



Raman study of lattice dynamics in the Weyl semimetal TaAs

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We report a polarized Raman study of the Weyl semimetal TaAs. We observe all the optical phonons, with energies and symmetries consistent with our first-principles calculations. We detect additional excitations assigned to multiple-phonon excitations. These excitations are accompanied by broad peaks separated by 140 cm^{-1} that are also most likely associated with multiple-phonon excitations. We also noticed a sizable B_1 component for the spectral background, for which the origin remains unclear.

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I. INTRODUCTION

Although predicted long ago as a solution of the Weyl equation describing relativistic spin 1/2 fermions [1], Weyl fermions have yet to be observed experimentally in high-energy physics. A few years ago the existence of Weyl nodes behaving as Weyl fermions has been predicted in condensed matter physics [2–4], in materials called Weyl semimetals. An isolated Weyl node can be assimilated in momentum space to a monopole of topological charge defined by its chirality [4]. However, only very recently has the existence of Weyl nodes been proven experimentally. In particular, the existence of Weyl nodes predicted [5,6] in TaAs and isostructural compounds TaP, NbAs, and NbP has been inferred experimentally from their topological surface states measured by angle-resolved photoemission spectroscopy (ARPES) [7–9] and from their negative magnetoresistance induced by the chiral anomaly [10–14], and more directly from their bulk electronic band structure determined from bulk-sensitive ARPES measurements [9,15]. Besides the interesting physics derived from its topological surface and the topological nature of Weyl nodes, TaAs has a great potential for applications. Indeed, not only it is a binary compound with a relatively simple crystal structure, but the Weyl nodes are associated with bulk properties, in contrast to topological insulators for which only the surface shows a particular interest. Despite a complete description of the electronic structure of this exotic material, there is only little known, both theoretically and experimentally, about the lattice dynamics of TaAs. A better characterization of the lattice dynamics would allow for an optimization of the crystal and film growth of TaAs for practical applications.

In this paper, we report a Raman study of TaAs. We observe all the optical modes of TaAs at the Brillouin zone (BZ) center (Γ), which consist in one A_1 mode, two B_1 modes, and three E modes. The experimental energies of these modes, along with their symmetries, are consistent with our first-principles calculations. We detect peaks beyond the range of the single-phonon excitations assigned to multiple-phonon excitations, as well as broader features separated by 140 cm^{-1} that also

likely correspond to multiple-phonon excitations. Finally, we report a sizable B_1 component for the spectral background, which has an undetermined origin.

II. EXPERIMENT

The single crystals of TaAs used in this study were grown by chemical vapor transport and characterized by x-ray diffraction to determine the crystal orientation [10]. Freshly prepared platelike samples with a typical size of $0.4 \times 0.4 \times 0.08\text{ mm}^3$ were prepared for Raman scattering measurements. The measurements were performed with the 514.5 and 488.0 nm excitations of an Ar-Kr laser focused on the flat sample surface regions with a $100\times$ objective mounted in a backscattering micro-Raman configuration. The power at the sample was smaller than 0.4 mW. The signal was analyzed by a Horiba Jobin Yvon T64000 spectrometer equipped with a nitrogen-cooled CCD camera.

III. CALCULATIONS

The noncentrosymmetric structure of TaAs is characterized by the space group $I41md$ (C_{4v}^{11} , group No. 109), with four atoms in one unit cell. An analysis in terms of the irreducible representations of this group shows that the vibration modes of this system decompose [16] into $[A_1 + E] + [A_1 + 2B_1 + 3E]$, where the first and second terms correspond to the acoustic and optical phonon modes, respectively. While all the optical modes are Raman (R) active, only the A_1 and E modes are infrared (IR) active. To determine the phonon vibrational configurations and estimate the phonon frequencies, we performed calculations using the first-principles pseudopotential plane wave method package QUANTUM ESPRESSO [17]. We set a $12 \times 12 \times 12$ Monkhorst-Pack momentum (k) point mesh and a 45 Ry cutoff for the electronic wave functions. The exchange and correlation functional was treated within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof [18]. The coordinates and the cell shape of the experimental data [19] have been fully relaxed until the forces acting on the atoms are all smaller than 10^{-4} Ry/aB and the pressure is smaller than 0.2 kbar. Using the information on the ground state, it is easy to use the PHONON package, which implements the density functional perturbation theory (DFPT) [20–22] to get the phonon frequencies and vibration modes at the Γ

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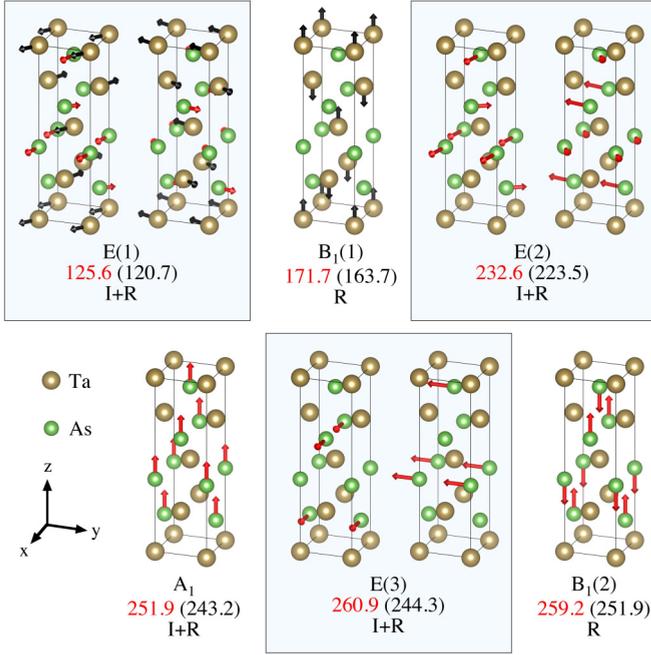


FIG. 1. (Color online) Main atomic displacements for the optical modes of TaAs. The displacements of Ta and As atoms are indicated by black and red arrows, respectively. We caution that the displacements of the Ta atoms are not represented when they are found to be too small compared to the displacements of the As atoms. The first line below each configuration of vibration indicates the mode symmetry in the C_{4v} group notation. The numbers in parentheses are used to specify modes when there is more than one mode with the same symmetry. The second line below each configuration of vibration indicates the experimental (calculated) mode energy. The last line below each configuration of vibration gives the optical activity, with I = infrared active, R = Raman active, and I + R = infrared and Raman active.

point. All the optical vibration modes of TaAs are illustrated in Fig. 1. For each mode we indicate the corresponding irreducible representation, the experimental and calculated phonon frequencies, as well as the optical activity. While the E modes are related to vibrations in the ab plane, the A_1 and B_1 modes are associated with vibrations along the c axis. In addition, we also calculated the phonon dispersion along the high-symmetry lines in the momentum space. We first applied DFPT calculations using the PHONON package on a coarse $4 \times 4 \times 4$ Monkhorst-Pack phonon momentum (q) point mesh to get their frequencies and modes. The dynamic matrix in real space is then obtained by a Fourier transformation of these modes. Finally, we transformed this real space dynamic matrix back to general q points and diagonalized it to get the dispersion.

IV. RESULTS AND DISCUSSION

Experimentally, the symmetry of the vibration modes can be described by the relevant Raman tensors of the C_{4v} group

(note that the A_2 channel is not Raman active):

$$A_1 = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}, \quad B_1 = \begin{pmatrix} c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$B_2 = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\left\{ E(x) = \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{pmatrix}, \quad E(y) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & e \\ 0 & e & 0 \end{pmatrix} \right\}.$$

In Fig. 2 we show the Raman spectra obtained in different ab -plane configurations of incident (\hat{e}^i) and scattered (\hat{e}^s) polarizations. Pure A_1 and B_1 symmetries are obtained in the $x'x'$ and $x'y'$ configurations of the polarizations, respectively. As expected from our group theory analysis, only one mode is observed in the $x'x'$ spectrum. Its energy, 251.9 cm^{-1} , is slightly higher than the calculated value (243.2 cm^{-1}). Similarly, we detected two peaks in the $x'y'$ configuration, in agreement with our analysis. The $B_1(1)$ peak is observed at 171.7 cm^{-1} while the $B_1(2)$ peak is detected at 259.2 cm^{-1} . In agreement with their symmetries, both the A_1 and the two B_1 modes are observed in the xx configuration while none of them appears in the xy spectrum.

In order to confirm further the symmetry of the Raman peaks observed, we performed an angular dependence study of the ab spectra. In Figs. 2(c) and 2(e) we display the intensity plots of the Raman spectra as a function of the in-plane angle θ defined with respect to the x axis for $\hat{e}^i \parallel \hat{e}^s$ and $\hat{e}^i \perp \hat{e}^s$, respectively. The intensity of the A_1 and B_1 modes for the corresponding plots are given in Figs. 2(d) and 2(f), respectively. As expected, the A_1 peak is observed only clearly for $\hat{e}^i \parallel \hat{e}^s$, with an intensity insensitive to the angle, as shown in Fig. 2(f). In contrast, the B_1 modes exhibit a strong angular dependence for both the $\hat{e}^i \parallel \hat{e}^s$ and $\hat{e}^i \perp \hat{e}^s$ configurations. For $\hat{e}^i \parallel \hat{e}^s$, we expect from the B_1 Raman tensor that the intensity should vary with angle such as $|c \cos(2\theta)|^2$, with a fourfold symmetry characterized by a maximum at 0° and a node at 45° , which is consistent with our observation, as shown in Fig. 2(d). For $\hat{e}^i \perp \hat{e}^s$, this pattern is shifted by 45° as the B_1 Raman tensor predicts an angular variation of the intensity proportional to $|c \sin(2\theta)|^2$, in agreement with our observation [see Fig. 2(f)]. Although this cannot be seen clearly from the individual spectra, we also point out a very small leak of the A_1 mode into the image plot displayed in Fig. 2(e), obtained with $\hat{e}^i \perp \hat{e}^s$. We attribute this leak to a small misalignment of the relative angle between \hat{e}^i and \hat{e}^s away from the perfect right angle.

We now describe the Raman measurements of the ac plane. For perfect alignment, no B_1 phonon should be observed while only the A_1 phonon should be detected when $\hat{e}^i \parallel \hat{e}^s$. This is consistent with the zz spectrum displayed in Fig. 2(b), which exhibits the A_1 mode at the same energy as in the ab plane spectra. Despite a much smaller intensity, we can detect some peaks in the zx configuration. In principle, only E modes should be observed in this configuration. However, four peaks (confirmed in several measurements) are detected instead of

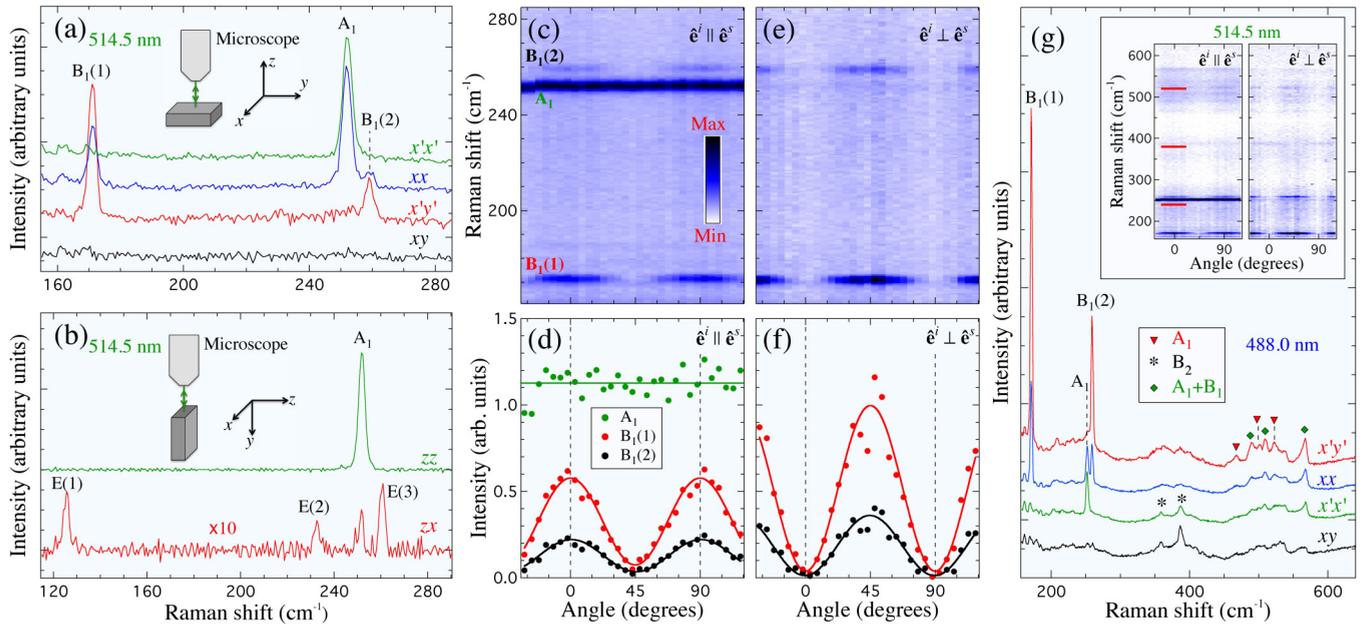


FIG. 2. (Color online) (a) Room temperature Raman spectra of TaAs for various *ab*-plane configurations of the incident and scattered light polarizations. The inset illustrates the experimental configuration. (b) Same as (a) but for the *ac* plane. The background of the *ac* spectra has been removed and the spectrum in the *zx* configuration has been multiplied by 10 for better visualization. (c) Intensity plot of the Raman shift as a function of the in-plane angle defined with respect to the *x* axis, for $\hat{e}^i \parallel \hat{e}^s$. (d) Angular dependence of the intensity of the Raman modes observed in (c) with $\hat{e}^i \parallel \hat{e}^s$. (e) Same as (c) but for $\hat{e}^i \perp \hat{e}^s$. (f) Same as (d) but for the Raman modes observed in (e) with $\hat{e}^i \perp \hat{e}^s$. (g) Long-range spectra of TaAs recorded with 488.0 nm laser excitation in several *ab*-plane configurations of polarization. The dominant symmetries of some sharp excitations at high energy are indicated. The inset shows the *ab*-plane angular dependence of the Raman intensity recorded with 514.5 nm laser excitation under the $\hat{e}^i \parallel \hat{e}^s$ and $\hat{e}^i \perp \hat{e}^s$ configurations of polarization. The red horizontal lines indicate the broad humps at 240, 380, and 520 cm^{-1} . The contrast has been adapted to illustrate a sizable B_1 symmetry component for the spectral background.

the three predicted. By matching the experimental data with the calculated values, we can unambiguously identify the $E(1)$ and $E(2)$ modes at 125.6 and 232.6 cm^{-1} , respectively. This leaves two candidate peaks at 251.7 and 260.9 cm^{-1} to be assigned to the $E(3)$ phonon, calculated to be located at 244.3 cm^{-1} , as shown in Fig. 1. The most likely explanation for the origin of the 251.7 cm^{-1} peak is its assignment to the A_1 mode, which has the same energy within error bars. Although this would be strictly forbidden for cross polarizations, we explained above a possible misalignment of the \hat{e}^i and \hat{e}^s polarizations away from the perfect right angle. Since the A_1 is much stronger in the *zz* spectrum as compared to the Raman intensity recorded in the *zx* spectrum, this hypothesis is quite plausible. Following this conclusion, we tentatively assign the peak at 260.9 cm^{-1} to the $E(3)$ phonon. Although this energy is close to that of the $B_1(2)$ mode (259.2 cm^{-1}), the energy difference is measurable. We note that none of the single-phonon peaks exhibits a Fano line shape or a particular broadening that would possibly be attributed to an electron-phonon coupling.

So far we have discussed single-phonon excitations, which have decent agreement with our calculations. The upper energy limit is 260.9 cm^{-1} . However, many Raman excitations are observed beyond that limit, as shown in Fig. 2(g). Considering that the phonon modes disperse in the momentum space, and allowing for small discrepancies between experiments and calculations, the energy range where these extra excitations are detected is consistent with double-phonon excitations, as confirmed by our calculation of the phonon dispersion along high-symmetry lines displayed in Fig. 3. It is worth noticing

at this point that these additional excitations are observed for all the samples that we measured, and also with the two laser wavelength excitations used in our study. For example,

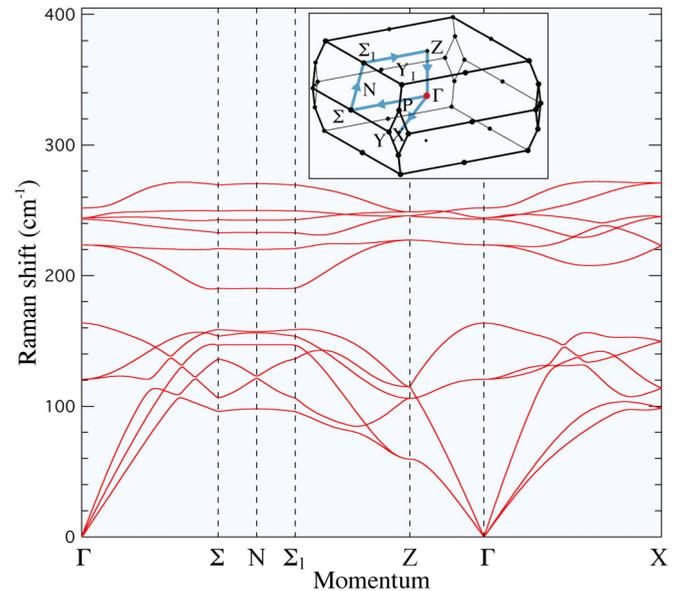


FIG. 3. (Color online) Calculation of the phonon band dispersions in TaAs along high-symmetry lines. The inset gives the definition of high-symmetry points in the momentum space. The blue arrows show the momentum path corresponding to the dispersion displayed.

Fig. 2(g) clearly shows their existence under 488.0 nm excitation while its inset shows clearly some intensity in the same energy range, as measured under 514.5 nm excitation. By comparing the spectra in Figs. 2(a) and 2(g), we report a variation of the relative intensity of the A_1 and B_1 phonons as the laser excitation varies. In contrast to the measurements performed using a 514.5 nm laser wavelength, for which the spectra show a stronger intensity of the A_1 peaks as compared to the B_1 peaks, the intensity of the B_1 peaks becomes larger than that of the A_1 mode under 488.0 nm laser excitation.

Double-phonon excitations can occur not only at the Γ point, but also anywhere on the BZ boundary, with the only restriction being that the total momentum is 0. A complete assignment of each feature is rather complicated and beyond the scope of our study, not only because modes disperse, but also because their symmetries vary with momentum. Nevertheless, the symmetries of many excitations can be described in terms of the C_{4v} point group and at least two of them can be tentatively identified as double excitations involving phonons at Γ . Indeed, we observe two sharp peaks at 358.8 and 386.7 cm^{-1} that appear clearly in the $x'y'$ and xy spectra. Such behavior is expected for a B_2 excitation. We also notice some reminiscence of that peak in the $x'y'$ spectrum, corresponding to a A_1 symmetry. As the ground state coincides with the A_1 representation, the symmetry of the excitation is directly determined by the tensor product of the irreducible representations characterizing the two phonon modes involved. The only three possibilities to get a double-phonon excitation at Γ with a B_2 symmetry are (1) $A_1 \times B_2 = B_2$, (2) $A_2 \times B_1 = B_2$, and (3) $E \times E = A_1 + A_2 + B_1 + B_2$. Since there is no A_2 and B_2 mode at Γ , the only possibility is to combine E modes. Interestingly, the excitations at 358.8 and 386.7 cm^{-1} coincide almost perfectly with $[E(1) + E(2)]$ ($125.6 \text{ cm}^{-1} + 232.6 \text{ cm}^{-1} = 358.2 \text{ cm}^{-1}$) and $[E(1) + E(3)]$ ($125.6 \text{ cm}^{-1} + 260.9 \text{ cm}^{-1} = 386.5 \text{ cm}^{-1}$), respectively.

We also observe additional features most likely related to double-phonon excitations, although a precise assignment of the modes involved and the corresponding momentum locations remains uncertain. Among peaks with a dominant

but not necessarily exclusive A_1 symmetry (as described within the C_{4v} point group), we detect features at 468.5, 501.7, and 523.1 cm^{-1} . Similarly, the peaks at 490.2, 509.2, and 567.7 cm^{-1} have a dominant $A_1 + B_1$ symmetry. Finally, we notice some broader features with a full width of about 100 cm^{-1} . The centers of these broad features are located at 240, 380, and 520 cm^{-1} , as shown in Fig. 2(g) and its inset. Interestingly, these broad humps are separated by 140 cm^{-1} . These features are detected in all the ab -plane configurations of polarization.

Interestingly, the inset of Fig. 2(g) suggests that the spectral background itself carries a sizable B_1 symmetry component. Indeed, we observe an intensity modulation with an angle that is similar to that of a B_1 phonon, with a lower intensity at 45° for $\hat{\mathbf{e}}^i \parallel \hat{\mathbf{e}}^s$, and at 0° and 90° with $\hat{\mathbf{e}}^i \perp \hat{\mathbf{e}}^s$. Whether this phenomenon originates from the lattice vibration, or is related to the Weyl semimetal nature of the electronic structure of TaAs, is unclear.

V. SUMMARY

In summary, we performed a polarized Raman study of the Weyl semimetal TaAs. We identified all the optical phonon modes of this material. Their energies and symmetries are consistent with our first-principles calculations. We observed additional features assigned to double-phonon excitations, as well as much larger humps separated by 140 cm^{-1} that are also likely to have a multiple-phonon origin. Finally, we identified a sizable B_1 component for the spectral background, whose origin is unknown.

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