Pressure-induced Lifshitz transition in NbP: Raman, x-ray diffraction, electrical transport, and density functional theory

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(Received 25 September 2017; published 5 February 2018)

We report high-pressure Raman, synchrotron x-ray diffraction, and electrical transport studies on Weyl semimetals NbP and TaP along with first-principles density functional theoretical (DFT) analysis. The frequencies of first-order Raman modes of NbP harden with increasing pressure and exhibit a slope change at $P_c \sim 9$ GPa. The pressure-dependent resistivity exhibits a minimum at P_c . The temperature coefficient of resistivity below P_c is positive as expected for semimetals but changes significantly in the high-pressure phase. Using DFT calculations, we show that these anomalies are associated with a pressure-induced Lifshitz transition, which involves the appearance of electron and hole pockets in its electronic structure. In contrast, the results of Raman and synchrotron x-ray diffraction experiments on TaP and DFT calculations show that TaP is quite robust under pressure and does not undergo any phase transition.

DOI: [10.1103/PhysRevB.97.064102](https://doi.org/10.1103/PhysRevB.97.064102)

I. INTRODUCTION

Soon after the discovery of the Dirac equation in 1928, it was pointed out that another massless solution of the Dirac equation represents a new kind of particle called Weyl fermions [1]. The recent developments in topological insulators and topological semimetals have paved the way to realizing Weyl fermions in terms of low-energy excitations where two nondegenerate linear dispersion electron bands cross each other at isolated points (called Weyl nodes) in the Brillouin zone [2]. This band structure has been observed in Weyl semimetals (WSMs) [3–7]. The Weyl nodes in WSMs always come in spatially separated pairs of opposite chirality, making WSMs different from Dirac semimetals, which have two degenerate Weyl nodes that form one Dirac node due to time-reversal and inversion symmetry. WSMs exhibit many exotic properties induced by Weyl nodes, such as topological surface states with Fermi arcs [3,4,6] and a negative longitudinal magnetoresistance due to the chiral anomaly [8–15]. Recently, the noncentrosymmetric TaAs, TaP, NbAs, and NbP have been predicted to be the candidate materials for WSMs with 12 pairs of Weyl nodes in their three-dimensional (3D) Brillouin zones [2,16]. The experimental evidence of Weyl nodes has been observed in this family by topological surface state and bulk electronic band-structure measurements using angle-resolved photoemission spectroscopy (ARPES) [3,17,18].

The Fermi surface topology of Weyl semimetals can be modified by a small change in the Fermi energy, due to their low intrinsic charge-carrier densities. Application of pressure is known to be a powerful approach to tune the electronic and lattice structure of the material. A high-pressure

synchrotron x-ray study of TaAs up to 53 GPa along with *ab initio* calculations [19] shows that TaAs goes to the hexagonal $P\bar{6}m2$ phase at 14 GPa from the ambient $I4_1md$ phase, along with changes in the electronic states. Another high-pressure magnetotransport study up to 2.3 GPa of NbAs [20] shows that the Fermi surface exhibits an anisotropic evolution under pressure. Similarly, a magnetotransport study of NbP up to 2.8 GPa [21] shows a significant effect on the amplitudes of Shubnikov–de Haas oscillations due to the subtle changes in the Fermi surface. Recently, first-principles calculations on NbP and NbAs predicted a structural phase transition at 63.5 GPa in NbP and three structural phase transitions at 23, 38, and 73 GPa in NbAs [22]. The effect of pressure on a lattice and phonons has not been studied in NbP or TaP. The objective of the present study is to examine NbP and TaP under pressure (carried out up to 25 GPa) using Raman spectroscopy and synchrotron x-ray diffraction as well as electrical transport (for NbP). Density functional theory (DFT) calculations have been done to gain microscopic insight into the pressure effect. Our main results for NbP are as follows: (i) The phonon frequencies of first-order Raman modes exhibit a slope change at $P_c \sim 9$ GPa, and (ii) the resistivity of NbP as a function of pressure passes through a minimum at P_c . The temperature-dependent resistivity at higher pressure ($P > P_c$) shows very different and complex behavior compared with the low-pressure metallic behavior expected for semimetals. (iii) The DFT calculations reveal that these anomalies at P_c are due to the Lifshitz transition involving the appearance of electron and hole pockets in its electronic structure. In comparison to NbP, our results on TaP show no phase transition up to 27 GPa.

II. EXPERIMENTAL DETAILS

High-quality single crystals of NbP and TaP were grown via a chemical vapor transport reaction using iodine as a trans-

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port agent [23]. Initially, polycrystalline powder of NbP was synthesized by a direct reaction of niobium (Chempur 99.9%) and red phosphorus (Heraeus 99.999%) kept in an evacuated fused silica tube for 48 h at 800 °C. Starting from this microcrystalline powder, the single crystals of NbP were synthesized by chemical vapor transport in a temperature gradient starting from 850 °C (source) to 950 °C (sink) and a transport agent with a concentration of 13.5 mg/cm³ iodine (Alfa Aesar 99,998%). A similar route was used for the growth of TaP crystals. Raman experiments were carried out at room temperature on these well-characterized single crystals of NbP and TaP [10,24] using a confocal Horiba 800 spectrometer, a peltier-cooled CCD, and a 532 nm diode pump solid state (DPSS) laser. The high-pressure synchrotron x-ray diffraction measurements were done at DESY on the beamline (P02) using 0.2888 Å x-ray radiation. Pressure was generated using a diamond anvil cell (DAC), where a thin platelet (~100 μm) of single crystals of NbP/TaP was embedded in a 4:1 methanol:ethanol pressure-transmitting medium along with a ruby chip for pressure calibration into a stainless-steel gasket inserted between the diamonds. The electrical resistivity at different pressures was measured using the direct current van der Pauw technique [25–27] in an in-house-designed diamond-anvil cell equipped with diamond anvils with a 500 μm culet. A cleaved NbP single crystal of a suitable size was cut and placed into the central hole of a tungsten gasket with an insulating cubic BN/epoxy layer without a pressure-transmitting medium. The electrical leads fabricated from 5-μm-thick Pt foil were attached to the sample. Initial sample thickness was 40 μm. Because visual observations indicated that linear dimensions of the sample (and thus the distance between the electrodes) did not change upon compression, we assume that only the thickness of the sample changed by the same value as the change of volume deduced from the experimental equation of state [28]. These thickness values were used to calculate the resistivity values at high pressure. The pressure was again determined by the ruby luminescence method.

III. COMPUTATIONAL DETAILS

Our first-principles calculations are based on density functional theory (DFT) as implemented in the QUANTUM ESPRESSO package [29], in which the interaction between ionic cores and valence electrons is modeled with ultrasoft pseudopotentials [30]. The exchange-correlation energy of electrons is treated within a local density approximation (LDA) using a functional form parametrized by Perdew and Zunger [31]. We use an energy cutoff of 60 Ry to truncate the plane-wave basis for representing Kohn-Sham wave functions, and an energy cutoff of 600 Ry on the basis set to represent charge density. We relaxed structures to minimize energy until the magnitude of Hellmann-Feynman force on each atom is less than 0.03 eV/Å. In self-consistent Kohn-Sham (KS) calculations with primitive cells, the Brillouin zone (BZ) integrations were sampled with a uniform mesh of 11 × 11 × 11 *k*-points. We determined electronic structure by including the spin-orbit coupling (SOC) through use of relativistic ultrasoft pseudopotentials [32]. We determined dynamical matrices and phonons at wave vectors on a 2 × 2 × 2 mesh in the BZ using DFT linear response (QUANTUM ESPRESSO implementation based on the Green's

FIG. 1. Crystal structure of bulk NbP and TaP with (a) conventional unit cells, (b) primitive unit cells, and (c) their Brillouin zone (BZ).

function). We used a scalar relativistic pseudopotential for phonon calculations as the inclusion of SOC changed phonon frequencies by a very small value ($<1 \text{ cm}^{-1}$) [Figs. 9(c) and 9(d)]. To determine the bulk modulus (B), we have fitted the P versus V plot to the Birch-Murnaghan equation of state,

$$P(V) = \frac{3B}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \times \left\{ 1 + \frac{3}{4} (B' - 4) \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\}, \quad (1)$$

where V is the volume at pressure P , V_0 is the reference volume, B is the bulk modulus, and B' is the pressure derivative of the bulk modulus. Fermi surfaces are interpolated on dense *k*-grids (equivalent to $33 \times 33 \times 33$ in the whole BZ).

IV. RESULTS AND DISCUSSIONS

A. Experimental results

NbP and TaP have the same geometric structure [noncentrosymmetric body-centered-tetragonal (bct) structure], which belongs to the space group of $I4_1md$ (C_{4v}^{11} , no. 109) [33] with two atoms each of a transition metal and phosphorus

FIG. 2. Raman spectrum of NbP (a) and TaP (b) at a few representative pressures. The solid lines (red and blue) are the Lorentzian fits to the measured spectra (black).

FIG. 3. Pressure dependence of phonons of NbP: (a) experiment; (b) theory. The solid lines are the linear fits to the data. The slope S in units of $\text{cm}^{-1}/\text{GPa}$ is given near each of the lines. The vertical dashed lines mark the transition pressure P_c .

per primitive cell [see Figs. 1(a) and 1(b)]. In this structure, Nb/Ta and P atoms have six nearest neighbors in a trigonal prismatic coordination. To understand the crystal structure, we can consider a stack of square lattice planes, where each plane is formed of either Nb/Ta or P atoms. Each plane is shifted by half a lattice constant in either direction (x or y) relative to the one below it. Due to these shifts, a screw pattern arises in the lattice along the z direction leading to a nonsymmorphic C_4 rotational symmetry that requires a translation along the z direction by $c/4$. It is clear from this crystal structure that

FIG. 4. (a) Measured resistivity of NbP as a function of pressure. The resistivity passes through a minimum at ~ 9 GPa as indicated by a vertical dashed line. (b) Temperature-dependent resistivity at different pressures, showing an electronic transition at ~ 10 GPa.

NbP and TaP lack spatial inversion symmetry. If time-reversal symmetry is respected, the broken inversion symmetry is an important condition for the Weyl semimetallic phase.

According to factor group analysis, this system has $[A_1 + E]$ acoustic phonons and $[A_1 + 2B_1 + 3E]$ optical phonons. All the optical phonons are Raman-active [34]. Figure 2(a) shows Raman spectra of NbP at a few typical pressures. Five Raman modes are observed in NbP and assigned to E^1 , B_1^1 , E^2 , A_1 , and B_1^2 irreducible representations, based on first-principles calculations (discussed later). The Lorentzian line shapes were fitted to the Raman spectra to extract the phonon frequencies and full width at half-maximum (FWHM). The Raman modes E^1 , B_1^1 , and E^2 become very weak after ~ 9 GPa, making it difficult to follow them. The extracted phonon frequencies at different pressures, plotted in Fig. 3(a), show clearly that the phonon frequencies of A_1 and B_1^2 modes exhibit a change in the slope $S(\frac{d\omega}{dP})$ at $P_c \sim 9$ GPa, signifying a phase transition. We note that the pressure-transmitting medium develops a nonhydrostatic component beyond 10 GPa, whose contribution will add to the linewidth and not much to the frequency shift, in a rather smooth manner. To further investigate this transition, we did resistivity measurements as

FIG. 5. (a) X-ray diffraction pattern of NbP as a function of pressure. (b) The Rietveld refinement of the x-ray diffraction pattern at 0.6 GPa pressure. (c) Pressure dependence of volume per formula unit (z) of NbP.

a function of pressure and temperature. Figure 4(a) shows that the resistivity first decreases with increasing pressure and then increases, showing a minimum at P_c . Figure 4(b) shows that the resistivity follows metallic behavior at low pressure as expected for semimetals, but it exhibits very different and complex behavior in the high-pressure phase. Thus our Raman and resistivity results as a function of pressure show a phase transition at P_c . To identify the structural changes, if any, at P_c , high-pressure x-ray diffraction measurements were carried out. Figure 5(a) shows x-ray diffraction patterns at a few representative pressures, revealing no new diffraction peaks or vanishing of the existing peaks until 25 GPa. This rules out the possibility of structural change at P_c . To get the lattice parameters, we performed Rietveld refinement using JANA 2006 [35] as shown, for example, at 0.6 GPa in Fig. 5(b).

The diffraction pattern is well fitted by JANA 2006 at all pressures. Figure 5(c) shows the pressure dependence of the unit-cell volume per formula unit (z). The solid red line is the fit to Eq. (1), signifying that volume is a smooth function of pressure until 25 GPa. Thus high-pressure x-ray data rule out the structural phase transition at P_c , consistent with the theoretical prediction [22].

We will now present our results on TaP. Figure 2(b) shows Raman spectra of TaP at a few representative pressures. As before, the solid red lines are the Lorentzian function fitted to the experimental data (black lines). At low pressure, only three modes could be recorded, and the two other modes (E^1 and E^2) could be seen at higher pressures. The zero-pressure extrapolated values of the frequencies of E^1 and E^2 modes are close to the values obtained from DFT calculations. The

FIG. 6. Pressure dependence of phonons of TaP: (a) experiments; (b) theory. The solid lines are the linear fit to the experimental data. The slope S in units of $\text{cm}^{-1}/\text{GPa}$ is given near the lines.

FIG. 7. (a) X-ray diffraction pattern of TaP as a function of pressure, and (b) pressure dependence of volume per formula unit (z) of TaP.

pressure dependences of phonon frequencies of E^1 , B_1^1 , E^2 , A_1 , and B_1^2 modes are shown in Fig. 6(a). It is clear from Fig. 6(a) that all the Raman modes harden with increasing pressure and there is no slope change with pressure, which is in contrast to the results obtained in NbP. Figure 7(a) shows the pressure dependence of synchrotron x-ray diffraction patterns of TaP at a few pressures. We note that the number of diffraction peaks remains the same in the entire pressure range, suggesting no structural phase transition. The lattice parameters were obtained by Rietveld refinement using JANA 2006 [35]. The pressure dependence of the volume per formula unit (z) is shown in Fig. 7(b). The solid red line is the fit to the Birch-Murnaghan equation of state [Eq. (1)], showing that there is no change in the bulk modulus of TaP over the entire pressure range [Fig. 7(b)]. We can thus conclude that TaP does not show any phase transition until 27 GPa.

B. Theoretical calculations

The calculated structural parameters are as follows: For NbP: $a = b = 3.31$ Å, $c = 11.23$ Å; for TaP: $a = b = 3.29$ Å, $c = 11.2$ Å. These values are in good agreement with experiments [36]. Lattice structural parameters of bulk NbP and TaP show smooth variation as a function of hydrostatic pressure [Figs. 8(a) and 8(b)], signifying the robustness of the crystal structure of NbP and TaP up to 20 GPa. Further, the absence of anomalies in the c/a ratio rules out the possibility of an isostructural phase transition. Calculated bulk moduli [from V versus P plotted in Figs. 8(a) and 8(b)] of the bct structure of NbP (TaP) are 196 ± 1 GPa (209 ± 0.8 GPa), which agree well with experimental values of 217 ± 7 GPa (218 ± 6 GPa).

The electronic structure and phonon dispersion of NbP and TaP with and without spin-orbit coupling at 0 GPa are shown in Fig. 9. In the absence of spin-orbit coupling, the valance-band maximum (VBM) and conduction-band minimum (CBM) cross the Fermi level along high symmetric paths (Γ - Σ - S - Z - N) of the Brillouin zone [Figs. 9(a) and 9(b)]. This crossing leads to the formation of a closed ring structure (nodal rings [2]) (in $k_x = 0$ and $k_y = 0$ planes), which is based on the fact that bands have opposite eigenvalues of mirror symmetry. As spin-orbit coupling is introduced, the nodal rings disappear, i.e., a gap opens up along these high-symmetry lines [see the red line in Figs. 9(a) and 9(b)] and Weyl nodes are generated

FIG. 8. Calculated lattice structural parameters a , c , c/a , and volume per formula unit of bulk NbP (a) and TaP (b) as a function of pressure.

[36]. This gap is smaller in NbP as compared to TaP, as expected from a weaker spin-orbit coupling in Nb as compared to Ta compounds. Our calculated phonon frequencies at the zone center are in good agreement with experiments (see Table I).

Our calculations of phonon frequencies of NbP as a function of hydrostatic pressure [Fig. 3(b)] reveal that A_1 and B_1^2 modes exhibit a change in S at $P_c^{\text{theory}} \sim 12$ GPa, while the other three modes, E^1 , E^2 , and B_1^1 , do not show any slope change until 24 GPa, consistent with the experimental results. The difference between the observed transition pressure $P_c \sim 9$ GPa and the calculated pressure $P_c^{\text{theory}} \sim 12$ GPa is partly due to the errors in calculated equilibrium lattice constants. Here, the calculated S for the A_1 mode increases above the transition pressure, whereas in experiment it decreases. While the difference in S of the A_1 mode below and above the transition pressure is ~ -0.5 $\text{cm}^{-1}/\text{GPa}$ in experiment, it is 0.7 $\text{cm}^{-1}/\text{GPa}$ in calculations. To understand this, we froze A_1 mode atomic displacements by 0.04 Å and determined the change in frequencies of other phonon modes. We find that the frequency of the A_1 mode changes by 4 cm^{-1} , revealing that there is a relatively strong coupling of the A_1 mode with itself. The A_1 mode also couples with other modes, but the strength of coupling is weaker. This anharmonic (phonon-phonon) coupling, not included in our analysis, may be responsible for the difference in S of the A_1 mode below and above the

TABLE I. Comparison of the observed and calculated frequencies of Raman-active modes of NbP and TaP at 0 GPa. Excellent agreement between theory and experiment is evident.

Modes	NbP (0 GPa, ω in cm^{-1})		TaP (0 GPa, ω in cm^{-1})	
	Experiment	Theory	Experiment	Theory
E^1	189	182	145	146
B_1^1	263	262	191	192
E^2	335	339	341	339
B_1^2	391	397	411	415
A_1	377	382	373	375

FIG. 9. Electronic structure (a,b) and phonon dispersion (c,d) of bulk NbP and TaP, respectively, at $P = 0$ GPa, calculated with and without inclusion of spin-orbit coupling.

transition pressure in the experiment and in theory. To identify whether it is a structural phase transition, we considered two high-symmetry crystal structures: (a) hexagonal (tungsten carbide structure with space group $P-6m2$, No. 162) and (b) cubic (CsCl structure with space group $Pm-3m$, No. 221), and we calculated the enthalpy differences between these phases and the low-pressure bct structure. Although the enthalpy difference (ΔH) between the hexagonal and bct phase first increases slightly with pressure and then decreases, it does not attain a negative value [Fig. 10(a)]. Thus, a structural phase transition from bct to hexagonal phase is ruled out. Similarly, ΔH between the cubic and bct phase decreases with pressure but does not crossover to a negative value up to 24 GPa [inset of Fig. 10(a)], ruling out a structural phase transition to the cubic phase as well. Our conclusion of the absence of a structural phase transition in NbP with pressure is consistent with our x-ray diffraction experiments.

FIG. 10. Pressure-dependent difference in enthalpy of body-centered-tetragonal (bct) and hexagonal (hex) structures of NbP (a) and TaP (b). ΔH of bct and cubic structures are given in the inset.

To understand the origin of change in pressure coefficients of Raman-active modes (A_1 and B_1^2 modes) of NbP above $P_c^{\text{theory}} = 12$ GPa, we study the evolution of electronic structure with pressure. At $P = 0$ GPa, NbP is semimetallic in nature, i.e., a finite density of states at the Fermi level. Near the Fermi energy, the electronic structure of NbP at 0 GPa shows the presence of an electron pocket along Γ - Σ and hole pockets along S - Z and Z - N lines [see Fig. 11(a)]. As the hydrostatic pressure does not alter the symmetry of the crystal, the energy levels do not split, but those near the Fermi energy change notably giving rise to pressure-induced transfer of electrons from one pocket to another in order to maintain the total number of carriers (i.e., the size of the electron and hole pockets changes with pressure) [37]. Interestingly, at 12 GPa a small hole pocket appears along the Γ - N path [see Fig. 11(c)]. To probe this further, we monitored the evolution of the Fermi surface with pressure, particularly the electron (red surface) and hole (blue surface) pockets [Fig. 12(a)]. Electron and hole pockets are almost semicircular and distributed along the rings [2,16] on the $k_x = 0$ and $k_y = 0$ mirror planes in the BZ [Fig. 12(b)]. At 8 GPa, the size of the electron pocket in the vicinity of the N point reduces, and a set of electron pockets (in between the existing hole pocket and the one appearing near the N point) and hole pockets (in the vicinity of the N point) appears [see Fig. 12(c)]. A further increase in pressure results in changes of the shape and size of the electron and hole pockets (see Fig. 12). Note that the electron pocket in the vicinity of the Σ point [Fig. 12(a)] does not disappear completely with increasing pressure. It is thus clear that there are notable changes in the topology of the Fermi surface with pressure. Since the Fermi surface changes with applied pressure without breaking

FIG. 11. Electronic structure of bulk NbP calculated at (a) 0 GPa, (b) 8 GPa, (c) 12 GPa, and (d) 16 GPa.

the structural symmetry, we assign it as a Lifshitz transition occurring at P_c^{theory} . We note that there are changes in S at 12 GPa [Fig. 3(b)]. Thus, there is a clear correlation between the pressure coefficients of Raman-active modes and the electronic phase transition. The small changes in the electronic band

topology or Fermi surface topology are driven by external parameters and reflected in the anomalies in the measurable quantities of two types: (a) the appearance or disappearance of electron and hole pockets, and (b) the rupturing of necks connecting Fermi arcs. In the present work, we observe a Lifshitz transition [38] associated with the former.

We now present our results for the pressure dependence of Raman-active modes of TaP. We show the variation of Raman-active modes as a function of pressure in Fig. 6(b). Calculated Raman-active modes do not exhibit any change in S , consistent with our experimental results on TaP [Fig. 6(a)]. To further check whether TaP would undergo a structural phase transition to either the hexagonal or cubic phases, we estimated the enthalpies of bct, cubic, and hexagonal crystal structures of TaP. Although the enthalpy difference (ΔH) [inset of Fig. 10(b)] between the cubic and bct phases decreases with pressure, it does not become negative even up to 24 GPa. Thus, a structural phase transition to the cubic phase of TaP is ruled out. Similarly, (ΔH) between the hexagonal and bct phases [Fig. 10(b)] also does not exhibit a crossover to negative values, signifying the absence of any structural phase transition, consistent with our experiments.

V. SUMMARY

The frequencies of A_1 and B_1^2 modes of NbP show a change in slope ($S = \frac{d\omega}{dP}$) at P_c , and its pressure-dependent resistivity exhibits a minimum at P_c . Further, the temperature-dependent resistivity at different pressures (3 and 10 GPa) shows that resistivity at $P > P_c$ exhibits a significant change from the metallic behavior observed at low pressure. We show that these anomalies are associated with a pressure-induced Lifshitz

FIG. 12. Evolution of the Fermi surface of NbP with pressure. Two views of the Fermi surface at 0 GPa (a,b). The Fermi surface at 8 GPa (c), 12 GPa (d), and 16 GPa (e) shows changes in the size of electron and hole pockets with pressure. Red represents hole pockets, whereas blue represents electron pockets.

transition at P_c using first-principles density functional theoretical analysis. The bct structure of NbP is robust as a function of pressure up to 24 GPa. Our experimental measurements and theoretical analysis of TaP show that its bct structure is quite robust under pressure, and it exhibits no structural or electronic phase transitions with pressure.

ACKNOWLEDGMENTS

We thank beam scientist K. Glazyrin (P02, DESY) for setting up the instruments to carry out the experiments. We grate-

fully acknowledge DESY, Germany synchrotron XRD facility for high pressure x-ray experiments. We thank the Department of Science and Technology (DST), India for financial support to carry out the experiments at DESY, Germany. A.K.S. thanks DST, India for the financial support. S.N.G. thanks DST, India for the fellowship. A.S. and K.P. are thankful to Jawaharlal Nehru Centre for Advanced Scientific Research, India for the research fellowship. U.V.W. acknowledges support from Indo-Korea Science and Technology (IKST) Center and a J. C. Bose National Fellowship of the Department of Science and Technology, Government of India.

A.S. and K.P. contributed equally to this work.

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