Ab initio optical and energy loss spectra of Weyl semimetals TaAs, TaP, NbAs and NbP

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Transition metal monopnictides represent a newly found class of topological semimetals exhibiting low-energy excitations akin to Weyl fermions. We report the optical properties in a wide energy range for TaAs, TaP, NbAs and NbP, obtained through density functional theory in an independent particle framework. We discover a rather independent behavior of the spectra from the anion and the light polarization. The spectral features are explained in terms of the upper $s$, $p$, $d$, and $f$ electrons. The corresponding absorption structures of the dielectric function yield characteristic frequency dependence of the Fresnel reflectivity. While the lower part of the energy loss spectra is dominated by plasmonic features, the high-energy structures are related to the same interband transitions as the absorption peaks.

I. INTRODUCTION

Topological Weyl semimetals (TWSs) represent a new class of materials, which has recently attracted great interest in the scientific community\textsuperscript{[1,2]} Their main feature is the presence of low-energy excitations behaving accordingly to the three-dimensional (3D) Weyl Hamiltonian, which describes band crossing near the Fermi energy known as Weyl nodes. The crossing points present a double degeneracy, in contrast with those of topological Dirac semimetals (TDSs) where a fourfold degeneracy is observed\textsuperscript{[3,4]} TWSs can be considered as TDSs where either the time-reversal or inversion symmetry has been lifted, causing the split of one Dirac point into two Weyl nodes\textsuperscript{[5]} The inclusion of spin-orbit interaction (SOI) in the theoretical models and calculations is fundamental in order to achieve such a split.

The presence of the Weyl nodes confers these materials with novel properties such as: Fermi arcs in the surface states\textsuperscript{[6]} anomalous and spin Hall conductivity\textsuperscript{[7,8]} negative magnetoresistance\textsuperscript{[9]} and the Adler-Bell-Jackiw chiral anomaly\textsuperscript{[10]} Interesting applications of TWSs as materials for Veselago lenses have been predicted\textsuperscript{[11]}

In order to realize a TWS, several ways have been proposed. One is the break of time-reversal symmetry, by stacking alternate layers of trivial and topological insulators with magnetic ordering\textsuperscript{[12]} This would produce a single pair of Weyl nodes, which are split in energy, but are quite challenging to realize experimentally. Recently, transition metal monopnictides, in their natural occurring bulk structure, have been proposed, because by crystallizing in the body-centered tetragonal (bct) non-symmorphic space group $I4_1$md which naturally lacks inversion symmetry\textsuperscript{[13]} Single crystals of these systems can be grown through chemical vapor transport techniques using iodine as the transport medium. Optimization of the growth procedure leads to single crystal larger than 1 cm in size\textsuperscript{[14]} \textit{Ab initio} calculations have predicted the presence of 12 pairs of Weyl nodes in the Brillouin zone (BZ) of TaAs, TaP, NbAs and NbP\textsuperscript{[15,16,17]}

The experimental confirmation through measurements of the Fermi arcs using angular resolved photoemission spectroscopy (ARPES) followed\textsuperscript{[18,19]} Optical studies have confirmed the Weyl picture\textsuperscript{[20]} but restricted to low-energy excitations\textsuperscript{[21]}

All these interesting findings spurred the interest into a deeper analysis of all the properties of the newly discovered TWSs. A better understanding of their electronic structures, optical and energy-loss spectra in a wide energy range is hence needed. One important step in this direction is the goal of the present study.

Our paper is organized as follows: In Sec. II we describe the theoretical methods employed in our calculations. In Sec. III we present and discuss the obtained optical and energy loss spectra. In Sec. IV we give a summary and conclusions.

II. THEORETICAL METHODS

The structural, electronic and optical properties of the transition metal monopnictides have been computed using density functional theory (DFT) as implemented in the Quantum ESPRESSO (QE) Package\textsuperscript{[22,23]} The exchange and correlation (XC) potential is generated within the generalized gradient approximation (GGA) scheme, as formulated by Perdew, Burke and Ernzerhof (PBE)\textsuperscript{[24,25]} The following electronic configuration have been employed in order to generate fully relativistic, norm-conserving pseudopotential\textsuperscript{[26]}: Ta($4f^{14}5s^25p^65d^56s^2$), Nb($4s^24p^64d^45s^2$), As($3d^{10}4s^24p^3$) and P($3s^23p^3$). The $4f$ states of Ta and $3d$ states of As have been included since they fall in the analyzed energy range. The cut-off radii and reference channels have been chosen so that the pseudo-wavefunctions agree with the all-electron ones, without the presence of any ghost states\textsuperscript{[27]} The SOI has been included by solving the radial Dirac equation for each isolated atom and then, by reducing the four-component Dirac spinors to two-component Pauli spinors\textsuperscript{[28]}

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The atomic geometries have been optimized starting from the reference Wyckoff positions for the \( \text{I}_{4}\text{mmd}(\text{No. 109}) \) group with multiplicity 4: \((0,0,u)\) and \((0,1/2,u+1/4)\) with \(u = 0\) for the cation and \(u \neq 0\) for the anion\(^{27}\). The convergence with the number of plane waves (PWs) has been tested, finding a suitable energy cut-off of 100 Ry. The BZ of the bct has been sampled by using a uniform grid of \(21 \times 21 \times 7\) Monkhorst-Pack \(k\) points\(^{36}\) in the self-consistent calculations. The energy eigenvalues and eigenfunctions of the single-particle Kohn-Sham equation are used to characterize the electronic properties of the TWSs.

The convergence for the optical properties in the energy range from 0.2 to 50 eV requires instead a \(36 \times 36 \times 12\) \(k\) point grid, with 190 empty bands. For the low-energy range a much more dense grid of \(192 \times 192 \times 64\) \(k\) points cropped around the Weyl nodes has been used. The optical properties have been computed within the single-particle approximation in the transverse gauge. The imaginary part of a diagonal element \(\epsilon_{jj}(\omega)\) of the frequency-dependent dielectric tensor is given as

\[
\text{Im}\epsilon_{jj}(\omega) = \left(\frac{2\pi e}{m_\pi}\right)^2 \frac{1}{V} \sum_\mathbf{k} \sum_{c,v} \left[ f(\epsilon_v(\mathbf{k})) - f(\epsilon_c(\mathbf{k}))\right] \times \\
\times \left|\langle c|p_j|v\rangle k\right|^2 \delta(\epsilon_c(\mathbf{k}) - \epsilon_v(\mathbf{k}) - \hbar\omega) \tag{1}
\]

with functions \(\nu|k\) of Bloch states with band index \(\nu = c,v\), wavevector \(\mathbf{k}\), energy \(\epsilon_\nu(\mathbf{k})\) and occupation \(f(\epsilon_\nu(\mathbf{k}))\) to compute the transition matrix elements of the momentum operator \(p_j\) in \(j\)-th Cartesian direction between valence \((v)\) and conduction \((c)\) bands. The effects of the non-local part of the pseudopotentials\(^{37}\) have been included\(^{38}\) as implemented in the Yambo package\(^{39}\). The real part of the dielectric function has been obtained by applying the Kramers-Kronig relation\(^{40}\)

\[
\text{Re}\epsilon_{jj}(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \text{Im}\epsilon_{jj}(\omega')}}{\omega'^2 - \omega^2} d\omega' . \tag{2}
\]

The energy loss spectrum \(L_j(\omega)\) is calculated for vanishing momentum transfer as:

\[
L_j(\omega) = -\text{Im} \frac{1}{\epsilon_{jj}(\omega)} , \tag{3}
\]

where \(\hbar\omega\) represents the loss energy. The plasma frequencies for the free electron approximation are calculated using the formula

\[
\omega_p = \sqrt{\frac{4\pi e^2 n_e}{m_e}} \tag{4}
\]

with \(n_e\) as the density of the electrons contributing to the loss.

### III. RESULTS AND DISCUSSION

#### A. Atomic and electronic structures

The transition metal monopnictides here studied crystallize in a body centered tetragonal structure. Each anion (As, P) coordinates with 6 cations (Ta, Nb), and vice versa. The local geometry of the bonds is trigonal prismatic, coming from a \(sp^3d^4\) hybridization.

The equilibrium atomic geometries have been obtained by relaxing the crystal cell while varying the lattice parameters \(a\), \(c\) and \(u\). The calculated structures\(^{27}\) are in agreement (with deviations smaller than 1\%) with results from X-ray diffraction measurements\(^{41-43}\) and other theoretical calculations\(^{20}\).

The band structures along the high-symmetry directions have been computed for all materials and are displayed in Fig. 1. Weyl nodes are not visible since they lay out of the high symmetry directions. We see that the \(d\) states of the cations give the dominant contributions to the bands close to the Fermi level. In general, the displayed valence and conduction bands are built by cation \(d\) and anion \(p\) states with smaller contributions from the cation \(s\) and \(p\). The separated valence bands with binding energy slightly larger than 10 eV are built by cation \(d\) and \(p\) states and anion \(s\) states. Many deeper core-level bands are also visible in Fig. 1. They are due to Nb 4\(p\) and Ta 5\(p\) states below \(−30\) eV, which are split by strong SOI. Around \(−20\) eV the SOI-split Ta 4\(f\) bands appear in Fig. 1 a and b. In Fig. 1 a and c the As 3\(d\) derived bands are observable at about \(−35\) eV.

#### B. Optical properties

Using a dense mesh of \(k\) points, we calculate the imaginary part of the dielectric function \(\text{Im} \epsilon_{jj}(\omega)\) through the \(\text{pw2gw sub-package of QE}\). The results are reported in Fig. 2, where convergence with the number of \(k\) points and empty bands has been carefully tested.

We observe that the absorption spectra \(\text{Im} \epsilon_{jj}(\omega)\) are fairly isotropic in the wide energy range. Only in the low energy range (below 5 eV) the tetragonal anisotropy of the crystal becomes evident as dependence on the light polarization. The strong anisotropy in the infrared spectral range has been demonstrated in a previous paper\(^{42}\).

It is worth noticing the rather identity of the optical spectra for the same cation and, hence, the weak influence of the anion. The high-energy range is dominated by the cation as demonstrated by comparing the the TaAs/TaP (NbAs/NbP) spectra in Fig. 2, while the anion only gives rise to small intensity changes for energies lower than 15 eV. The distinct features that characterize the high-energy transitions for TaX (X=As,P),
FIG. 1. Band structure along the high-symmetry directions for (a) TaAs, (b) TaP, (c) NbAs and (d) NbP. The projected DOS (in arbitrary units) shows the contribution of the cation (solid lines) and of the anion (dashed lines). The states $s$ (cyan), $p$ (red), $d$ (blue) and $f$ (green) are resolved. The Fermi level is used as energy zero.

FIG. 2. Imaginary part of the dielectric function for $j = x, y$ polarization (solid lines) and $j = z$ polarization (dashed lines) for TaAs (black), TaP (red), NbAs (blue) and NbP (green). Inset: real part of the dielectric function.

visible in the range $19 \sim 27$ eV, are caused by transitions between the $f$ states of Ta and the conduction bands. For
all materials a broad peak structure, visible in the range 30 \( \sim \) 38 eV, is caused by transitions originating from the \( p \) orbitals of the cation, visible around \(-30\) eV in the band structure. In the case of TaX, another structure is visible at 43 eV. This is also originated by transitions from the \( p \) orbitals, which, in the case of TaX, produce two structure instead of one because of the large SOI split. In contrast, the structure at 43 eV is not present in NbX (X=As, P) due to the smaller spin-orbit splitting.

The reflectivity at normal incidence can also be calculated from the knowledge of the dielectric function via the Fresnel formula

\[
R_j(\omega) = \left| \frac{\sqrt{\epsilon_{jj}(\omega)} - 1}{\sqrt{\epsilon_{jj}(\omega)} + 1} \right|^2. \tag{5}
\]

The reflectivity presented in Fig. 3 in the wide energy range shows several structures that are connected to the same transitions described for \( \text{Im} \ \epsilon_{jj}(\omega) \). In particular we note that the reflectivity is negligible around 18 eV (29 eV) for TaX (NbX) and X=As, P, where also \( \text{Im} \ \epsilon_{jj}(\omega) \) vanish. In these energy windows the transmission is hence maximized. In the intermediate energy range, 5 \( \sim \) 15 eV for TaX and 5 \( \sim \) 18 eV for NbX, the reflectivity is less frequency-dependent, with values around \( R_j(\omega) \approx 0.5 \sim 0.6 \). Only below 5 eV down to vanishing energy, a strong increase of the reflectivity is visible. In this range, the transition metal monopnictides reflect but also strongly absorb light. The infrared region (insets in Fig. 3) finally, characterizes the semimetallic character of the monopnictides with vanishing gaps and topological electron and hole pockets but also trivial hole pockets.\(^{[20]}\) Caution should be taken when relating the low-energy behavior to the Weyl fermion picture. In fact, although an ideal Weyl node would give a constant infrared behavior of the imaginary part of the dielectric function, the non-local dependence shown in equation (2) for the derivation of \( \text{Re} \ \epsilon \) does not allow to guess any special behavior in the infrared limit of the reflectivity.

Above the vanishing reflectivities, around 18 and 29 eV, respectively, further spectral features with intermediate reflectivity strength appear in Fig. 3. They are strongly related to the spectral features in the absorption in Fig. 2. They represent the same interband transitions. The finite reflectivities in the high-energy range are important if real part of the optical conductivity, even in the infrared region, is constructed from measured reflectivity spectra and Kramers-Kronig relations.\(^{[20]}\)

### C. Energy losses

By implementing Eq. (5) we can calculate the energy loss for zero exchanged momentum. Only averaged values are shown in Fig. 4 since the polarization dependence of the response functions is very weak. We also present the low-energy spectra (Fig. 4 insets) which provides useful information in order to characterize the Weyl nodes, when separated from the elastic scattering peak and from the contribution of the trivial points. Consequently, low-electron energy loss spectroscopy is suggested as complementary experimental method to study Weyl fermions.

The first main peak in the energy loss is a consequence of the second zeros of \( \text{Re} \ \epsilon_{jj}(\omega) \) when \( \text{Im} \ \epsilon_{jj}(\omega) \) simultaneously almost vanishing (see insets of Fig. 2). The spectra show typical plasmon losses of valence electron gases as indicated by the positions \( h\omega_p \) of the first main peak, which are in the range of the plasmons of TaAs and NbAs compounds (\( \sim 18 \) eV) and TaP and NbP (\( \sim 19 \) eV), if the \( d^3s^2 \) electrons of the cation and \( p^3 \) electrons of the anion are considered as free electrons. For all compounds these values do not vary with the propagation direction of the inelastically scattered particles.

While the first main peak can be explained within the free electron plasmon picture, the other high-energy structures that appear in Fig. 4 are related to the optical transitions already discussed for \( \text{Im} \ \epsilon_{jj}(\omega) \) from semi-core states to the conduction bands. In particular for TaX we see transitions from the \( f \) cation states associated with the 2nd peak at 28 eV. The 3rd and 4th peak (around 38 and 44 eV) are instead associated with transitions from the SOI-splitted \( p \) states of the cation. For NbX only one other peak appears at 38 eV, associated with transitions from the \( p \) states of the cation.

### IV. SUMMARY AND CONCLUSIONS

Results on the optical properties of transition metal monopnictides TaAs, TaP, NbAs and NbP, in a wide range of photon energies obtained \textit{ab initio} via DFT and independent particle approximation, were presented. The investigations on the projected DOS and optical properties show the importance of the \( f \) states of Ta, while the \( d \) states of As give negligible contributions. The energy loss and reflectivity spectra are presented as possible tools to further characterize the properties of the topological semimetals. The high-energy peaks in the optical properties are related to transitions from cation \( f \) and \( p \) semi-core states to conduction bands. The materials show high optical reflectivity in the range 0 \( \sim \) 15 eV of 50 \( \sim \) 60\%, which still amounts to 20\% around 35 \( \sim \) 40 eV. The first peak of the energy loss is explainable through a plasmon picture by taking into account the cation \( d^3s^2 \) and anion \( p^3 \) electrons as free particles.

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FIG. 3. Reflectivity for $j = x, y$ polarization (solid lines) and for $j = z$ polarization (dashed lines) for TaAs (black), TaP (red), NbAs (blue) and NbP (green). Inset: infrared reflectivity for $x, y$ and $z$ polarizations.

FIG. 4. Energy loss spectra for TaAs (black), TaP (red), NbAs (blue) and NbP (green). Inset: low-energy range of the same quantities.

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