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Exploring the Interplay between Structure and Electronic Behavior across Pressure-Induced Isostructural and Structural Transitions in Weyl-Type Semimetal NbAs
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Abstract: NbAs is a Weyl semimetal and belongs to the group of topological phases that exhibit distinct quantum and topological attributes. Topological phases have a fundamentally different response to external perturbations, such as magnetic fields. To obtain insights into the response of such phases to pressure, we conducted a comprehensive study on the pressure-induced electronic and structural transitions in NbAs. We used micro-X-ray diffraction (XRD) and micro-X-ray spectroscopy (XAS) techniques to elucidate the changes at different atomic and electronic length scales (local, medium, and bulk) as combined with theoretical calculations. High-pressure XRD measurements revealed a rather common compression behavior up to ~12 GPa that could be fitted to an equation of state formalism with a bulk modulus of $K_0 = 179.6$ GPa. Complementary Nb K-edge XAS data unveiled anomalies at pressure intervals of ~12–15 and ~25–26 GPa in agreement with previous literature data from XRD studies. We attribute these anomalies to a previously reported topological Lifshitz transition and the tetragonal-to-hexagonal phase transition, respectively. Analysis of EXAFS results revealed slight changes in the mean next-nearest neighbor distance Nb–As $(\sim 2.6 \text{ Å})$ at ~15 GPa, while the second nearest neighboring bond Nb–Nb $(\sim 3.4 \text{ Å})$ shows a pronounced anomaly. This indicates that the electronic changes across the Lifshitz transition are accommodated first in the medium-range atomic structure and then at the local range and bulk. The variances of these bonds show anomalous but progressive evolutions close to the tetragonal-to-hexagonal transition at ~25 GPa, which allowed us to derive the evolution of vibration properties in this material. We suggest a prominent displacive character of the $I4_1md \rightarrow P\bar{6}m2$ transition facilitated by phonon modes.

Keywords: Weyl semimetal; NbAs (niobium arsenide); high-pressure X-ray diffraction; high-pressure X-ray absorption

1. Introduction
Weyl semimetals (WSMs) represent an advancement beyond previously known topological phases [1–3], such as the topological insulators. The intriguing aspect of WSMs lies in the potential to realize Weyl fermions at lower energy scales, in contrast to the typical GeV–TeV ranges needed for high-energy physics [4,5]. In fact, a high-energy Weyl fermion was postulated to be a massless spin-1/2 particle back when the Dirac equation was derived [6], and it was later interpreted as a neutrino. In WSMs, all of the aspects behind the chirality property can be probed as a reliable condensed matter analogous. This unique property gives rise to fascinating bulk and surface phenomena, including the chiral
anomaly, which is associated with a negative magnetoresistance observed in transport experiments under simultaneous low-temperature and high magnetic fields \cite{7,8}. The electronic band structure of a WSM exhibits definite chiral charges, characterized by band crossings known as Weyl nodes resulting from strong spin-orbit coupling, paving the way for novel applications and technologies based on these materials \cite{2,9}, such as efficient thermoelectric generators, topological electronics (or Weyltronics), and magnetic devices.

The realization of Weyl semimetals faces a significant bottleneck due to the difficulty in obtaining large single crystals without multiple nucleation spots \cite{10,11}. These extrinsic defects may hinder a precise characterization of the electronic properties at both surface and bulk levels. Among the few known systems, the most significant include the family of pnictogens containing tantalum or niobium elements, such as TaP, TaAs, NbP, and NbAs. For instance, the Weyl semimetallicity in TaP was confirmed through the observation of negative magnetoresistance in this system at low temperatures and high magnetic fields, attributed to the chiral anomaly \cite{12}. In NbAs, the Weyl fermion state through Weyl nodes and their chiral charge were confirmed by numerical calculations and experimental results \cite{5}. In fact, NbAs has unique physical properties, for example, large electron mobility and magnetoresistive coupling \cite{5,7}, that make it promising for different applications, such as novel thermoelectric generators and quantum computing. From the topological point of view, the anomalous Hall effect of this system was already reported and attributed to the Berry curvature induced by the pairs of Weyl points near the Fermi level \cite{9,13}. However, further studies are necessary to precisely elucidate its topological features and evaluate its potential applications in quantum technologies.

At ambient conditions, NbAs crystalizes in a tetragonal unit-cell within the non-centrosymmetric space-group \textit{I}4\textsubscript{1}md. The broken inversion symmetry is crucial for the existence of the Weyl semimetal phase, which in contrast preserves time-reversal symmetry \cite{14,15}. It is known that exotic phase transitions in materials can be induced through the application of pressure, potentially leading to the emergence of new electronic or magnetic quantum phases \cite{16–25}. In NbAs, theoretical calculations predicted a sequence of pressure-induced structural transitions from tetragonal-to-hexagonal (another topological phase with different Weyl node geometry) and subsequently the transition from monoclinic to cubic as follows: \textit{I}4\textsubscript{1}md $\rightarrow$ \textit{P}6\textsubscript{m}2 $\rightarrow$ \textit{P}2\textsubscript{1}/c $\rightarrow$ \textit{Pm}3\textsubscript{m} \cite{26}. The tetragonal-to-hexagonal transition has been confirmed by previous experimental studies, but the onset pressure differs between ~23 \cite{26} and ~26 GPa \cite{11}. In addition, Gupta et al. \cite{27} found evidence for an isostructural topological Lifshitz transition in NbAs at ~15 GPa. This transition is characterized by a slight change in volume compression and the hardening of phonon modes as observed from complementary Raman data. Detailed knowledge of the underlying structural and electronic changes across these transitions at various length scales (local, medium, and bulk) would be needed to uncover new functionalities in NbAs and in topological materials in general. However, such data are presently not available due to the experimental challenges.

In Weyl semimetals, the bulk and local properties are as significant as the surface topological features, which are typically examined using UPS and ARPES techniques \cite{5}. This amplifies the importance of bulk and local probe techniques, such as structural methods like X-ray diffraction \cite{8,28} and X-ray absorption spectroscopy \cite{29}. Here, we examined the electronic and structural phase transitions in NbAs under high pressure from 0 to 40 GPa at room temperature at various length scales using XRD (bulk scale), XANES (medium scale), and EXAFS (local scale). Through the combination of XANES and EXAFS techniques at Nb K-edge, we could confirm the previously reported topological Lifshitz transition. Our data further provide important details of this transition mechanism, revealing abrupt changes in the bond length evolution. In addition, the pressure-induced tetragonal-to-hexagonal phase transition in this system was thoroughly characterized using EXAFS data. Based on the observed progressive evolutions of local structural parameters across this transition, we argued that this structural phase transition exhibits a prominent displacive character, facilitated by phonon modes.
2. Materials and Methods

2.1. NbAs Single Crystals

The crystal growth and initial laboratory-based characterizations were performed by Zhiwei Hu’s group, confirming the crystallization of niobium arsenide (NbAs) within the non-centrosymmetric tetragonal phase ($I4_1md$). Selected crystal pieces were finely ground into powder for X-ray diffraction and X-ray absorption spectroscopy studies.

2.2. Synchrotron X-ray Diffraction and Analysis

High-pressure X-ray diffraction studies were conducted on the high-pressure/microdiffraction station of beamline BL04-MSPD (ALBA, Barcelona) [30], with an incident monochromatic beam with $\lambda = 0.4246$ Å (Cd K-edge). A Rayonix CCD detector placed at 220.125 mm to the sample position was used for recording the 2D X-ray images. Both sample-to-detector distance and beam center position were calibrated from the LaB$_6$ diffraction patterns collected under the same conditions as the sample. The X-ray images were recorded in continuous $\omega$-scan in a range of $-3^\circ \leq \omega \leq +3^\circ$.

The pressure generation was enabled by a membrane-type LeToullec-type diamond anvil cell (DAC), equipped with Ia-type single-crystalline diamonds having culet sizes of 400 µm. The sample chamber consisted of a pre-indent stainless-steel gasket of 35 µm thickness in which a hole diameter of 140 µm was laser drilled. The sample chamber was filled with micro-grains of NbAs after fine grinding in an agate mortar and placed in the center, and several micro ruby spheres near the sample served as the pressure gauge using the EOS reported by Shen et al. [31]. The error in pressure estimation was found to be within the range of 0.05–0.1 GPa, based on the average measurements from various rubies. The remaining sample chamber was filled with silicone oil serving as the pressure-transmitting medium (PTM).

X-ray diffraction images were integrated using the Dioptas software [32]. The integrated 1D patterns were subsequently refined using the Rietveld method and Fullprof software [33]. The parameters refined comprised the zero-point error, background parameters, scaling factor, and lattice parameters. A preferential orientation along the (0 0 1) direction (c-axis) hindered a precise evaluation of the atomic positions and isotropic displacements of Nb and As atoms. Therefore, these parameters were kept fixed during the structural refinements.

2.3. X-ray Absorption Spectroscopy

High-pressure X-ray absorption measurements at the Nb K-edge (18.986 keV) were conducted on the X-ray absorption beamline BM23 (ESRF, Grenoble, France) [34,35]. The incoming beam was monochromatized by a fixed-exit double crystal monochromator containing two LN$_2$-cooled Si(1 1 1) crystals. For pressure-dependent measurements, the X-ray beam was focused down to $3 \times 3$ µm$^2$ (FWHM) using two Pt-coated mirrors in the standard Kirkpatrick–Baez geometry (an incidence angle of 2 mrad), also acting for higher harmonics rejection.

The pressure was generated using a membrane-driven LeToullec-type DAC. This cell was equipped with nanopolycrystalline diamond (NPD) anvils of 250 µm culet size. For the sample chamber, a pre-indent reheminum gasket was used, having a final thickness of 40 µm and a laser-drilled hole in the center of 120 µm in diameter. The sample chamber was filled with ground NbAs powder together with ruby spheres serving as pressure sensors [31] and silicone oil as the PTM. All absorption measurements were recorded in axial geometry (i.e., in transmission mode) through the NPD anvils [36]. An edge jump ($\Delta\mu\chi$) of 0.9 at ~0.1 GPa was obtained for this 40 µm pre-indentend sample chamber.

The XAS spectra were recorded up to 22 Å$^{-1}$ in $k$-space with a precise step scanning of 0.25 eV for the near-edge range (XANES) and $\delta k$ stepping of 0.035 Å$^{-1}$ for EXAFS. The data reduction was performed using a dedicated Python code, which included obtaining the edge position $E_0$ from the XANES first derivative, the subtraction of the pre-edge background, and the mono-atomic background subtraction in the post-edge range. This
allowed a normalization of the edge jump and the extraction of the EXAFS function $\chi(k)$ from the absorption coefficient $\mu(k)$, in agreement with the relation $\mu(k) = \mu_0[\chi(k) + 1]$, where $\mu_0$ represents the absorption coefficient of the isolated absorber atom.

2.4. EXAFS Fitting

EXAFS data were fitted using the Artemis software [37]. For this purpose, the theoretical scattering paths for the tetragonal phase of niobium arsenide within the space-group $I4_1md$ [38] were calculated using FEFF software [39]. Our local structural model for NbAs comprised four single scattering paths: Nb–As$_{(1)}$ (~2.63 Å, CN = 6), Nb–Nb$_{(1)}$ (~3.47 Å, CN = 8), Nb–As$_{(2)}$ (~4.36 Å, CN = 4), and Nb–Nb$_{(2)}$ (~4.87 Å, CN = 8). Here, CN stands for the coordination number or coordination environment. A diagram of these single scattering paths is shown in Figure S1. The pair Nb–As$_{(1)}$ forms a trigonal prismatic [NbAs$_6$] unit, which serves as the building blocks of the NbAs crystal structures [38]. The backscattering amplitude [$F(k)$] and phase [$\phi(k)$] for individual paths calculated using FEFF are shown in Figure S2. For the hexagonal high-pressure phase of NbAs, the same paths Nb–As$_{(1)}$, Nb–Nb$_{(1)}$, Nb–As$_{(2)}$, and Nb–Nb$_{(2)}$ having the same coordination number and similar distances can be employed. As will be discussed later, a high-pressure phase with a hexagonal unit-cell is observed for NbAs. We tested the EXAFS fitting using both phases, and the results are quite similar. This occurs because both $F(k)$ and $\phi(k)$ are quite identical for the tetragonal and hexagonal phases. For the fitting procedure, the Fourier transforms (FT) of $k$-weighted EXAFS functions $\chi(k) \cdot k^2$ were performed using a Hanning-type window. The window size was set in $k$- and $R$-spaces to the ranges of $\Delta k = 3.5–19.5$ Å$^{-1}$ and $\Delta R = 1.5–5.0$ Å, respectively. Fitting parameters included the mean pair distances ($R_\Gamma$) and their variances ($\sigma^2_\Gamma$), while the coordination numbers were kept as fixed parameters [40]. The amplitude reduction factor ($S^2_\mu \approx 1.05$) was deduced from the fit of a Nb foil EXAFS spectrum measured during the same experiment.

2.5. Computational Methods

Theoretical Nb K-edge XANES spectra were calculated in the energy range $-10–70$ eV (in units of $E - E_F$, where $E_F$ is the Fermi level energy), using the real-space FDMNES code [41]. Green’s method was applied to solve the relativistic extension of the Schrödinger equation expanded up to the quadrupole term. The Nb-centered cluster radius was set to 9 Å. We used four structural models of NbAs, as detailed in Table S1, as the input crystal structures. The self-consistency (SCF) of the potential was used for a better estimation of the energy cutoff level. The spectral broadening was generated by an energy-dependent Lorentzian to represent the XANES spectra from the density of states (DOS).

Wilson’s GF-matrix method was utilized to perform the lattice dynamics calculations of the first-order Raman and infrared active modes of the tetragonal NbAs crystal structure. For these calculations, we employed the VIBRATZ software written by Dowty [42]. Further details and application examples of this method can be found elsewhere [43–46].

3. Results

The results section of this paper is organized as follows: First, the results from X-ray diffraction data on the pressure evolution of the bulk crystal structure up to 14.1 GPa are presented. Then, the results from X-ray absorption spectroscopy up to 40 GPa are shown, including, first, the findings from XANES that allow us to access structural and electronic properties of NbAs at the medium-range order, followed by the observations from EXAFS that provide detailed insights into the local atomic structure evolution and vibrational properties in NbAs.

3.1. Pressure Evolution of the Bulk Structure of NbAs

The integrated X-ray diffraction patterns of NbAs as a function of pressure are shown in Figure 1a. All of the peaks in these patterns could be fitted using the tetragonal phase of NbAs within the space-group $I4_1md$ (#109) and four formula units ($Z = 4$). We ob-
served no apparent changes in the peak distribution up to 14.1 GPa and only shifts of the peak positions to higher 2θ angles as a result of unit-cell compression. We measured points under decompression, and the crystal structure was completely recovered down to ~0 GPa (see Figure S3). For the tetragonal phase, Nb occupies 4a sites (0, 0, z ≈ 0), As is at 4a (0,0,0.416) [38], and the lattice parameters found here at 0 GPa are a = 3.4537(9) Å and c = 11.684(4) Å. These values are in close agreement with the reported crystal structure of NbAs at room conditions [5,11].

Figure 1. Panel (a): Raw X-ray diffraction pattern collected under pressure in the interval 0–14.1 GPa. The Miller index (hkl) for each peak is shown. The green vertical bars at the bottom denote the expected Bragg reflections from the tetragonal phase (I4_1 md). Panel (b): Unit-cell volume as a function of pressure and best fitting using three EOS formulations for NbAs, namely Murnaghan (M) [47], Birch–Murnaghan (BM) [48], and Rose–Vinet (RV) [49]. Panel (c): The difference between experimental points with comparable curve fitting. The difference between experimental and fitted points is shown.

The tetragonal structural model was also taken for the refinement of the pressure-dependent XRD data up to 14.1 GPa. From the obtained lattice parameters, the experimental volume data were derived, as shown in Figure 1b and listed in Table S2. At 14.1 GPa, the unit-cell volume of tetragonal NbAs contracted by ~5.5% compared to ambient pressure. To describe the volume contraction, we fitted three different equation of state formulations (EOS), namely Murnaghan (M) [47], Birch–Murnaghan (BM) [48], and Rose–Vinet (RV) [49]. This analysis enabled a precise evaluation of the following parameters: unit-cell volume at 0 GPa (V_0), bulk modulus (K_0), and its first derivative [(K'_0 = \partial K_0/\partial P, kept as a free variable). The best-fitted parameters for the EOS of NbAs are listed in Table 1. In Figure 1b, all of the equations of state (EOS) formulations effectively matched the experimental points with comparable curve fitting. The difference between experimental and fitted points is shown in Figure 1c. In Table 1, the goodness of fit parameters (R^2) for all formulations presented quite uniform values. In this way, the mean EOS parameters can be set as \( V_0 = 139.2 \text{ Å}^3, \langle K_0 \rangle = 179.6 \text{ GPa} \), and \( \langle K'_0 \rangle = 10.9 \). Our mean bulk modulus aligns closely with that reported by Gupta et al. \( K_0 = 180(6) \text{ GPa} \) [27] and that calculated using DFT methods \( K_0 = 163 \text{ GPa} \) [50].
Table 1. Parameters of the EOS derived by least-squares fit of the experimental high-pressure data for niobium arsenide (NbAs).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Murnaghan †</th>
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<th>Rose–Vinet †</th>
<th>DFT #</th>
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<td>139.23 (0.14)</td>
<td>139.24 (0.13)</td>
<td>141.92</td>
</tr>
<tr>
<td>K₀ (GPa)</td>
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<td>179.3 (16.6)</td>
<td>179.2 (15.1)</td>
<td>163</td>
</tr>
<tr>
<td>K'₀</td>
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<td>11.4 (3.5)</td>
<td>11.0 (2.7)</td>
<td>-</td>
</tr>
<tr>
<td>R²</td>
<td>0.99573</td>
<td>0.99565</td>
<td>0.99567</td>
<td>-</td>
</tr>
</tbody>
</table>

† Three EOS formalisms were tested, namely Murnaghan (M) [47], Birch–Murnaghan (BM) [48], and Rose–Vinet (RV) [49]. # Extracted from structural dataset on the Materials Project webpage [50].

3.2. XANES Analysis

Normalized Nb K-edge XANES spectra recorded in the range of 0.1–40 GPa are shown in Figure 2a (vertically shifted). The ambient XANES spectrum exhibits four clear features or peaks characterized by elevated absorption values at specific energies (labeled as α, β, γ, and δ in Figure 2). The energy position and the shape of the features γ and δ show the most pronounced variations with pressure. All of the features evolve progressively without discontinuity. For instance, the feature γ at ~19.024 keV, which defines a very weak shoulder on the second XANES peak at ambient conditions, intensifies progressively and can be clearly distinguished up to ~14 GPa. In contrast, the intensity of the δ feature found at ~19.046 keV, which defines the third XANES peak, decreased systematically until 40 GPa, accompanied by the broadening of the third XANES peak.

![Figure 2](image-url)  
Panel (a): Raw normalized Nb K-edge under high pressure in the range of 0.1–40 GPa. Panel (b): Theoretical XANES spectra calculated using four crystal structures as follows: I₄₁md (tetragonal), P₆₃m2 (hexagonal), P2₁/c (monoclinic), and Pm₃m (cubic) [26]. The energy scale is represented in units of E − E_F (E_F, the Fermi level energy). Panel (c): These crystal structures predicted by DFT [26] are represented. Vertical dashed lines are guides for the eye to follow the features (α, β, γ, and δ).

The theoretical XANES spectra calculated for the four crystal structures of NbAs are presented in Figure 2b. These structural models comprised the tetragonal I₄₁md...
already observed at room conditions and the predicted high-pressure phases, including the hexagonal $P\overline{6}m2$, the monoclinic $P2_1/c$, and the cubic $Pm\overline{3}m$ structures [26] (see Figure 2c), as summarized in Table S1. From the comparison between the theoretical and experimental XANES spectra, it is evident that both tetragonal and hexagonal phases closely resemble the experimental data, as all the XANES features ($\alpha$, $\beta$, $\gamma$, and $\delta$) can be accurately reproduced. This is not the case for both monoclinic and cubic phases, which exhibited significant spectral changes and an increased number of spectral features. We note that the simulated XANES spectra of the hexagonal $P\overline{6}m2$ exhibit a more enhanced $\gamma$ feature compared to the tetragonal phase. It can be therefore used as an indicator for the phase transition previously observed from XRD [27]. Indeed, with increasing pressure, this feature intensifies also in the experimental data above ~25 GPa.

In Figure 3, the pressure dependency of the edge energy shift [$\Delta E(P) = E(P) - E(P_0)$, $P_0 = \sim$-0.1 GPa] is shown. The edge position $E(P)$ was extracted from the first maximum of the XANES first derivative and compared to the position at ~0.1 GPa [$E(P_0)$]. The edge energy distinctly shifted toward higher energies under compression, displaying an almost linear trend until ~12 GPa. Between ~12 and ~13 GPa, a clear discontinuity in the pressure evolution of the edge energy shift is apparent. Above this pressure, the edge energy shift stagnates up to ~26 GPa before it increases again up to the maximum probed pressure of ~40 GPa.

![Figure 3](image.png)

**Figure 3.** Edge energy shift of Nb K-edge energy as a function of pressure. The pressure-induced shift was assessed relative to edge position under near ambient pressure (~0.1 GPa).

### 3.3. EXAFS Analysis

We first evaluated the local atomic structure of NbAs under near-ambient conditions, principally because under these conditions, the most reliable structural data are reported. In Figure 4a, the $k$-weighted raw oscillation $\chi(k)\cdot k^2$ (open symbols) at ~0.1 GPa is presented. Individual contributions from the single scattering paths (orange and green lines) are also shown together with the best fit (black lines). In Figure 4b, the modulus and real part of FT signals in $R$-space are plotted (here, $R$ is not phase-shift corrected). The fitted EXAFS parameters for NbAs at ~0.1 GPa are listed in Table 2, as well as the corresponding pair distances from extracted XRD data. The alignment between the raw data and the fitted EXAFS indicates the reliability of our structural model. This is evidenced by the low-level fit residuals observed in both panels (a) and (b).
The same EXAFS model was applied to fit the pressure-dependent spectra. The fitting convergence remained satisfactory, with R-factors varying between ~0.010 and ~0.023, with maximum values occurring in the range of 23–30 GPa. The experimental and best-fitted weighted oscillations $\chi(k) \cdot k^2$ for niobium arsenide, at selected pressure points, are shown in Figure 5a. In the range of 0–13 GPa, clear features at ~8 Å in $k$-space started progressively to disappear. The corresponding Fourier transforms (FT) of $|\chi(k)|^2$ are displayed in Figure 5b. In fact, four FT peaks can be recognized at ~0.1 GPa, occurring at ~2.2, 3.2, 4.0, and 4.5 Å (not phase-shift corrected), corresponding to the paths Nb–As(1), Nb–Nb(1), Nb–As(2), and Nb–Nb(2), respectively. Under pressure, the first peak shifted to lower radial distances. Interestingly, those peaks located in the $R$-range 3–5 Å display a significant intensity reduction above the interval 13–15 GPa.

![Figure 4](image)

**Figure 4.** Panel (a): Raw Nb K-edge EXAFS oscillations under near-ambient conditions (~0.1 GPa) (blue open symbols) together with individual single scattering paths [orange: Nb–As(1), green: Nb–Nb(1), Nb–As(2), and Nb–Nb(2)] and the fitted EXAFS signal (black line). Panel (b): Fourier transform of $\chi(k) \cdot k^2$ raw data, individual scattering paths, and summed paths. The fit residuals are depicted at the bottom of each panel.

<table>
<thead>
<tr>
<th>Path</th>
<th>$R_F$ (Å)  †</th>
<th>$\sigma^2_\Gamma \times 10^{-3}$ Å² †</th>
<th>CN †</th>
<th>$d$ (Å) †</th>
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<tr>
<td>Nb–As(1)</td>
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<td>3.4 (1)</td>
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<td>2.635</td>
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<td>6.5 (3)</td>
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<td>3.443</td>
</tr>
<tr>
<td>Nb–As(2)</td>
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<td>5.3 (9)</td>
<td>4</td>
<td>4.357</td>
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<td>$R$-factor</td>
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<tr>
<td>$\Delta k$ (Å⁻¹)</td>
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<td>$\Delta R$ (Å)</td>
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</tr>
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<td>35</td>
<td>$N_0$</td>
<td>9</td>
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† $R_F$ represents the mean pair distances, $\sigma^2_\Gamma$ the pair-distance variances, CN the coordination numbers (kept as fixed variables), and $d$ the mean pair distances from XRD data under room condition [38].

The same EXAFS model was applied to fit the pressure-dependent spectra. The fitting convergence remained satisfactory, with R-factors varying between ~0.010 and ~0.023, with maximum values occurring in the range of 23–30 GPa. The experimental and best-fitted weighted oscillations $\chi(k) \cdot k^2$ for niobium arsenide, at selected pressure points, are shown in Figure 5a. In the range of 0–13 GPa, clear features at ~8 Å in $k$-space started progressively to disappear. The corresponding Fourier transforms (FT) of $|\chi(k)|^2$ [moduli $|\chi(R)|$] are displayed in Figure 5b. In fact, four FT peaks can be recognized at ~0.1 GPa, occurring at ~2.2, 3.2, 4.0, and 4.5 Å (not phase-shift corrected), corresponding to the paths Nb–As(1), Nb–Nb(1), Nb–As(2), and Nb–Nb(2), respectively. Under pressure, the first peak shifted to lower radial distances. Interestingly, those peaks located in the $R$-range 3–5 Å display a significant intensity reduction above the interval 13–15 GPa.

Table 2. Structural parameters of NbAs under near-ambient conditions (~0.1 GPa) extracted from EXAFS fitting to the Nb K-edge spectrum. The data are compared to those extracted from XRD refinement of the pattern under ambient conditions.

<table>
<thead>
<tr>
<th>Path</th>
<th>$R_F$ (Å) †</th>
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</table>

† $R_F$ represents the mean pair distances, $\sigma^2_\Gamma$ the pair-distance variances, CN the coordination numbers (kept as fixed variables), and $d$ the mean pair distances from XRD data under room condition [38].
Figure 5. Panel (a): Pressure-dependent EXAFS data at selected pressures: $k^2$-weighted oscillations $\chi(k) \cdot k^2$ in $k$-space. Panel (b): Moduli of Fourier transform $\chi(R)$ in $R$-space. The open symbols represent the raw experimental data collected under compression, while the black lines denote the best EXAFS fit. Vertical dashed lines are guides for the eye.

The mean pair distances ($R_\Gamma$) and their variances ($\sigma_\Gamma^2$) for the paths Nb–As$_{(1)}$ and Nb–Nb$_{(1)}$ are shown in Figure 6. As can be seen in Figure 6a, the bond distance Nb–As$_{(1)}$ reduces by ~5.2% during the compression from 0.1 to 40 GPa. We noticed a subtle change in the evolution of the bond compressibility above ~15 GPa and 25 GPa. Interestingly, the pressure evolution of mean distance for the path Nb–Nb$_{(1)}$ also exhibits changes in the slope above ~12 GPa and 25 GPa (Figure 6c). In Figure 6b, the pressure evolution of the variances ($\sigma_\Gamma^2$) of the Nb–As$_{(1)}$ bond can be recognized. It displays a constant decrease until ~25 GPa and an increase above this pressure. In contrast to the Nb–As$_{(1)}$ bond, the distance variance of the Nb–Nb$_{(1)}$ bond increased monotonically until ~15 GPa, as shown in Figure 6d. Above this pressure, it increases rapidly up to ~25 GPa and then remains almost constant until ~40 GPa. We noticed an increase in error bars for the path Nb–Nb$_{(1)}$ parameters above ~15 GPa, which is possibly related to the decreasing signal strength with pressure, as shown in Figure 5b.
Figure 6. Pressure dependence of the EXAFS parameters and mean pair distances ($R_{p}$) and their respective variances ($\sigma_{R_{p}}^2$). Panel (a): scattering path Nb–As(1) and Panel (b): its length variance. Panel (c): scattering path Nb–Nb(1) and Panel (d): its length variance.

4. Discussion

4.1. Pressure Evolution of the Bulk Structure

The XRD results of this study suggest that the tetragonal NbAs remains stable up to 14.1 GPa (Figures 1 and S4). Although a slight change in compression behavior above ~12 GPa can be observed, the variation remains within the error bars, and, thus, a potential transition cannot be clearly assigned at this pressure. Two previous experimental studies have also reported on the high-pressure behavior of the bulk structure of NbAs using XRD methods coupled to the DAC technique, employing silicone oil [11] and a methanol–ethanol mixture [27] as PTM. Gupta et al. [27] reported a topological Lifshitz transition at ~15 GPa, which was characterized by a slight change in volume compression and the hardening of phonon modes as observed from complementary Raman data. This transition does not affect the bulk crystal structure but the Fermi surface, and it is accompanied by a drastic alteration of the electronic properties, evident as a drop in resistivity [27]. Zhang et al. [11] also argued that tetragonal NbAs maintains stability up to the highest probed pressure in this study of 26 GPa. These observations from experimental works agree with those reported from first-principles calculations [26]. Afterward, the tetragonal NbAs undergoes a sequence of pressure-induced transitions as follows: the tetragonal phase transforms at 23 GPa to the hexagonal phase ($P6_{3}m2$), at 38 GPa to the monoclinic phase ($P2_1/c$), and subsequently to a cubic phase ($Pm3m$) at 73 GPa. The cubic phase remains stable up to the highest point simulated (~200 GPa).

4.2. Pressure Evolution of the Medium-Range Structure

From the spectral simulations of experimental XANES spectra, we could show that the proposed monoclinic and cubic high-pressure phases did not match the experimental XANES features ($\alpha$, $\beta$, $\gamma$, and $\delta$). In contrast, the simulated spectra of the tetragonal and hexagonal phases exhibited remarkable similarity, in particular the feature $\gamma$, which is slightly more intense for the hexagonal phase. Interestingly, the experimental data also show an intensifying of this feature above ~25 GPa, which could indeed indicate...
a progressive transition from tetragonal-to-hexagonal NbAs consistent with previous works [11,26,27].

Electronic transitions can lead to pronounced changes in the energy position of the white line of a XANES spectrum as it is directly linked to the DOS and Fermi level. As can be seen in Figure 3, the evolution of the edge energy shift revealed a clear discontinuity at ~12 GPa. Because of the absence of strong anomalies in the bulk structure and in the pressure evolution of the Nb–As or Nb–Nb bonds at this pressure (Figure 6), this discontinuity suggests a change in the electronic configuration of NbAs. This observation may likely support the Lifshitz-type transition [27]. In fact, a key aspect of this transition is the reduction in the density of states due to changes in the Weyl points at the Fermi level [51]. In this process, DFT calculations have shown that high pressure induces variations in the size and shape of electron-hole pockets at the $\Sigma$- and $N$-points of the Fermi surface, beginning at 12 GPa and completing at 16 GPa [27]. Based on our XANES results, we can infer that this variation at the Fermi surface can be detected from the edge position discontinuity at ~12 GPa and blueshift, as illustrated in Figure 3. We may also consider strain effects from the PTM used for XAS experiments, such as silicone oil, as a potential catalyst for the anomaly at ~12 GPa. However, this effect appears to be more crucial for bulk properties observed in XRD data and has a lesser impact on the medium and local structure [52–55].

At higher pressures and above 26 GPa, we observed another change in the evolution of the edge energy shift, possibly related to the completion of the structural transition from $I4_1m\bar{d}$ to $P6m2$. This structural transition has been associated with a change in the electronic properties of NbAs from semimetal to metal [26].

4.3. Pressure Evolution of the Short-Range Structure

The analysis of Nb K-edge EXAFS data unveiled that both mean pair distances Nb–As(1) and Nb–Nb(1) exhibited pronounced changes in their compression behaviors at ~15 GPa. These discontinuities appear at slightly higher pressures compared to the one observed in the XANES edge energy shift at ~12 GPa. This may suggest that the change in electronic configuration due to the Lifshitz transition may act on the bond compressibility. Across the Lifshitz transition, no anomalies in the pair-distance variances of Nb–As(1) could be noticed (Figure 6b). The path variances of Nb–As(1) and $\sigma^2_{\text{Nb-As}(1)}$ decreased progressively in the range of 0–25 GPa, denoting a hardening of the associated main bond vibration that contributes to this pair-distance variance. In contrast, the pair-distance variance of Nb–Nb(1) and $\sigma^2_{\text{Nb-Nb}(1)}$ exhibited a distinct sudden increase above ~15 GPa, which suggests that the electronic changes associated with the Lifshitz transition act on the vibrational properties of the medium-range structure, notably in enhancing a softmode behavior that may be a precursor of the tetragonal-to-hexagonal transition that follows at higher pressure (Figure 6d).

The pressure evolutions of all of the examined local structural parameters unveil no discontinuities across the tetragonal-to-hexagonal phase transition and evolve progressively. The bond distances Nb–As(1) and Nb–Nb(1), as well as the bond distance variance Nb–Nb(1), revealed only a slight change in the compression behavior or stagnation. Most interestingly is the variation of the Nb–As(1) bond length variance, $\sigma^2_{\text{Nb-As}(1)}$, that decreases progressively in the tetragonal phase after the Lifshitz transition up to 25 GPa. Above this pressure, $\sigma^2_{\text{Nb-As}(1)}$ increases again with a softmode-type behavior [56]. The pressure evolution of $\sigma^2_{\text{Nb-As}(1)}$ is consistent with the proposed stiffening of all of the Raman-active modes in both NbAs near the tetragonal-to-hexagonal transition [27].

The EXAFS findings unravel the significant contribution of vibrational mode changes in the Nb site during the structural transition from the tetragonal to the hexagonal phase. In the tetragonal structure, Nb atoms occupy 4a sites, characterized by point symmetry $C_2h$. This symmetry is distinguished by its principal axis ($C_2$) and includes two vertical mirrors ($\sigma_v$). In the hexagonal phase, Nb atoms are positioned on higher symmetry 1c sites described by dihedral point symmetry $D_{3h}$. This dihedral group encompasses the
axes $C_3$, $C_2$, and $C_{3h}$, along with the vertical ($\sigma_v$) and horizontal ($\sigma_h$) mirrors. The local structural environments around the Nb sites in both the tetrahedral and hexagonal phases are illustrated in Figure 7, highlighting the changes in the pair distances Nb–As(1) and Nb–Nb(1) near ~25 GPa.

Figure 7. Panel (a): Representation of local environment around Nb atom at the onset of structural transition from tetragonal to hexagonal phases in NbAs, with scattering path Nb–As(1) forming the trigonal prismatic [NbAs₃] units and Panel (b): scattering path Nb–Nb(1). Symmetry elements belonging to the point group $C_{2v}$ ($C_2$ and $\sigma_v$, in tetragonal phase) and $D_{3h}$ ($C_{3h}$ and $\sigma_h$, in hexagonal phase) are also shown.

Notably, the coordination numbers equal to six and eight for paths Nb–As(1) and Nb–Nb(1), respectively, were maintained across the phase transition, as shown in Figure 7. However, changes in bonding topology due to the $C_{2v} \rightarrow D_{3h}$ transition of the trigonal prismatic [NbAs₃] units can be recognized. For instance, the spatial arrangements of the Nb–As bond were altered from $[4 \times \text{As} \oplus 2 \times \text{As}]$ to $[3 \times \text{As} \oplus 3 \times \text{As}]$, as shown in panel (a). In this sense, pressure initially confines the Nb–As vibration (hardening effect) and, subsequently, induces a change at ~25 GPa in the bond topology, leading to an increase in $\sigma_{\text{Nb–As}(1)}^2$. Near pressure-induced structural transitions, indeed, typical anomalies in pair-distance variance may occur in several compounds, as, for example, in YH₃ [57], CuO [58], and La₁/₃NbO₃ [59]. For the pair Nb–Nb(1) in Figure 7b, it is noteworthy that the formation of both the $C_{3h}$ axis and horizontal mirror ($\sigma_h$) continuously alters the vibrational patterns, which may explain the increase in the value of $\sigma_{\text{Nb–Nb}(1)}^2$ above ~25 GPa.

In Table S3, a detailed factor-group analysis predicting the Brillouin zone center vibrational modes [60] for both the tetrahedral and hexagonal phases revealed that the $C_{2v}$ site ($I4_1md$) contributes with four modes: $A_1(R,IR) \oplus B_1(R) \oplus 2E(R,IR)$. In contrast, the $D_{3h}$ site ($P6m2$) provides two modes: $A''_2(1R) \oplus E'(R,IR)$. Here, R and IR designate the Raman and infrared activity, respectively. Both NbAs phases are non-centrosymmetric; therefore, it is expected that some modes are both Raman- and infrared-active, as exemplified by the $A_1$ mode in the $I4_1md$ phase and the $E'$ mode in the $P6m2$ phase. A brief description of the vibrational modes of tetragonal NbAs is presented in Figure S5. Here, theoretical calculations were performed employing Wilson’s GF-matrix [42], with details provided in Table S4. Attention should be directed toward the $A_1(R,IR)$ mode at 230 cm⁻¹ (expt. 270 cm⁻¹), distinguished by the out-of-phase translation of Nb and As along the c-axis, potentially representing the most influential vibration for $\sigma_{\text{Nb–As}(1)}^2$. The $E(R,IR)$ mode is also particularly interesting due to its strong bending behavior, which
reduces atomic displacements along the Nb–As bond. As a result, it can be influenced by motion stiffness before the transition. In the hexagonal phase, only one Raman mode is expected to occur, \( E'(R, 1R) \), which results from the symmetrization of the unit-cell and from the collapse of \( A_1(R, 1R) \) and \( B_1(R, 1R) \) vibrations. This collapse typically results in frozen vibrational modes due to symmetry restrictions and is associated with a displacive mechanism \([56]\), leading to the emergence of a high-symmetry phase after the transition completion, as, for example, in ReO\(_3\) \([61]\) or BaZrO\(_3\) \([62]\). In this scenario, we can argue that the tetragonal-to-hexagonal transition has a strong displacive character, as mediated by phonons, evident through the softening in Figure 6b,d.

5. Summary and Conclusions

In this work, we investigated in detail the pressure-induced structural and electronic transitions occurring in NbAs up to 40 GPa at different atomic length scales. For this purpose, we combined micro-XRD and micro-XAS measurements with the diamond anvil cell technique. Initial lab-based XRD measurements of the starting material confirmed that NbAs crystallized in the non-centrosymmetric tetragonal phase. The main findings observed using XRD and XAS related to pressure-induced isostructural and structural transitions in the Weyl-type semimetal NbAs are summarized in Table S5.

The high-pressure micro-XRD data provided information on the bulk structural evolution up to 14.1 GPa. These data suggest that the tetragonal phase is stable up to the highest pressure in agreement with previous works \([11,26,27]\). A slight anomaly in the volume compression behavior could be distinguished at \(~12\) GPa (Figure 1c). This anomaly is characterized by a slight anomalous volume increase with pressure, which could potentially be related to the occurrence of a previously suggested topological Lifshitz transition in NbAs \([27]\). This anomaly remains, however, within the error bars, and a clear association with a potential topological transition is not warranted from the data. We noticed that isostructural electronic topological transitions are very difficult to study from structural data because of their very weak effect on the latter \([28]\). We fitted the volume compression data up to 14.1 GPa to different EOS formalisms and retrieved a bulk modulus of \( K_0 = 179.6 \) GPa for all methods.

The high-pressure micro XAS data up to 40 GPa provided information on the local and medium-range atomic arrangement from EXAFS and XANES techniques, respectively. The detailed analysis of the Nb K-edge white line position evolution with pressure could also be used to extract information on the electronic structure. Indeed, for both the isostructural Lifshitz transition around 12 GPa and the topological transition at 25 GPa, prominent increases in the white line energy position could be observed. This attests to a strong change in electronic properties. We observed that local structural parameters show lower sensitivity to the Lifshitz transition but that medium-scale parameters show stronger effects. The pressure evolution of the mean pair distances Nb–As\(_{(1)}\) (next nearest neighbor) displays only a slight change in compression behavior above \(~15\) GPa, while the mean pair distances Nb–Nb\(_{(1)}\) (second next nearest neighbor) displays a stronger non-continuous evolution already at \(~12\) GPa. Together with the observations from XRD, the pressure offset of these anomalies and their difference in intensity suggest that the Lifshitz transition affects predominantly the medium-range electronic and structural arrangement. The longer pair distance Nb–Nb\(_{(1)}\) exhibited a softmode behavior, with a noticeable slope change above \(~15\) GPa, while the vibrational properties of the Nb–As\(_{(1)}\) bond were only marginally affected.

In conclusion, our XRD and XAS data suggest that the Lifshitz transition involves, first, changes in the medium and bulk structure followed by changes in the very local structure. In contrast to the mean pair-distance parameters, the pair-distance variance for the pairs Nb–As\(_{(1)}\) and Nb–Nb\(_{(1)}\) exhibited only an anomalous trend at \(~25\) GPa. At higher pressures, this bond changes its vibrational properties drastically and exhibits a softmode tendency with a continuous increase in the bond length variance. Our data also allowed us to reexamine the local bonding topology and vibrational modes in NbAs across the \(I\_4\_1md \rightarrow P\_6m2\) transition. This transition occurs at \(~25\) GPa and possesses a
prominent displacive character, facilitated by phonon modes, as indicated by the observed softening for the scattering path Nb–As \(_{1}(1)\). This conclusion is supported by the XANES data that reveal an edge energy shift anomaly of the white line at ~26 GPa, which indicates a concomitant change of topological structure.

Our data provide important new insights into how pressure modulates topological phase transitions both structurally and electronically at various length scales. This new knowledge is important to elucidate if the properties of topological materials can be individually shaped for quantum applications. We could show that structural and vibrational properties show either progressive variations in the vicinity of topological phase transitions or stagnate. Electronic changes across the isostructural Lifshitz are manifested in clear discontinuities of the relevant followed parameter (white line energy position), while this parameter shows only progressive changes across structural topological phase transition such as the tetragonal-to-hexagonal transition at 25 GPa. Based on the topological features of NbAs and the understanding of pressure-induced transitions presented here, we can argue that this compound can be used to engineer functionalities by manipulating its selected ground states, such as those stabilized via epitaxial strain. This may have significant implications for device design in quantum technologies based on Weyl semimetals.

Supplementary Materials: The supporting information is available at: https://www.mdpi.com/ article/10.3390/cryst14070578/s1. Figure S1: Sketch of the single scattering paths employed to model EXAFS fitting. Figure S2: Amplitude and phase for single scattering paths calculated using FEFF method. Figure S3: Comparison between XRD patterns collected at ~0 GPa before and after the compression run. Figure S4: Integrated diffraction pattern of NbAs at ~14.1 GPa. Figure S5: Vibrational patterns for five modes in the tetragonal structure of the Weyl semimetal NbAs. Table S1: Structural parameters theoretically predicted for different phases of NbAs. Table S2: Pressure dependence of the structural parameters \((a, c, V)\) extracted from Rietveld refinements. Table S3: Factor-group analyses for both tetragonal and hexagonal crystal structures of NbAs. Table S4: List of experimental and calculated modes at ambient conditions for tetragonal NbAs. Table S5: The main observations from the multiscale length structural analysis of the pressure-induced transitions in Weyl semimetal NbAs, using XRD and XAS data, obtained in this work.


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References


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