

Local Atomic Structure in InAs at Low Pressures. Fourier-Transform Analysis of As X-ray Absorption Spectra

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Abstract. Local structural distortions in Indium Arsenide at 11 GPa are studied applying the Fourier-transform analysis to As K-edge XAFS restricted to a short exploitable energy range of ~ 250 eV above the edge, due to the Bragg reflections from the diamond anvils. The best model for the radial distribution of In-atoms around As is obtained by combining available XRD data with a fitting procedure of the XAFS data, where alternative models for As coordination have been tested. InAs at 0.4 GPa was used as reference compound to minimize the number of variable parameters.

Keywords: InAs, pressure, XAFS, local structure distortions.

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INTRODUCTION

The structural analysis of $A^N B^{(8-N)}$ octet semiconductors under increasing pressure shows the transformation of structures with low densities to denser phases with increased coordination. This may be accompanied by a decrease of the structural symmetry [1] and in some cases [2,3] by a site disorder in the atomic local environment. The structural sequence as a function of pressure of the $A^N B^{(8-N)}$ compounds has been extensively studied by using X-Ray diffraction (XRD) [3,4]. Nonetheless, the issue of the site ordering of the high-pressure structures can be hardly assessed by XRD only, because of the Bragg peaks broadening with pressure. X-ray Absorption Spectroscopy (XAS) may be able to distinguish site order from site disorder within the nearest-neighbor distance from the photoabsorber since it probes selectively its local environment and is sensitive to the nature of the surrounding neighbors. Previous studies on InAs using different techniques have shown that up to 11 GPa this compound undergoes to a first-order phase transition from the four-fold coordinated zincblende (ZB) structure to the six-fold coordinated rocksalt structure. In a recent study [5] the analysis of As K-edge XAFS spectra of InAs in the six-fold coordinated phase has shown that the use of a single shell model for the nearest neighbor environment leads to a large Debye-Waller (DW) parameter which indicates the presence of local distortions with respect to the rocksalt structure. An accurate analysis of these distortions by XAS requires a large number of fitting variable parameters. However, the exploitable energy range of spectra at high pressure (often restricted to ~ 250 eV above the edge due to the Bragg reflections from the diamond anvils), limits the number of independent variables to $\sim 5-6$. In the present paper distortions in the local atomic structure of InAs at 11 GPa are studied by the FT-analysis of [6,7] applied to As K-edge XAFS spectra over the available range of photoelectron wave numbers ($k < 8.5 \text{ \AA}^{-1}$) and using a fitting procedure based on alternative models for the radial distribution of atoms around the ionized As. The present approach allows us to decrease the needed number of variables and the most likely model is chosen by comparing the obtained values of reduced χ^2 or χ_v^2 [8]. An additional decrease in the number of variables is obtained by fixing some parameters to values obtained from InAs at 0.4 GPa, used as the reference compound.

InAs AT PRESSURE 0.4 GPa

Diffraction data shows that InAs adopts an undistorted ZB structure in which As is tetrahedrally coordinated to four In-atoms at the same distance ($R_{\text{As-In}}$) and hence InAs at 0.4 GPa can be used as a reference compound for the structural analysis of the XAFS spectra at high pressure. Structural parameters from XRD were used for As K-XAFS calculations by the SELCOMP-code [9] based on the Hartree-Fock (HF) MT-potential [10] and by the FEFF8-code [11] with Hedin-Lundqvist exchange-correlation potential. Both theoretical spectra are in good agreement with the experimental As K-XAFS at 0.4 GPa. Figure 1 shows the experimental As K-edge XAFS of InAs at 0.4 GPa (curve 1), the theoretical spectrum for the ZB structure calculated by FEFF8 (curve 2) and the single scattering contribution of the 4 coordinating In atoms calculated by SELCOMP (curve 3). The FT analysis of the theoretical and experimental spectra was performed with FEFFIT-code [8] over the Δk -range $\sim 4.0 \text{ \AA}^{-1}$. The k_{min} value was chosen at energy $E \sim 11915 \text{ eV}$ (above the first edge-crest features) so as to minimize: i) inaccuracies in the background removal procedure in the near edge region and ii) the contribution of multiple-scattering (MS) processes into the FT resulting function $F(R)$ [7]. The FT and the fit were performed using photoelectron scattering amplitudes and phase shifts calculated by HF MT-potential model, which provides, for four-coordinated As in InAs, an interstitial potential value $E_{\text{MT}} = 11848 \text{ eV}$. This value was used to determine the photoelectrons k -scale as $k = (0.2625 (E - E_{\text{MT}}))^{1/2}$. With increasing coordination number, the E_{MT} value shifts by $\sim +1.5\text{-}2 \text{ eV}$ [9]. The FT analysis of contributions of As-In bonds with different $R_{\text{As-In}}$ distances using scattering amplitudes calculated at $R_{\text{As-In}} = 2.7 \text{ \AA}$ revealed that these HF-amplitudes are suitable for structural analysis of samples with radial distribution of As-In distances from 2.45 to 2.95 \AA . Nevertheless, the stability of the determined structural parameters was tested using the scattering amplitudes calculated also at $R_{\text{As-In}} = 3.0 \text{ \AA}$.

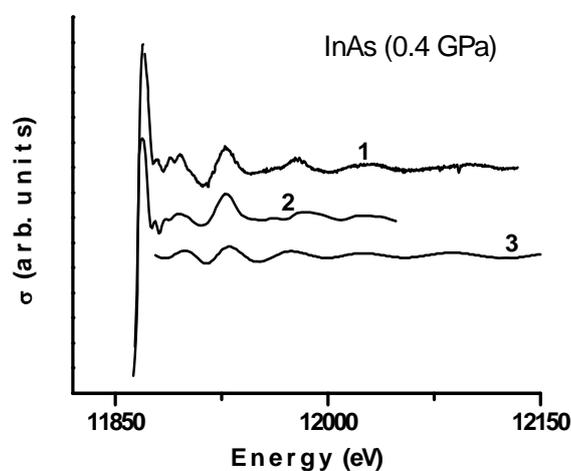


Fig. 1. Experimental As K-edge XAFS in InAs at pressure 0.4 GPa (curve 1), theoretical spectrum for the ZB-structure (curve 2) and the single scattering component of theoretical spectrum accounting for the four coordinating In-atoms (curve 3).

The results of As K-XAFS simulations and application of FT-analysis to theoretical spectra using the chosen k_{min} value show that: 1) in agreement with [6,7] the MS-processes contribution in the $F(R)$ can be neglected in the R -range up to $\sim 6 \text{ \AA}$; 2) Although Δk used for the FT is limited to 4 \AA^{-1} , this range is sufficient to determine with accuracy the structural parameters of the nearest coordinated In polyhedron without including the As-As second shell. This remains valid as long as ΔR between the As-In first shell and the As-As second shell is more than $\sim 0.7 \text{ \AA}$ (the contribution of the As-As second neighbors was accounted with As scattering amplitudes calculated at $R_{\text{As-As}} = 3.4$ and 3.8 \AA). This last condition is expected to be broken at higher pressures.

The FT-analysis was applied to experimental data at 0.4 GPa also to establish the values of parameters which can be fixed in the analysis of the high-pressure data and to test the accuracy of the used approach. For example, the value of parameter Γ , used to account for experimental energy resolution, the energy width of the core hole and the excited electron states, was chosen according to [7] giving the effective electron mean free path $\lambda_{\text{eff}}(k)$ for FEFFIT. The value of the reduction factor $S_0^2=0.82$ for the photoelectron intrinsic losses was obtained through the fit of the experimental $\chi(k)$ contribution in $F(R)$ performed with three variables S_0^2N , $R_{\text{As-In}}$, σ^2 and fixing the E_{MT} value of the HF MT-potential, by using $N=4$ for the ZB structure. The value obtained for $R_{\text{As-In}} = 2.610 \text{ \AA}$ is in excellent agreement with the XRD value (2.613 \AA). The obtained value of $\sigma^2 = 0.007 \text{ \AA}^2$ is also reasonable. To illustrate the fit quality, characterized by $\chi_v^2 = 3.2$ and R-factor = 0.005, the magnitude $|F(R)|$ and the imaginary part $\text{Im} F(R)$ of the FT of experimental As K-edge XAFS in InAs at 0.4 GPa are compared to the corresponding functions of the In single-shell model for As coordination in the ZB structure (Figure 2).

The adequacy of the values of the fixed parameters and the stability of the determined fitting parameters were tested by varying the values of the fixed parameters around the established values in physically reasonable ranges: $\Delta\Gamma = \pm 1.0 \text{ eV}$, $\Delta E_{\text{MT}} = \pm 1.0 \text{ eV}$ and observing the changes in values of the fitted parameters S_0^2N , $R_{\text{As-In}}$ and σ^2 . The above deviations showed minor divergences in the values of these parameters. The results obtained for the reference crystal InAs at 0.4 GPa show that the FT analysis of As K-edge XAFS with the available restricted energy interval yields inaccuracies in interatomic distances R determination of $\pm 0.005 \text{ \AA}$ ($\sim 1\%$) and in N -determination of $\sim 5\text{-}7\%$ which is in agreement with the results of papers [6,7] obtained through the study of smaller XANES k -ranges in disordered and amorphous compounds. It must be noted that for the structures to be determined (as for InAs at 11 GPa) the N -determination accuracy can be obtained only by using the appropriate reference compound (as InAs at 0.4 GPa) which helps to establish the S_0^2 value.

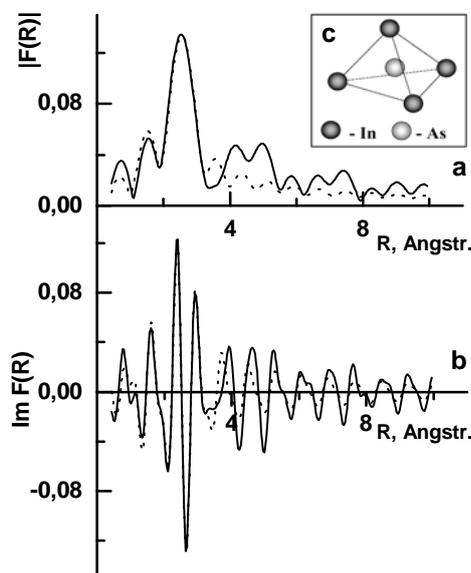


Fig. 2. (a) FT magnitudes $|F(R)|$ and (b) imaginary parts $\text{Im}F(R)$ of As K-edge XAFS in InAs at 0.4 GPa (solid curves) and of the single-shell model for coordinating In-tetrahedron (dash-dotted curves). Insert (c) shows the coordination of As at this pressure.

InAs AT PRESSURE 11 GPa

To study the expected local distortions in InAs around As at 11 GPa the FT method was applied to As K-edge XAFS spectra measured at this pressure. The fit of $F(R)$ was performed first via a single-

shell model that considers As coordinated to 6 In atoms according to [3]. Three variable parameters $R_{\text{As-In}}$, σ^2 and e_0 (the last is taken relative to E_{MT}) were used in the fit together with the other non-structural parameters obtained from the reference InAs at 0.4 GPa. An average As–In distance $R_{\text{As-In}} = 2.70 \text{ \AA}$, $e_0 = -1.7 \text{ eV}$ (typical shift value between CN= 4 and 6 [3,9]) and $\sigma^2 = 0.014 \text{ \AA}^2$ were found by this fit, characterized with the values of R-factor = 0.067 and $\chi_v^2 = 25.8$. The poor single-shell fit quality and the big value of σ^2 compared to the reference InAs at 0.4 GPa indicates, in agreement with [5], that the local environment of As in InAs at 11 GPa is not given by a single shell of 6 In atoms, but that a dispersion of As–In distances for the coordinating In atoms has to be considered. Therefore, in order to simulate the local distortion around As in InAs at 11 GPa, two- and three-shell models for the radial distribution of coordinating In atoms around ionized As have been used in the fit of $F(R)$. Table 1 shows results for some of the studied fit models with variable parameters: $R_{\text{As-In}}$ for each subshell and common σ^2 (at first) are presented. The comparison of the fit quality performed via the χ_v^2 values, unambiguously indicates the advantage of the distortion model (1+4+1) with the following radial distribution of In atoms relative to As: 1 atom at $2.55(1) \text{ \AA}$, 4 atoms at $2.73(4) \text{ \AA}$, 1 atom $3.06(1) \text{ \AA}$ and $\sigma^2 = 0.005 \text{ \AA}^2$. The fit quality of this model is illustrated in Figure 3.

TABLE 1. Fit results for coordinating In-atoms models.

Model	$R_{1,1}, \text{ \AA}$	$R_{1,2}, \text{ \AA}$	$R_{1,3}, \text{ \AA}$	$\sigma^2, \text{ \AA}^2$	χ_v^2
2+4	2.68	2.72		0.014	23.8
3+3	2.70	2.72		0.014	25.9
1+4+1	2.55	2.73	3.06	0.005	3.6
2+2+2	2.68	2.71	2.72	0.014	38.6

The validity of the selected model (1+4+1) and stability of the structural parameters obtained by it, were confirmed: i) by the fit with different fixed values of σ^2 (from 0.004 to 0.02 \AA^2) for each subshell of In atoms and ii) through the fit performed under the presence of contribution (or a background) in $F(R)$ caused by the second As–As shell. Under the limited number of variables the effect of this contribution was simulated approximately by twelve second-neighbor As atoms (according to their total number in NaCl structure), with a variable average distance $R_{\text{As-As}}$ and a variable $\sigma^2(\text{As-As})$.

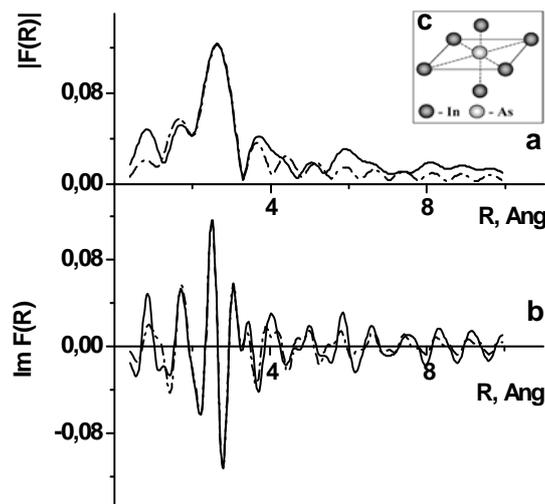


Fig. 3. (a) FT magnitudes $|F(R)|$ and (b) imaginary parts $\text{Im} F(R)$ of As K-edge XAFS in InAs at 11 GPa (solid curves) and of the (1+4+1) model for In-octahedron distortion (dash-dotted curves). Insert shows the revealed (1+4+1) model for the As local structure.

Combining the XRD value of the lattice parameter $a = 5.469 \text{ \AA}$ obtained at 14 GPa [4] with the above determined value $R_{\text{As-In}} = 2.73 \text{ \AA}$ for four In atoms, one can conclude that ionized As is located in the same plane of these four In atoms, giving the model of As local structure presented in the inset of Figure 3, compatible with the orthorhombic distortion from NaCl to Cmc structure.

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REFERENCES

1. R. J. Nelmes, M. I. McMahon, and S. A. Belmonte, *Phys. Rev. Lett.* **79**, 3668 (1997).
2. C.B. Vanpeteghem, R.J. Nelmes, D.R. Allan, M.I. McMahon, A.V. Sapelkin, S.C. Bayliss, *Physica. Status Solidi B* **223**, 405-409 (2001).
3. S. Pascarelli, G. Aquilanti, W. A. Crichton, T. Le Bihan, M. Mezouar, S. De Panfilis, J. P. Itie, and A. Polian, *Europhys. Letters* **61**, 554-560 (2003).
4. S. Pascarelli, G. Aquilanti, W. Crichton, T. Le Bihan, S. De Panfilis, E. Fabiani, M. Mezouar, J. P. Itie, and A. Polian, *High Pressure Research* **22**, 331-335 (2002).
5. G. Aquilanti and S. Pascarelli, *J.Phys.: Condens. Matter* **17**, 1811-1824 (2005).
6. L. A. Bugaev, A. P. Sokolenko, H. V. Dmitrienko, and A.-M. Flank, *Phys.Rev. B* **65**, 0241051-0241058 (2002).
7. L. A. Bugaev, J. A. van Bokhoven, A. P. Sokolenko, Ya. V. Latokha, and L. A. Avakyan, *J.Phys.Chem. B* **109**, 10771-10778 (2005).
8. M. Newville, B. Ravel, D. Haskel, J. J. Rehr, E. A. Stern, and Y. Yacoby, *Physica B* **208&209**, 154-157 (1995).
9. L. A. Bugaev, Ph. Idefonse, A.-M. Flank, and A. P. Sokolenko, *J. Phys. C* **10**, 5463-5473 (1998).
10. L. Bugaev, R. Vedrinskii, I. G. Levin, and V. M. Airapetian, *J. Phys. C* **3**, 8967-8979 (1991).
11. A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson, *Phys, Rev. B* **58**, 7565 (1998) .