Spectroscopy and Structural Investigation of Iron Phosphorus Trisulfide—FePS$_3$

Adam K. Budniak,* Szymon J. Zelewski,* Magdalena Birowska, Tomasz Woźniak, Tatyana Bendikov, Yaron Kauffmann, Yaron Amouyal, Robert Kudrawiec, and Efrat Lifshitz*

1. Introduction

The rediscovery and intense interest in 2D materials began with the exfoliation of a single graphite layer, called graphene, and presenting its extraordinary electronic[1] and mechanical[2] properties. An entire catalog of such materials emerged,[3] dividing them by many criteria, for example, their electronic conductivity (including superconducting states[4,5] and excitonic insulators[6,7]), optical properties, or characteristic element groups forming the crystals which can help predict the character of neighboring compounds by chemical trends.[8] A discovery of bandgap change from indirect to direct in a single layer of MoS$_2$,[9,10] and then other transition metal dichalcogenides (TMDs),[11] opened up broad interest in potential applications of semiconducting 2D materials in optoelectronics.[12,13] Prototypes of single-layer devices often exhibit performance superior to the ones fabricated in bulk semiconductors,[14,15] at the same time offering tightly confined (<1 nm[14,16]) systems for exploration of quantum effects.[17,18]

A unique group of 2D materials receiving growing attention is transition metal phosphorus trichalcogenides.[19–21] They are described by the empirical formula MPX$_3$, where M denotes the transition metal, P phosphorus, and X the chalcogenide. With sulfur being the most common chalcogenide, multiple transition metal trisulfides are formed. Their crystal structure is Lamellar structures of transition metal phosphorus trisulfides possess strong intralayer bonding, albeit adjacent layers are held by weak van der Waals interactions. Those compounds received enormous interest due to their unique combination of optical and long-range magnetic properties. Among them, iron phosphorus trisulfide (FePS$_3$) gathered special attention for being a semiconductor with an absorption edge in the near-infrared, as well as showing an Ising-like anti-ferromagnetism. A successful growth of centimeter size bulk FePS$_3$ crystals with a chemical yield above 70% is reported, whose crystallographic structure and composition are carefully identified by advanced electron microscopy methodologies, including atomic resolution elemental mapping, along with photoelectron spectroscopy. The knowledge on the optical activity of FePS$_3$ is extended utilizing temperature-dependent absorption and photoacoustic spectroscopies, while measurements are corroborated with density-functional theory calculations. Temperature-dependent experiments show a small and monotonic band-edge energy shift down to 115 K and expose the interconnected importance of electron-phonon coupling. Most of all, the correlation between the optical behavior and the magnetic phase transition is revealed, which shows the practical utilization of temperature-dependent optical absorption to investigate magnetic interactions.
determined by the hexathiohypo diphosphate anion: $P_2S_6^{4-}$ (simplified as $PS_3^{2-}$) undergoing elongation or distortion to sandwich different transition metals.[22] Many of them reveal a peculiar combination of physicochemical properties: 2D layered structure, semiconducting nature with open bandgap[23,24] and magnetic ordering[25,26] relevant for spintronics and magneto-optics. Optical absorption edges covering the spectral range from near-infrared up to ultraviolet[23,24] raised interest in applications of various MPX$_3$ materials as photodetectors and other opto-electronic devices.

Iron phosphorus trisulfide, FePS$_3$, attracts a lot of attention in that term. It has been shown to exhibit extraordinary photoconductive performance[27–29] arising from high carrier mobility and broadband optical absorption above the bandgap (1.2–1.5 eV depending on the experimental technique[23,24,29]) close to the optimal for solar cells as determined by the Shockley–Queisser limit. Negative photoconductivity[28] has also been observed in thin layers of FePS$_3$ for illumination with photons of energy around trap states within the conduction band, switchable in sign and magnitude by applying a gate voltage,[27] giving another parameter to control the device performance. Despite that, reports on optical properties of FePS$_3$ at low temperatures, providing details on the typical temperature range of artificially (cryogenics, thermoelectrics) or naturally (space environment[30]) cooled photodetectors, are lacking. Numerous reports cover the magnetic phase transitions in MPX$_3$ compounds based on magnetization measurements,[31–33] though the impact on their (including FePS$_3$) optical properties often remains unknown, as the spectroscopic studies are limited to room temperature. Its photosensitivity, competitive among other 2D materials, makes detailed optical and structural studies a necessary step in the development of MPX$_3$-based devices and sensors.

Our work aims to extend the knowledge on the optical activity of FePS$_3$ under conditions typical for cooled, low-noise photodetectors. Bulk FePS$_3$ crystals synthesized with high yield via chemical vapor transport (CVT) were characterized by powder X-ray diffraction, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS). Then the crystals were thinned by mechanical exfoliation to confirm the crystallographic structure, employing both transmission electron microscopy (TEM) to determine crystallographic planes, and the high-resolution scanning TEM (HR-STEM) with energy dispersive spectroscopy (EDS) mapping with sub-nanometer resolution for determining atomic arrangement. Then, we performed photoacoustic spectroscopy (PAS) and temperature-dependent optical absorption experiments, revealing a discontinuity of trend in the fundamental absorption edge energy upon the paramagnet to antiferromagnet transition. A $d$-$d$ intra-atomic transition forms another below-gap absorption band, and the analysis of its broadening served as a benchmark parameter for evaluating the electron-phonon coupling strength. The final remarks are complemented by comparing the STEM and optical spectroscopic results with the crystal and band structure calculated in the framework of the density-functional theory (DFT).

2. Results and Discussion

2.1. Preparation and Characterization of Bulk FePS$_3$

FePS$_3$ single bulk crystals have been synthesized from pure elements in quartz ampoules via CVT.[22,34,35] The reaction yield exceeded 70% and formed single crystals which approached lateral dimensions of a centimeter (Figure 1a).

Figure 1. A) Photograph of FePS$_3$ flakes as prepared in a sealed quartz ampoule (top) and a few individual flakes out of an ampoule (bottom). B) X-ray diffraction of a powder (green) and a single FePS$_3$ crystal (red). Vertical lines present the position of FePS$_3$ diffraction peaks according to PDF#04-005-1516.[36] C) HR-SEM image of FePS$_3$ single-crystal registered by the in-lens detector, exposing the lamellar structure. D) HR-SEM picture registered with secondary electron (SE) detector and three corresponding EDS maps (Fe, P, and S) presenting uniform distribution of the elements across the crystal.
X-ray diffractograms of both ground crystals and a single crystal were recorded (Figure 1b), showing agreement with the diffractions reported previously.[36] Figure S1, Supporting Information, introduces the EDS spectrum received with a SEM, confirming the presence of all three elements in the obtained material. A qualitative analysis delivers the atomic ratio Fe:P:S close to 1:1:3, thus confirming the composition of FePS$_3$. Furthermore, a high-resolution SEM (HR-SEM) image in combination with EDS mapping confirmed the lamellar structure and equal distribution of all elements across the whole crystal (Figure 1c,d).

2.2. TEM Study of Mechanically Exfoliated FePS$_3$

Figure S2, Supporting Information, presents the FePS$_3$ unit cell along three main directions. FePS$_3$ has monoclinic symmetry $C2/m$ with lattice parameters $a = 5.947 \ \text{Å}, \ b = 10.300 \ \text{Å}, \ c = 6.722 \ \text{Å}$, and $\beta \approx 107.16^\circ$. To precisely explore the structural properties of FePS$_3$, a bulk crystal was mechanically exfoliated directly onto a TEM grid.[37,38] A detailed description of the mechanical exfoliation and the transfer procedures were given in the Supporting Information and also were elaborated in the previous work.[37] Structural models presented in Figure S3, Supporting Information, show geometrical aspects of TEM of FePS$_3$ in different zone axes (Z.A.): [001] and [103]. Figure S4, Supporting Information, presents a low magnification micrograph of the whole flake, with the area marked where high-resolution TEM (HR-TEM) and selected area electron diffraction (SAED) experiments were performed. Figure 2a,c present HR-TEM images after average background subtraction examined along the [001] and [103] Z.A., respectively. Figure 2b,d portray the corresponding SAED patterns, confirming examination at the [001] and [103] Z.A., respectively. For [001] Z.A. electrons are moving along the $c$ direction and three different planes can be described: (200), $d = 0.28 \ \text{nm}$; (060), $d = 0.17 \ \text{nm}$ and (260), $d = 0.15 \ \text{nm}$. Although the diffraction pattern (DP) of FePS$_3$ in [001] Z.A. has locally a hexagonal arrangement of diffraction spots, the DP has globally only twofold symmetry. Consequently, in the HR-TEM micrograph of FePS$_3$ in [001] Z.A. only twofold symmetry is observed. This is in agreement with the crystal structure of FePS$_3$, which is a monoclinic system. Even though P$_2$ pairs and Fe atoms are hexagonally arranged, the FePS$_3$ crystal has two-fold symmetry as sulfur planes lower the symmetry. For [103] Z.A. electrons go along the $c^*$ axis, viz.,
normal to the ab-plane (normal to the surface of the flake). Registration of three equal planes: (060), (331), and (331), with \( d = 0.17 \) nm, and a sixfold symmetry (for both HRTEM image and DP) for a monoclinic system, agrees with an observation described by Murayama et al.,[39] who explained it by forming of rotational twin structure.

Previously, HRTEM experiments were discussed, that usually do not allow observing columns of atoms directly, but lattice fringes. High angle annular dark-field (HAADF) scanning TEM (STEM) has a different image forming mechanism and, for most cases, columns of atoms can be more directly imaged and interpreted.

Figure 3a presents a HAADF STEM micrograph of a mechanically exfoliated FePS₃ crystal[37,38] along the [001] Z.A. The micrograph is overlapped with a crystallographic model (Fe – red spheres, P – blue spheres, and S – yellow spheres).[36] Based on the HAADF signal, the mutual distance of 0.35 nm between adjacent Fe–Fe and Fe–P₂ columns were determined. Furthermore, Figure 3b–d depict, for the first time, atomically resolved EDS maps of any MPS₃ compound acquired along the [001] Z.A. Those maps unprecedently exposed the hexagonal arrangement of the Fe atoms and the columns of phosphorus pairs which are placed in the middle of the Fe hexagons. This conclusion is based on the fact that in the middle of the Fe hexagon, the EDS signal of phosphorus is much higher than that of iron. This observation is in agreement with the crystal structure in this Z.A. The mixing of Fe and P maps can be explained by sample drift, which cannot be avoided at such high magnification. The maps reveal a distance of 0.35 nm between neighboring Fe columns, in agreement with the Fe–Fe distance obtained with the HAADF detector. Moreover, the maps expose a spacing of 0.59 nm between adjacent P₂ columns. The described structure and measured inter-atomic distances agree with DFT calculations described further.

2.3. Optical Investigation of Bulk FePS₃

The excellent crystallographic quality confirmed by several electron microscopy and X-ray techniques served as a base for choosing a good quality material for optical studies of FePS₃.

Section 3 and Figure S5, Supporting Information, present XPS and UPS investigations of bulk FePS₃. With both techniques (different energy sources, penetration depth, cross-sections for the electronic transitions, etc.), the same values (0.6 eV) of the valence band maximum (VBM) and the second electronic transition (at 2.2 eV, with respect to the Fermi level in Au) were obtained, further strengthening the reliability of these measurements.

Figure 4a shows a comparison of room temperature optical absorption and photoacoustic spectra of a bulk FePS₃ crystal. Both spectroscopic methods reveal a broad, symmetric absorption feature centered around 1 eV, followed by a steep absorption edge in the 1.4–1.6 eV range. It is worth noting that both methods use monochromatic light illumination with varying wavelengths as opposed to broad-spectrum probing which could cause additional unwanted effects, including excessive sample heating or photovoltaic carrier generation. The photoacoustic spectrum follows the optical absorption profile up to 270 cm⁻¹ at 1.4 eV when it saturates, which is a typical effect in photoacoustic detection performed at low modulation frequencies.[40] The phase of the photoacoustic signal undergoes a steep decrease in the vicinity of the amplitude saturation region,
related to the heat source appearing closer to the sample surface due to the strong absorption of photons above the bandgap. PAS does not rely on analysis of light reflected or passed through a studied material and is intrinsically linked with optical absorption, further confirming the nature of any electromagnetic wave extinction below the saturation. The 1 eV absorption peak agrees with the $3d-3d$ atomic-like metal ($Fe^{2+}$) transition from fundamental $^5T_{2g}$ to the first excited state $^5E_g$ (further called the $d-d$ transition for simplicity), appearing within the forbidden energy region, previously reported on FePS$_3$ and other MPX$_3$ compounds.[23,41–43] Despite the prediction of $d-d$ transitions at higher energies,[41] derivatives of optical spectra shown in Figure 4b contain only symmetric extrema (each well fitted with a single Gaussian peak) indicating the absence of other hidden transitions, even in the low-temperature spectrum presented in Figure 4c. Oscillations observed in the 0.6–1.2 eV region are a result of numerical differentiation and have no physical meaning. The high-energy absorption feature (onset around 1.9 eV) cannot be precisely analyzed (including the temperature dependence) due to significant overlap with the main absorption edge and saturation on the high-energy region resulting from low sample optical transparency.

The low-energy $d-d$ transition can be approximated with a Gaussian shape. As shown in Figure 5a, subtraction of the
fitted curve from the original spectrum leaves a clean sub-gap absorption residue (Figure 5b). A comparison of Tauc plots for the absorption edge around 1.4 eV proves that the d-d transition does not affect the bandgap determination even at room temperature when the transition is the broadest (difference of a few meV), see insets of Figure 5a,b. The temperature dependence of the d-d feature shown in Figure 5c reveals a small redshift of the transition peak and a significant decrease of its broadening upon increasing the temperature. The transition energy and full width at half maximum (FWHM) are determined in the full temperature range in Figure 5d, following the procedure previously shown in Figure 5a. The bandgap-related absorption edge shown in Figure 5d also redshifts with the increasing temperature, as revealed by applying Tauc plots to analyze the spectra.

The determined transition energies are summarized in Figure 6a. The fundamental absorption edge at 10 K is 1.44 eV and quickly decreases with an abrupt change in the 100–120 K region. The trend is followed by an almost linear shift up to room temperature (≈1.40 eV at 300 K), resembling typical models for the temperature dependence of a semiconductor bandgap. For comparison, the original Brec’s work[23] reports the bandgap energy of FePS3 to be 1.5 eV, though it was determined arbitrarily in the middle of the absorption edge. Our room temperature result is in good agreement with the absorption onset at ≈880 nm (≈1.41 eV) measured on a thin (11 nm) exfoliated film reported by Gao & Lei et al.[27] Monotonic and predictable absorption edge shift within the temperature range covered by present state-of-the-art thermoelectric cells (200–250 K)[46] is relevant for extending the usefulness of FePS3 as the active material for low-noise cooled photodetectors covering a broad spectral range from near-infrared up to ultraviolet. The characteristic region of anomalous temperature dependence coincides with a transition from the paramagnetic (PM) to the antiferromagnetic (AFM) phase of FePS3 (Néel temperature). The same behavior has been observed on a few samples of the synthesized material and during multiple heating/cooling cycles on the same sample, proving good reversibility of the phase transition. Monotonic absorption edge blueshift upon cooling in the range covering the PM-AFM transition has already been observed for other MPX3 materials, including MnPS3[51,52] and NiPS3.[53] This observation might be a link between the magnetic ordering and changes in the band structure of the material resulting from crystal lattice distortion, as previously reported based on temperature-dependent structural studies.[39]

The d-d transition peak energy, depicted by a purple curve in Figure 6a, goes parallel with the temperature dependence of the fundamental absorption edge, ranging from 1.095 to 1.055 eV. The sudden slope shift around 110 K proves that the localized d levels respond to the phase transition via the crystal field effect. Derivatives of both curves and their single Gaussian fits, shown in insets of Figure 6a, reveal more accurately the transition temperatures as (112 ± 1) K for the bandgap absorption and (114 ± 1) K for the d-d transition, accordingly. In addition, these results show that the phase transition in MPX3 and other (anti)ferromagnets can be indirectly (through transition-induced changes in crystal parameters) detected by purely optical methods such as simple absorption measurements.

Figure 6b shows the temperature dependence of d-d transition broadening represented by the FWHM of the fitted Gaussian curve. The huge change from ≈220 up to ≈500 meV at room temperature suggests strong electron-phonon coupling with various possible carrier scattering mechanisms. By applying the formula:

$$\Gamma(T) = \Gamma_0 + \frac{\gamma_{LO}}{e^{\frac{E_{LO}}{kT}} - 1} + \gamma_{AC}T$$

the contributions of longitudinal optical (LO, Fröhlich) and acoustic (AC) phonons can be distinguished in the...
broadening parameter. \( \gamma_b \) stands for inhomogeneous broadening, \( E_{LO} \) the LO phonon energy, \( k_B \) the Boltzmann constant, \( \gamma_{LO} \) and \( \gamma_{AC} \) the coupling constants for LO and AC phonons, respectively. The FHWM experimental points are fitted with Equation (1) with and without the acoustic phonon contribution. With the AC coupling parameter left as a free parameter, the fit quality is slightly worse (\( R^2 \) 0.9981 versus 0.9997) and does not approximate the data well in the low-temperature range. A low \( \gamma_{AC} \) value of \( 2.4 \times 10^{-4} \) causes the fitted curves to overlap above 100 K. The proper analysis of acoustic phonon contribution in the broadening requires narrow features in optical spectra, typically found in ultra-pure inorganic semiconductors such as GaN.\(^{[55]}\) For determining the dominating coupling parameters with LO phonon the \( \gamma_{AC} \) is thus omitted. The obtained \( E_{LO} \) is \( (28.1 \pm 0.1) \) meV, in excellent agreement with the 225 cm\(^{-1} \) (27.9 meV) \( A_g/B_g \) mode found in the Raman spectrum (Figure 6c) well above the phononic bandgap separating the acoustic and optical branches, which also agrees with previously reported results.\(^{[56,57]}\) All high-energy peaks (>150 cm\(^{-1} \)) originate from vibrational modes of the \( \text{P}_2\text{S}_6^4^- \) anion,\(^{[58,59]}\) suggesting that electron-phonon coupling strength might be evaluated based on differences in atomic weights of the transition metals.\(^{[57]}\) It is relevant to mention that Raman modes above the AFM transition temperature are only affected by intra- and interlayer coupling, from commonly studied TMDs known to cause energy shifts of particular peaks. In the case of FePS\(_3\), mode frequencies between bulk material and thin films down to the monolayer (ML) regime do not change significantly, most likely due to relatively weak van der Waals interaction.\(^{[24,59]}\) Scarce information about the Fröhlich coupling can be found for MPX\(_3\) materials, though recent analysis of temperature-dependent absorption and modulated thermoreflectance spectra have been reported on NiPS\(_3\).\(^{[53]}\) Significantly higher electron-phonon interaction strength of \( (1800 \pm 800) \) meV for one of the optical transitions has been explained by flat spin-orbit split-off band dispersion. Our \( \gamma_{LO} \) value of \( (520 \pm 2) \) meV can be explained in a similar matter taking into account the localized character of the \( d-d \) transition\(^{[60]}\) and therefore complements the physical understanding of physical processes affecting the optical activity of transition metal phosphorus trisulfides.

### 2.4. FePS\(_3\) Band Structure Calculations

To extend the analysis of optical properties of FePS\(_3\) and point out aspects differentiating it from other layered semiconductors, we performed electronic band structure calculations employing the DFT + \( U \) method. The FePS\(_3\) is an Ising-like antiferromagnet (AFM) with a honeycomb lattice.\(^{[20]}\) The magnetic ground state of a bulk system exhibits the AFM zigzag order within the plane, and the adjacent layers are antiferromagnetically aligned.\(^{[22]}\) However, the magnetic ground state is not commensurate with the lattice structure, thus, we have chosen the smallest possible magnetic unit cell (see Figure 7a) which contains 40 atoms. It is worth mentioning that the position of the band edges depends on the choice of the Hubbard \( U \) of the 3d states, which has been shown to have a minor impact in the case of MnPS\(_3\),\(^{[61]}\) but remains significant for FePS\(_3\). This difference stems from the fact that in the case of MnPS\(_3\) there is a smaller contribution of the 3d states to the band edges than for FePS\(_3\). In particular, the Hubbard \( U \) affects the position of the Fe 3d states with respect to the Fermi

**Figure 7.** Electronic structure of the bulk FePS\(_3\), obtained with GGA + D3 + \( U \) (\( U = 2.6 \) eV) approach. A) A magnetic unit cell (solid black lines) used in the calculations (for clarity only iron atoms are shown) with B) the corresponding first BZ with high symmetry \( k \)-points and recommended high symmetry \( k \)-path\(^{[62]}\) plotted in blue. C) The fundamental indirect bandgap equal to 1.44 eV is visible. The difference between the direct and indirect transitions is 60 meV and may depend on the Hubbard \( U \). The 3d band projections of the Fe atoms (denoted in red) and projected density of states (PDOS) are presented. The main contribution close to the Fermi level comes from the 3d states of Fe atoms. The valence and conduction band edges are denoted by blue circles. Note that the two conduction band minima are visible (two valleys). The arrows in (A) indicate the spin arrangements on iron atoms.
level, which might result in a different bandgap character. Notably, for the $U = 2.6\; eV$, the indirect bandgap is obtained, whereas for the $U = 5.3\; eV$ the direct character is clearly visible for the ML FePS$_3$ (see Figure S4, Supporting Information). Thus, the proper Hubbard $U$ is of significant importance (details in SI) and was set to be equal to 2.6 eV, which nicely reproduces the experimental bandgap as well as the positions of the 3d orbital projections similar to the hybrid functional. Our theoretical results for the FePS$_3$ bulk structure reveal an indirect character of the electronic bandgap, which is equal to 1.44 eV (see Figure 7) and matches perfectly the experimental bandgap of 1.4 eV obtained here from several optical measurements. Nevertheless, the bands close to the Fermi level are flat and the difference between the indirect and direct transitions is 60 meV. In addition, a much smaller bandgap equal to 1.23 eV has been previously reported for the bulk system,$^{29}$ which is consistent with the choice of the $U$ ($U = 2.2\; eV$). However, the transition reported in this work occurs at different k-points in the Brillouin zone (BZ), which points to a different unit cell, not commensurate with the magnetic unit cell of a bulk (see Figure 7a). In addition, the comparison between the ML and bulk system reveals that the theoretical bandgap of bulk is 0.4 eV smaller than for the ML case ($U = 2.6\; eV$, please refer to Supporting Information). This is in line with the general trend of the bandgap behavior for the van der Waals materials.

The structural parameters, as well as distances for the bulk system, are in good agreement with our structural characterization (compared in Figure 8) and with previously reported ab initio results.$^{63}$

### Table

|          | HR-STEM experiment (Å) | DFT calculations (Å) |
|----------|------------------------|----------------------|
| $d_{Fe-Fe}$ | 3.5                    | 3.438                |
| $d_{P-P}$   | -                      | 2.204                |
| $d_{P1-P2}$ | 5.9                    | 5.969                |
| $d_{Fe-P}$  | 3.5                    | 3.591                |

Figure 8. Side view model of FePS$_3$ monolayer: Fe (red spheres), P (blue spheres), and S (yellow spheres). The (001) plane is presented also with inter-atom distances that are discussed in the table. The table introduces a comparison between experimental (atomic resolution EDS mapping and HR-STEM imaging presented in Figure 3) and theoretical distances between the atoms. Structural parameters for the bulk obtained in the GGA + D3 + U approach are in good agreement with previously reported values.$^{63}$

### 3. Conclusions

We demonstrated a CVT synthesis of large, centimeter size FePS$_3$ crystals, providing 70% product yield. The extensive structural characterization confirms the compositional uniformity of the synthesized material. To the best of our knowledge, for the first time on any transition metal phosphorus trisulfide, different positions of atomic columns were revealed by high-resolution STEM coupled with EDS mapping. FePS$_3$ was further investigated independently via XPS and UPS, showing a valence band maximum for 0.6 eV and a second electronic transition at 2.2 eV. The optical activity of FePS$_3$ has been evaluated at room temperature by photoacoustic and optical spectroscopy, distinguishing the d-d intraatomic-like transition from the fundamental absorption edge. Temperature-dependent absorption spectra provide new insight into the potential usefulness of FePS$_3$ as the active material in cooled photodetectors, as the bandgap energy (1.4 eV) shift is monotonic and relatively small down to the magnetic phase transition temperature around 115 K. Additionally, the demonstrated fully optical approach to study phase transitions in (anti)ferromagnetic materials reveals the link between magnetic arrangement and band structure changes, paving the way toward future explorations of magneto-optic coupling effects. Huge absorption broadening sheds new light on the localized nature of the observed d-d transition and leads to an analysis of electron-optical phonon interaction strength. The calculated band structure within the DFT + U approach, first used to verify the findings of optical spectroscopy, points out the relevance of considering a proper Hubbard parameter ($U$) value on electronic structure results, affecting the band edges and the determined bandgap character. We believe that our results will support future research and increase the interest in iron phosphorus trisulfide as a representative of unique magnetic layered semiconductors.

### 4. Experimental Section

All experimental details and methodology are given in the Supporting Information (SI). VESTA software$^{65}$ was used for crystal structure visualization, including the Supporting Information.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

A.K.B. and E.L. were supported by the European Commission via the Marie Sklodowska-Curie action Phonsi (H2020-MSCA-ITN-642656). S.J.Z. and R.K. performed research within the grant of the National Science Centre Poland (OPUS 11 no. 2016/21/B/ST3/00482). S.J.Z. is a beneficiary of the START scholarship from the Foundation for Polish Science. M.B. acknowledges financial support from the National Science Centre Poland (SONATA 12 grant no. 2016/23/D/ST3/03466). Access to computing facilities of TU Dresden (ZIH) within the project “TransPheMat”, PL-Grid Polish Infrastructure for Supporting Computational Science in the European Research Space, and of the
Interdisciplinary Center of Modeling (ICM), University of Warsaw are gratefully acknowledged. E.L. acknowledges the financial support from the Israel Science Foundation (No. 2528/19) and from the USA National Science Foundation—USA/Israel Binational Science Foundation (NSF-BSF, No. 2017637). The authors thank Prof. Pawel Scharoch (Wroclaw University of Science and Technology, Poland) for fruitful discussions. The authors want to acknowledge Prof. Reshef Tenne, Dr. Rita Rosentsveig, and Dr. Marco Serra (Weizmann Institute of Science, Israel) with an appreciation for the introduction to the synthesis of FePS₃. The authors thank Dr. Alex Berner (Technion — Israel Institute of Technology, Israel) for advice for SEM microscopy, and Mr. Michael Kalina (Technion — Israel Institute of Technology, Israel) for his technical support.

**Conflict of Interest**

The authors declare no conflict of interest.

**Author Contributions**

A.K.B. and S.J.Z. contributed equally to this work. A.K.B. synthesized materials and performed structural experiments (XRD, electron microscopy). S.J.Z. did temperature-dependent absorption and photoacoustic spectroscopy experiments. M.B. implemented DFT calculations for monolayer and bulk material with T.W. support. Y.K. photoacoustic spectroscopy experiments. M.B. implemented DFT microscopy). S.J.Z. did temperature-dependent absorption and UPS experiments. R.K. supervised optical measurements. E.L. and T.W. support. Y .K. superintended materials preparation. S.J.Z., A.K.B., M.B., and T.B. and interpreted results and wrote the manuscript with input from all authors.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

density-functional theory, electron microscopy, FePS₃, layered semiconductors, spectroscopy, van der Waals materials

Received: November 16, 2021
Revised: December 31, 2021
Published online: February 12, 2022

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Science 2004, 306, 666.
[2] C. Lee, X. Wei, J. W. Kysar, J. Hone, Science 2008, 321, 385.
[3] P. Miró, M. Audiffred, T. Heine, Chem. Soc. Rev. 2014, 43, 6537.
[4] Y. Saito, T. Nojima, Y. Iwasa, Nat. Rev. Mater. 2017, 2, 16094.
[5] D. Qiu, C. Gong, S. Wang, M. Zhang, C. Yang, X. Wang, J. Xiong, Adv. Mater. 2021, 33, 2006124.
[6] Y. Wakisaka, T. Sudayama, K. Takubo, T. Mizokawa, M. Arita, H. Namatame, M. Taniguchi, N. Katayama, M. Nohara, H. Takagi, Phys. Rev. Lett. 2009, 103, 264602.
[7] L. Li, W. Wang, L. Gan, N. Zhou, X. Zhu, Q. Zhang, H. Li, M. Tian, T. Zhai, Adv. Funct. Mater. 2016, 26, 8281.
[8] M. A. Susner, M. Chyasnavichyus, M. A. McGuire, P. Ganesh, P. Maksymovych, Adv. Mater. 2017, 29, 1602852.
[9] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C. Y. Chim, G. Galli, F. Wang, Nano Lett. 2010, 10, 1271.
[10] K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, Phys. Rev. Lett. 2010, 105, 136805.
[11] W. Shi, M.-L. Lin, Q.-H. Tan, X.-F. Qiao, J. Zhang, P.-H. Tan, 2D Mater. 2016, 3, 025016.
[12] W. Zhang, Q. Wang, Y. Chen, Z. Wang, A. T. S. Wee, 2D Mater. 2016, 3, 022001.
[13] K. F. Mak, J. Shan, Nat. Photonics 2010, 6, 216.
[14] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, Nat. Nanotechnol. 2011, 6, 147.
[15] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, A. Kis, Nat. Nanotechnol. 2013, 8, 497.
[16] S. B. Desai, S. R. Midhavpathy, A. B. Sachid, J. P. Llinas, Q. Wang, G. H. Ahn, G. Ptnr, M. J. Kim, J. Bokor, C. Hu, H.-S. P. Wong, A. Javey, Science 2016, 354, 99.
[17] C. Chakraborty, K. M. Goodfellow, S. Dhara, A. Yoshimura, V. Meunier, A. N. Vamivakas, Nano Lett. 2017, 17, 2253.
[18] M. Parzefall, A. Szabó, T. Taniguchi, K. Watanabe, M. Lusier, L. Novotny, Nat. Commun. 2019, 10, 292.
[19] L. Wang, P. Hu, Y. Long, Z. Liu, X. He, J. Mater. Chem. A 2017, 5, 22855.
[20] R. Samal, G. Sanyal, B. Chakraborty, C. S. Rout, J. Mater. Chem. A 2021, 9, 2560.
[21] Y. Zhang, T. Fan, S. Yang, F. Wang, S. Yang, S. Wang, J. Su, M. Zhao, X. Hu, H. Zhang, T. Zhai, Small Methods 2021, 5, 2000168.
[22] R. Brec, Solid State Ionics 1986, 22, 3.
[23] R. Brec, D. M. Schleich, G. Ouvrard, A. Louisy, J. Rouxel, Inorg. Chem. 1979, 18, 1814.
[24] K. Z. Du, X. Z. Wang, Y. Liu, P. Hu, M. I. B. Utama, C. K. Gan, Q. Xiong, C. Kloc, ACS Nano 2016, 10, 1738.
[25] M. Gibertini, M. Koperski, A. F. Morpurgo, K. S. Novoselov, Nat. Nanotechnol. 2019, 14, 408.
[26] M. Blei, J. L. Lado, Q. Song, D. Dey, O. Ertzen, V. Pardo, R. Comin, S. Tongay, A. S. Botana, Appl. Phys. Rev. 2021, 8, 021301.
[27] Y. Gao, S. Lei, T. Kang, L. Fei, C. L. Mak, J. Yuan, M. Zhang, S. Li, Q. Bao, Z. Zeng, Z. Wang, H. Gu, K. Zhang, Nanotechnology 2018, 29, 244001.
[28] Z. Ou, T. Wang, T. Tang, X. Zong, W. Wang, Q. Guo, Y. Xu, C. Zhu, L. Wang, W. Huang, H. Xu, Adv. Opt. Mater. 2020, 8, 2000201.
[29] M. Ramos, F. Carrascoso, R. Frisenda, P. Gant, S. Mañas-Valero, D. L. Esteras, J. J. Baldovi, E. Coronado, A. Castellanos-Gomez, M. R. Calvo, npj 2D Mater. Appl. 2021, 5, 1.
[30] R. Thirsk, A. Kuipers, C. Mukai, D. Williams, Can. Med. Assoc. J. 2009, 180, 1216.
[31] C. C. Mayorga-Martinez, Z. Sofer, D. Sedmidubský, Š. Huber, A. Y. S. Eng, M. Pumera, ACS Appl. Mater. Interfaces 2017, 9, 12563.
[32] Y. Peng, S. Ding, M. Cheng, Q. Hu, J. Yang, F. Wang, M. Xue, Z. Liu, Z. Lin, M. Avdeev, Y. Hou, W. Yang, Y. Zheng, J. Yang, Adv. Mater. 2020, 32, 2001002.
[33] M. J. Coak, D. M. Jarvis, H. Hamidov, A. R. Wildes, J. A. M. Paddison, C. Liu, C. R. S. Haines, N. T. Dang, E. C. Kichanov, N. B. Savenkov, S. Lee, M. Kratochvillová, S. Klotz, T. C. Hansen, D. P. Kozlenko, J.-G. Park, S. S. Saxena, Phys. Rev. X 2021, 11, 011024.
[34] W. Klingen, R. Ott, H. Hahn, Z. Anorg. Allg. Chem. 1973, 396, 277.
[35] B. E. Taylor, J. Steger, A. Wold, J. Solid State Chem. 1973, 7, 461.
[36] G. Ouvrard, R. Brec, J. Rouxel, Mater. Res. Bull. 1985, 20, 1181.
[37] A. K. Budniak, N. A. Killilea, S. J. Zelewska, M. Sytnyk, Y. Kaufmann, Y. Amouyal, R. Kudrawiec, W. Heiss, L. Wong, I. Kaminer, Nat. Photonics 2020, 14, 686.
[39] C. Murayama, M. Okabe, D. Urushihara, T. Asaka, K. Fukuda, M. Isobe, K. Yamamoto, Y. Matsushita, J. Appl. Phys. 2016, 120, 142114.
[40] P. Poulet, J. Chambron, R. Unterreiner, J. Appl. Phys. 1980, 51, 1738.
[41] M. Piacentini, F. S. Khumalo, G. Leveque, C. G. Olson, D. W. Lynch, Chem. Phys. 1982, 72, 61.
[42] V. Grasso, S. Santangelo, M. Piacentini, Solid State Ionics 1986, 20, 9.
[43] E. J. K. B. Banda, Phys. Status Solidi B 1986, 138, K125.
[44] Y. P. Varshni, Physica 1967, 34, 149.
[45] K. P. O’Donnell, X. Chen, Appl. Phys. Lett. 1991, 58, 2924.
[46] D. Zhao, G. Tan, Appl. Therm. Eng. 2014, 66, 15.
[47] G. L. Flem, R. Brec, G. Ouvard, A. Louisy, P. Segransan, J. Phys. Chem. Solids 1982, 43, 455.
[48] K. Kurosawa, S. Saito, Y. Yamaguchi, J. Phys. Soc. Jpn. 1983, 52, 3919.
[49] P. A. Joy, S. Varshni, Phys. Rev. B 1992, 46, 5425.
[50] D. Lançon, H. C. Walker, E. Ressouche, B. Ouladdiaf, K. C. Rule, G. J. McIntyre, T. J. Hicks, H. M. Rønnow, A. R. Wildes, Phys. Rev. B 2016, 94, 214407.
[51] V. Grasso, F. Neri, P. Perillo, L. Silipigni, M. Piacentini, Phys. Rev. B 1991, 44, 11060.
[52] V. G. Piryatinskaya, I. S. Kachur, V. V. Slavin, A. V. Yeremenko, Y. M. Vysotskikh, Low Temperature Physics 2012, 38, 870.
[53] C.-H. Ho, T.-Y. Hsu, L. C. Muhammah, npj 2D Mater. Appl. 2021, 5, 8.
[54] A. D. Wright, C. Verdi, R. L. Milot, G. E. Eperon, M. A. Pérez-Osorio, H. J. Snaith, F. Giustino, M. B. Johnston, L. M. Her, Nat. Commun. 2016, 7, 11755.
[55] A. K. Viswanath, J. I. Lee, Phys. Rev. B 1998, 58, 16333.
[56] M. Bernasconi, G. Benedek, L. Miglio, Phys. Rev. B 1988, 38, 12100.
[57] F. Kargar, E. A. Coleman, S. Ghosh, J. Lee, M. J. Gomez, Y. Liu, A. S. Magana, Z. Barani, A. Mohammadzadeh, B. Debnath, R. B. Wilson, R. K. Lake, A. A. Balandin, ACS Nano 2020, 14, 2424.
[58] M. Scagliotti, M. Jouanne, M. Balkanski, G. Ouverard, G. Benedek, Phys. Rev. B 1987, 35, 7097.
[59] J. U. Lee, S. Lee, J. H. Ryoo, S. Kang, T. Y. Kim, P. Kim, C. H. Park, J. G. Park, H. Cheong, Nano Lett. 2016, 16, 7433.
[60] R. Atta-Fynn, P. Biswas, D. A. Drabold, Phys. Rev. B 2004, 69, 245204.
[61] M. Birowska, P. Faria Junior, J. Fabian, J. Kunstmann, Phys. Rev. B 2021, 103, L121108.
[62] Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Comput. Mater. Sci. 2017, 128, 140.
[63] B. L. Chittari, Y. Park, D. Lee, M. Han, A. H. Macdonald, E. Hwang, J. Jung, Phys. Rev. B 2016, 94, 184428.
[64] K. Momma, F. Izumi, J. Appl. Crystallogr. 2011, 44, 1272.