general with trivial lebelling modifications, the first structure at 3653.8 eV can be associated with the lowest conduction band, that is partially formed by the In 5s orbitals. Since the initial core 2p state practically is not split by the anysotropic crystal field, such transitions do not depend on polarization. The second structure at 3656.5 eV is likely to originate from the third group of bands, where some mixture with higher excited In s states probably occurs.

In conclusion, by means of the Ga K, as well as In L, absorption spectra we have probed part of the conduction band wavefunctions of the III-VI layer semiconductors GaS, GaSe and InSe. In agreement with recent calculations, we find that the lowest conduction band has a strong Ga 4s (In 5s) character, with very little Ga $4p_z$ contribution. The third group of conduction bands instead has Ga $4p_x p_y$ character, probably with some contribution from more excited Ga s orbitals.

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