



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

**Experiment title:**

Investigation of impurity site configuration in layered semiconductors (InSe,GaSe) by means of EXAFS

Experiment**number:**

HE-740

Beamline:	Date of experiment: from: 22/05/01 to: 29/05/01	Date of report: 28/08/02
Shifts:	Local contact(s): Lilian Jacquamet	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):**Proposer: Alfredo SEGURA****Departamento de Física Aplicada Edificio de Investigación, c/ Dr. Moliner 50, 46100 Burjasot (Valencia), Spain, Phone: 34 96 3864792, Fax: 34 96 3983146,****email: Alfredo.Segura@uv.es****Co-proposers;****Chantal FERRER, email: Chantal.Ferrer@uv.es****Julio PELLICER, email: Julio.Pellicer@uv.es****Report:****1) Introduction**

The object of the experiment was to investigate the local structure of impurities in III-VI layered semiconductors, specially in Indium Selenide (InSe). Arsenic (As) was proposed to be a single substitutional acceptor in Se site [5], but the possibility of As substituting to In and giving rise to a double donor could not be excluded. The interest of the As related acceptor is based on the fact that the highest solar efficiency in a layered material was obtained on ITO/p-InSe:As solar cells [1], due to the lower resistivity of As-doped p-InSe.

2) Experimental

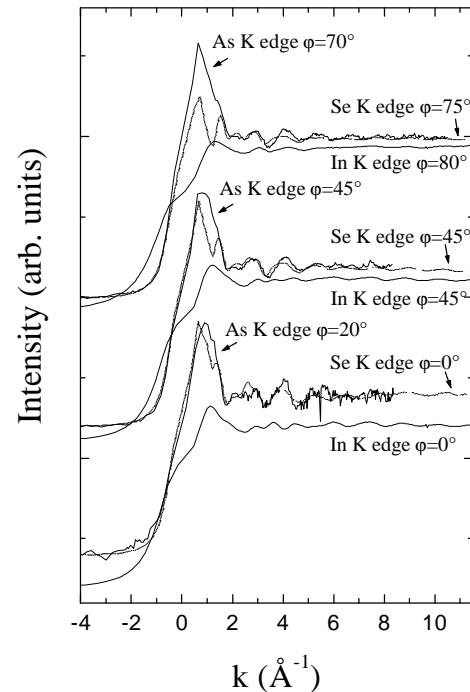
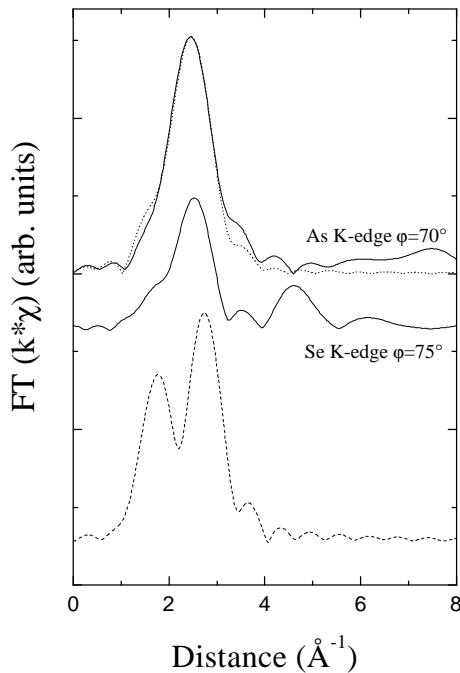
Large single crystals of InSe have been grown by the Bridgman method. Doped crystals have been prepared by adding different doping agents, in different proportions, to the polycrystalline melt before the Bridgman growth process. The crystal studied in the experiment were prepared with impurity nominal proportions of about 0.5 %. Given the high segregation coefficient in these materials, only a small part remains in the crystal, the rest being rejected to the end of the ingot [2]. The crystals were previously characterized so as EXAFS results can be correlated to previous results on transport, DLTS and photoluminescence measurements [3]. Spectra were collected in the fluorescence mode. We employed grazing incident angles in order to minimize elastic scattering. The fluorescence yield was measured a function of the X-ray photon energy using a p-i-n diode detector. Different filters (10 μ absorbance) were used to further minimize unwanted elastic scattering. Spectra were taken at the K-edge of impurities with a energy range of about 400 eV above the absorption edge. The availability of large monocrystals made it possible to take advantage of the polarized character of synchrotron radiation in order to study the possible anisotropy of the next neighbor distances around the impurity atom, by rotating the sample in order to change the angle between the c-axis of InSe and the X-ray polarization direction.

3) Results

Figure 1 shows the XAS spectra of an As doped InSe sample taken at different incidence angles. For comparison, in addition to the spectra measured at the As K-edge, we have included in the figure the spectra taken at the Se and In K-edges (shifted by their energy difference with respect to the As K edge).

The XANES (x-ray absorption near edge structure) part of the spectrum involves multiple scattering processes and is consequently sensitive to medium-range order. In Fig. 1 it is observed that at the As and Se K-edges the XANES are similar, and change in the same way when the incidence angle is varied. On the opposite, the XANES corresponding to the In K-edge presents a completely different structure that changes when the incidence angle. These observations suggest that the As and Se environments may be similar, and different from the In one. In Fig. 1 it is also evident that the main frequency associated with EXAFS (extended x-ray absorption fine structure) oscillations is higher at the Se K-edge than at the As K-edge, indicating that the Se-In bondlength is longer than the distance from the As to their first neighbors.

The pair-pseudo-distribution function (PPDF) was obtained from Fourier Transformation of the EXAFS oscillations using a Bessel type ($\tau=4$) apodization window. With an incidence angle between the normal to the sample and the incident radiation of $\varphi=70^\circ$ (grazing incidence), we included in the analysis a wave vector range comprised between 2.6 and 7.6 \AA^{-1} . When the incidence angle diminishes the effective depth sampled by the incident radiation becomes smaller and at the same time the fluorescence signal crosses a thicker part of the sample before reaching the detector. Consequently, the XAS signal degrades as the incident radiation approaches the normal. With an incidence angle of $\varphi=45^\circ$ the wave vector range used in the EXAFS analysis is reduced to the interval between 2.6 and 5.6 \AA^{-1} .



At $\varphi=20^\circ$ the quality of the experimental signal does not allow a quantitative analysis. In Fig. 2 we present the PPDF corresponding to $\varphi=70^\circ$ and $\varphi=45^\circ$.

4) Discussion

The fact that no linear dichroism is observed in EXAFS spectra taken at different incidence angles is a clear indication that all first neighbors are at the same distance. The single substitutional acceptor, As in Se site (As_{Se}), is the only acceptor configuration compatible with this result. Any other configuration including a bond along the c-axis of the crystal would give rise to a linear dichroism as it is actually observed in substitutional Ga in In site in the alloy $Ga_{0.01}In_{0.99}Se$. In that case a clear linear dichroism in the XANES spectra at the K-edge of Ga in at different incidence angles, due to the presence of a covalent bond along the c-axis [4].

On the other side, comparison of the XANES part of the spectrum at the As K-edge with that of the spectra at the Se edge, shown in figure 1 is a clear indication of the similarity of the local surrounding of the normal Se site in InSe and the As related center, supporting the hypothesis of the single substitutional acceptor.

Let us discuss now the next neighbor distance obtained from our fit. The in-layer In-Se covalent bond distance is 2.63 Å. In order to check the behaviour of the In-As bond distance in different compounds, let us compare this distance with the one in the $\text{In}_x\text{Ga}_{1-x}\text{As}$ alloys, where the As environment is tetrahedral. The In-As distance does not follow the Vegard's law, and remains near [18,19] to the one in InAs, 2.623 Å. In thin $\text{In}_x\text{Ga}_{1-x}\text{As}$ epitaxial alloys grown on GaAs substrates the In-Ga distance has been found [5,6] to vary between 2.57 and 2.59 Å. The bond-length is reduced with respect to the bulk value due to the constraints imposed by the lower cell parameter of the substrate with respect to the alloy. As more monolayers of the alloy are added it becomes energetically favorable for the film to collapse through a network of misfit dislocations [5]. The In-As distance is then relaxed to the bulk value. In a similar way, if the alloy becomes amorphous by ion bombardment, the bond-length also changes to the bulk value [6]

The distance we obtain is 2.56 ± 0.02 Å. This bond length is smaller than the in-plane In-Se covalent bond length in InSe (2.63 Å) and the In-As bond length in InAs (2.623 Å). This reduction can be explained on the basis of two factors:

- i) We do not expect As to be in a strained configuration when substituting Se, as happens in thin $\text{In}_x\text{Ga}_{1-x}\text{As}$ epitaxial alloys grown on GaAs substrates, because the covalent In-As bond is very close to the In-Se one. One of the reasons for the bond-length reduction could be the fact that in InSe the As impurity is bound to only 3 In atoms, in a trigonal configuration. If one compares with the standard tetrahedral configuration in InAs compound one should expect a bond length reduction, as the attractive force of the three In first neighbors in the layer is much stronger than the weak Van der Waals interlayer forces.
- ii) On the other side one has to take into account the acceptor character of substitutional As in Se site. Most substitutional acceptors in InSe have hydrogenic character, with ionization energies of the order of 50 to 60 meV and effective Bohr radii of the order of 13-14 Å [5,23]. The effective Bohr radius is much larger than the bond length and, consequently, even if the acceptor center is neutral, the proportion of the hole positive charge present at the As atom would be of the order of 0.1%. Then, from a local point of view, the As atom is singly ionized (with negative charge -e) independently of the fact that the acceptor center is ionized or neutral. This negative charge on the As_{Se} center increases the attractive force with the first neighbor cations and the repulsive force with the second neighbors (Se anions of the adjacent layer), contributing to a bond length reduction.

EXAFS analysis exclude other configurations, like an As atom substituting to In (that would yield a much shorter bond length). If such centers exist, they must be in a concentration below the detection limit of the ESRF-ID26 system, and then, well below than the As_{Se} centers that are actually detected.

References

- 1) J.P.Martinez, A.Segura, J.L.Valdes and A.Chevy, J. Appl. Phys. **62**, 1477 (1987).
- 2) A. Chevy: J. Appl. Phys. 56, 978 (1984).
- 3) A.Segura, C. Martínez, B. Marí, A. Casanovas, A. Chevy: Appl. Phys. A 44, 249 (1987).
- 4) J. Pellicer-Porres, to be published
- 5) J. C. Woicik, K. E. Miyano, J. G. Pellegrino, P. S. Shaw, S. H. Southworth and B. A. Karlin, Appl. Phys. Lett. **68**, 3010 (1996)
- 6) K. M. Yu and L. Hsu, Appl. Phys. Lett. **69**, 824 (1996).

PUBLICATIONS

A part of the results of the experiment has been published in the following paper:

J. Pellicer-Porres, Ch. Ferrer-Roca, A. Segura, L. Jacquamet and A. Chevy
"Investigation of the local structure of As-related acceptor centres in InSe by means of fluorescence detected XAS",
Semiconductor Science and Technology **17**, ---- (2002)

One other paper on $\text{In}_{1-x}\text{Ga}_x\text{Se}$ alloys is under preparation.