

Rich Polymorphism of Layered NbS₃

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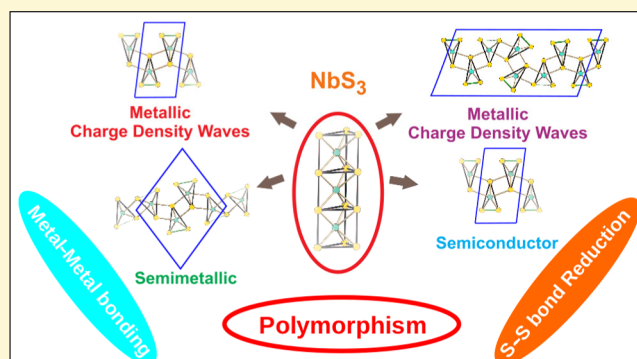
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ABSTRACT: Layered group V transition-metal trichalcogenides are paradigmatic low-dimensional materials providing an ever increasing series of unusual properties. They are all based on the same basic building units, one-dimensional MX₃ (M = Nb, Ta; X = S, Se) trigonal-prismatic chains that condense into layers, but their electronic structures exhibit significant differences leading to a broad spectrum of transport properties, ranging from metals with one, two, or three charge density wave instabilities to semimetals with potential topological properties or semiconductors. The different physical and chemical properties are shown to be related with subtle structural differences within the layers that result in half-, third-, or quarter-filled quasi-one-dimensional Nb d_{z²}-type bands, providing a clear-cut illustration of the intimate link between structural and electronic features within a family of solids. An interesting yet not sufficiently explored feature of these solids

is the polymorphism. Based on both experimental and new theoretical results, we examine this aspect for NbS₃ and show that at least seven different polymorphs with a stability compatible with the presently known phases of this compound are possible. We discuss a simple rationale for the physical properties of the presently known polymorphs as well as predictions for those that have still not been characterized or prepared. It is argued that some of the presently unknown polymorphs may have been prepared in an uncontrolled way as mixtures of different phases which could not be structurally characterized. The rich landscape of structures and properties found for this van der Waals material is suggested to represent an ideal platform for the preparation of flakes with fine-tuned properties for applications in new electronic and optoelectronic devices.



INTRODUCTION

Layered group V transition-metal trichalcogenides display a plethora of challenging physical and chemical properties such as charge density waves (CDW), superconductivity, easy chemical intercalation, and so forth.¹ Very recently, it has been shown that they may also provide useful platforms for next-generation electronic and optoelectronic 2D materials.^{2,3} The CDW material NbSe₃ for instance is one of the archetypal systems in low-dimensional materials science.^{4,5} It was the first inorganic solid found to exhibit Fröhlich-type conductivity, and this observation launched a huge and continued interest on it. Almost 40 years later, very fundamental aspects of its physical and chemical behavior still remain challenging.^{6–9} NbSe₃^{10,11} is a room-temperature quasi-one-dimensional metal¹² which undergoes two successive Fermi surface-driven incommensurate CDW transitions at 145 and 59 K, respectively.^{11,13,14} After the second CDW transition, NbSe₃ still exhibits metallic character so that the Fermi surface is not completely removed by the CDWs. Interestingly, monoclinic-TaS₃ (*m*-TaS₃),¹⁵ which is isostructural with NbSe₃ and also exhibits two successive incommensurate CDWs at 240 and 160 K,¹⁶ becomes semiconducting after the second transition, indicating that the Fermi surface has been indeed completely destroyed in this case.

Such contrasting low-temperature behavior has been related to the different strength of the inter-chain interactions.^{9,17}

The crystal structure of NbSe₃,¹¹ as those of all systems to be discussed in this work, is built from a series of MX₃ chains where the transition-metal atoms are in a trigonal prismatic coordination (see Figure 1a). It may be considered as a less symmetric variation of the TiS₃-type structure¹⁸ (Figure 1b). While all trigonal prismatic chains are structurally equivalent in the TiS₃ structure, three nonequivalent chains, marked as I, II, and III in Figure 1a, can be distinguished in the NbSe₃ structure. The high-symmetry TiS₃-type structure has been found for all group IV MX₃ solids (M = Ti, Zr, Hf; X = S, Se, Te). It is important to note that since in this type of structures two adjacent chains are displaced by half the repeat vector along the chain direction (*b*), the transition-metal atom is actually coordinated to six X-atoms of its own chain and two additional X-atoms of the neighboring chains, leading to an MX₃ layer. A

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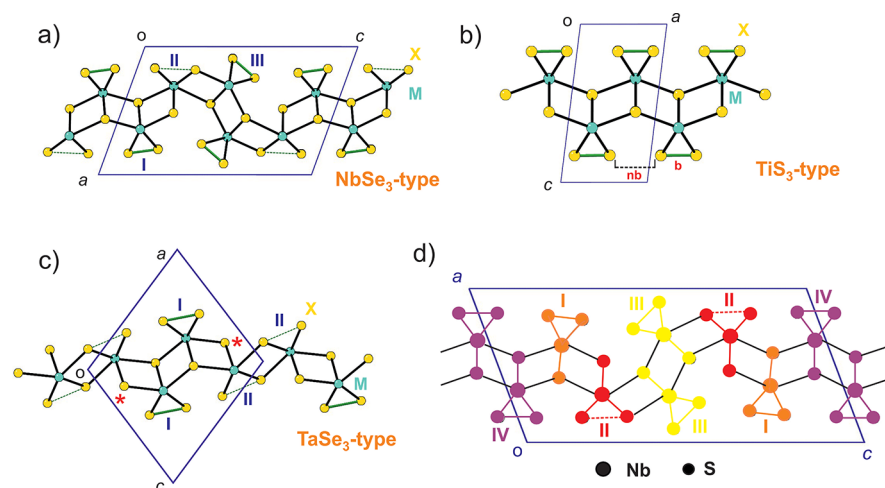


Figure 1. Top view of different MX_3 crystal structures: (a) $\text{NbSe}_3/m\text{-TaS}_3$, (b) TiS_3 , (c) TaSe_3 , and (d) $\text{NbS}_3\text{-II}$. In all cases, adjacent chains are shifted by $1/2$ the repeat vector along the chain direction (i.e., b). In (a–c), the short and relatively long $\text{X}\cdots\text{X}$ contacts important for electron counting are shown as full and dashed green lines, respectively. Labels I, II, III, and IV denote different trigonal prismatic chains (see text). In (d), the four different types of chains are shown with different colors using the same color coding as in the experimental structural determination.¹⁹ The short and relatively long $\text{X}\cdots\text{X}$ contacts are shown as full and dashed lines, respectively. By analogy with NbSe_3 (a), the chain with a long $\text{S}\cdots\text{S}$ triangular side is labeled as chain II and the chain which is tilted with respect to the c -direction of the layer will be referred to as chain III.

very important structural observation is that in the group IV MX_3 phases, the X_3 triangles are not equilateral-like but isosceles since one of the $\text{X}-\text{X}$ contacts, highlighted in green in Figure 1b, is compatible with an $\text{X}-\text{X}$ bond, whereas the other two are equivalent but considerably longer. Thus, for electron counting purposes, the isolated X -atoms must be considered as X^{2-} and the $\text{X}-\text{X}$ bonded pair as $(\text{X}_2)^{2-}$, leaving the transition-metal atom as d^0 . For group V MX_3 compounds, the additional electron per transition-metal atom leads to two significant structural changes that strongly affect the electronic structure. First, as a result of the additional electrons, some $\text{X}-\text{X}$ bonds are broken and the X_3 triangles become almost equilateral (see the chains labeled II in Figure 1a where the broken bond has been shown as a dashed line). Second, as a consequence of the local strain generated by the increased $\text{X}-\text{X}$ distance, the layer rearranges at this region and one pair of trigonal prismatic chains is tilted with respect to the layer horizontal c -axis (see chains III in Figure 1a).

What these simple structural observations are telling us is that the extra electron provided by the transition-metal atom in group V trichalcogenides may be used to induce either (i) metal–metal bonding (i.e., commensurate or incommensurate CDW or Peierls distortions) or (ii) $\text{S}-\text{S}$ bond reduction (i.e., the formation of equilateral-type chains). The ratio between the number of electrons used in the two processes will impose the shape of the trigonal prismatic-based layers and subtly change the d^x ($0 < x < 1$) electron count of the transition-metal atoms and consequently the electronic structure and properties of the solid. This observation immediately suggests that group V trichalcogenides should be prone to occur in several polymorphic forms (here, we are mostly interested in polymorphic forms with different types of layers because as it will be seen, polymorphs due to different layer stacking do not change the transition-metal electron count and thus have little effect on the transport properties) with different properties and that the presently known systems may well be just the tip of the iceberg.

Different polymorphic forms were in fact early observed for some of these solids. For instance, TaS_3 occurs in orthorhombic

and monoclinic structures differing in their layer packing.^{1,16} For a long time, the only crystal structure known for NbS_3 (labeled as $\text{NbS}_3\text{-I}$ from now on)²⁰ was based on the TiS_3 one (Figure 1b). Since in this structure all S_3 triangles are isosceles, the Nb atoms are thus formally d^1 . The observation of a semiconducting behavior, together with a doubling of the periodicity along the chain direction, where Nb–Nb short and long distances alternate, was considered as the result of a Peierls transition due to the occurrence of a formally half-filled band that opens a band gap at the Fermi level. However, it has been recently shown that a metallic state is induced under pressure,²¹ and thermoelectric power measurements suggest that $\text{NbS}_3\text{-I}$ is not a usual Peierls distorted system.²² The existence of a second polymorph, $\text{NbS}_3\text{-II}$, has also been known for a long time.¹ Although different superstructures of the basic $\text{NbS}_3\text{-I}$ structure were proposed for this polymorph, a clear-cut structural determination remained elusive until recently (Figure 1d).¹⁹ $\text{NbS}_3\text{-II}$ is metallic²³ and has been reported to exhibit three CDWs at around 450–475, 360, and 150 K, respectively.²⁴ This behavior is reminiscent of the NbSe_3 and $m\text{-TaS}_3$ systems, but now with an additional CDW transition. In fact, the situation is considerably more complex. The existence of two additional polymorphs, $\text{NbS}_3\text{-III}$ ²⁵ and $\text{NbS}_3\text{-HP}$ (obtained under pressure),²⁶ has been reported, but their crystal structures are not known. It has been suggested that $\text{NbS}_3\text{-III}$, which exhibits a CDW transition at 155 K,²⁵ may be a subphase of $\text{NbS}_3\text{-II}$.²⁴

Very recently, the crystal structure of two additional phases, $\text{NbS}_3\text{-IV}$ and $\text{NbS}_3\text{-V}$, was reported.²⁷ $\text{NbS}_3\text{-IV}$ is essentially the $\text{NbS}_3\text{-I}$ phase with a doubling of the cell along the inter-layer direction. The $\text{NbS}_3\text{-V}$ structure is, however, quite different. It is essentially that of $\text{NbS}_3\text{-I}$ without the doubling along the chain direction, that is, really a TiS_3 -type structure. Consequently, this phase is expected to be metallic, although this aspect has not been studied in any detail yet. However it is worth pointing that although a full structural characterization was not possible, Izumi et al. reported²⁸ the preparation of NbS_3 samples without a doubling of the b -cell parameter which are metallic and even superconducting at 2.15 K.

Table 1. Calculated Cell Parameters, Band Gap, and Relative Stability for Different NbS₃ Polymorphs Using the HSE06 Functional (See the [Supporting Information](#) for Details)^a

	NbS ₃ -I	NbS ₃ -IV	"NbSe ₃ "	NbS ₃ -II	"TaSe ₃ "	NbS ₃ -V'	NbS ₃ -V
a/Å	4.967 (0.1%)	6.746 (−0.1%)	9.692	9.714 (0.6%)	10.278	4.828	4.944 (−0.1%)
b/Å	6.745 (0.2%)	4.967 (−0.1%)	3.356	3.352 (0.2%)	3.392	3.346	3.340 (−0.5%)
c/Å	9.215 (0.8%)	18.277 (0.8%)	14.680	19.551 (−1.5%)	9.253	9.113	9.254 (1.9%)
β/°	97.21 (−0.1%)	90.21 (0.1%)	108.64	108.73 (−1.8%)	109.51	81.79	96.63 (−0.7%)
V(f.u.)/Å ³	76.570 (1.1%)	76.548 (0.6%)	75.415	75.360 (0.5%)	76.030	72.860	75.885 (1.4%)
band gap (eV)	0.91	1.06	metallic	metallic	0.33	metallic	metallic
rel. energy (meV)/NbS ₃	0.0	0.49	46.9	47.7	118.4	198.7	211.1

^aThe errors with respect to the experimental cell constants for polymorphs whose structure has been determined are given in parentheses.

Since metallic MX₃ phases of group V (M = Nb, Ta; X = S, Se) elements have been at the origin of some of the more celebrated discoveries in low-dimensional materials science,^{1,4} these results bring to the fore the need for further attention to the polymorphism of these materials. This is all the more interesting in view of the recent interest on MX₃ systems as single- or few-layer systems with promising applications in electronic and optical devices as a result of their very anisotropic electronic structure.^{2,29–32} In fact, nanoribbons of both NbS₃-I and NbSe₃,³³ nanofibers of TaS₃,³⁴ microwires of TaSe₃,^{35,36} and single-layer TaSe₃ nanoribbons on SiO₂/Si substrates³⁷ have already been reported.

Our purpose here is to point out that numerous polymorphs associated with different physical and chemical behaviors, some of which are not yet prepared or characterized, are possible because of the intimate connection between the S–S bond reduction and metal–metal bonding abilities of these layers. We will emphasize the subtle link between structural and electronic features on the basis of recent experimental results and new theoretical data. To illustrate our claim, we will consider in some detail the case of NbS₃ and we will provide a rationale for recent experimental results on the new polymorphs. Similar ideas should apply to the other M/X combinations.

■ RESULTS AND DISCUSSION

Stability of Different NbS₃ Polymorphs. Since the available experimental information suggests a rich polymorphism for NbS₃, we first carried out a density functional theory (DFT) study of different NbS₃ polymorphs (see the [Supporting Information](#) for details of the calculations). We were able to locate seven different polymorphs with a fully optimized structure. The calculated cell parameters, relative energy, and band gaps are reported in [Table 1](#). One of them is the well-known NbS₃-I phase,²⁰ three correspond to the recently characterized NbS₃-II,¹⁹ NbS₃-IV,²⁷ and NbS₃-V²⁷ phases, and the remaining three are so-far unreported polymorphs with the structures of NbSe₃, TiS₃, and TaSe₃. The agreement between experimental and theoretical structures for the four presently characterized compounds is excellent, thus lending reliability to these calculations.

The labeling used all along this work to designate the different polymorphs is the following: (1) **NbS₃-I**: the semiconducting system with the crystal structure determined by Rijnsdorf and Jellinek²⁰ exhibiting two trigonal prismatic chains in the unit cell with an alternation of short and long Nb–Nb distances ([Figure 1b](#) with periodicity doubled along *b*), (2) **NbS₃-II**: the polymorph exhibiting three CDWs whose crystal structure has been recently reported¹⁹ (see [Figure 1d](#)), (3) **"NbSe₃"-type**: the hypothetical phase exhibiting the NbSe₃^{10,11} or *m*-TaS₃¹⁵ crystal structure ([Figure 1a](#)), (4) **"TaSe₃"-type**: the hypothetical phase

exhibiting the TaSe₃ structure type³⁸ ([Figure 1c](#)), (5) **NbS₃-IV**: the structure²⁷ closely resembling NbS₃-I, that is, with dimerized trigonal prismatic chains but containing two symmetry related layers per unit cell, (6) **NbS₃-V**: the recently reported structure²⁷ exhibiting the same structure as NbS₃-I without the doubling along the direction of the chains, that is, the structure of TiS₃ ([Figure 1b](#)), and (7) **NbS₃-V'**: another hypothetical structure very close to NbS₃-V, but with a variation in the sulfur sublattice.

The main results emerging from this study are the following:

- (1) The NbS₃-I structure, which for a long time was the only structurally well-characterized polymorph, is found to be the lowest-energy phase. The recently reported NbS₃-IV polymorph is, however, only marginally less stable as expected from the fact that the intralayer structure is practically identical to that of NbS₃-I and only the layer stacking differs between both structures (see [Figure S5](#) in the [Supporting Information](#)).
- (2) A pair of polymorphs, NbS₃-II and "NbSe₃"-type, with different structures but very small energy differences are the next more stable phases. This is a very appealing result because NbS₃-II exists and it is now well characterized so that there are all the reasons to think that the so-called "NbSe₃"-type structure may actually exist. In fact, the two phases are but two members of a structural family (see [Figure 1a,d](#)). As it will be discussed later, in both phases, one pair of trigonal prismatic chains (type II) has the short S–S side of the sulfur triangles too long to be considered a single bond. Thus, the two phases have a different number of chains with short S–S contacts compatible with a single S–S bond (two pairs, types I and III, in the "NbSe₃"-type phase and three pairs, types I, III, and IV, in NbS₃-II) and the same number of chains without an S–S bond (one type II pair). Consequently, both phases should be low-dimensional metals but with a different filling of the partially filled bands. This raises the possibility of changing the number and nature of the modulation of the CDWs for these structurally related polymorphs.
- (3) The next more stable polymorph ("TaSe₃"-type) exhibits a structure similar to that of TaSe₃ (see [Figure 1c](#)), with one pair of chains per unit cell where the short S–S side is compatible with a single bond and another pair of chains where it is not. Thus, in a certain sense, it can be considered as the first member of the previously mentioned family even if there are some subtle differences in the crystal structure.
- (4) The less stable polymorphs that we have been able to locate are NbS₃-V and NbS₃-V'. Both structures correspond to the popular TiS₃ structural type without the doubling along the chain direction. The two structures

somewhat differ in the sulfur sublattice, and both contain just one layer per unit cell. One of them, NbS₃-V, has been recently reported as a stable polymorph,²⁷ thus providing support to the potential existence of all other so-far unknown polymorphs of Table 1.

NbS₃-II: CDWs in a Polymorph with Average One-Third Filled Nb d_z^2 Bands. Links between the Crystal and Electronic Structure. The NbS₃-II polymorph is the first reported low-dimensional system exhibiting three different CDWs. In this section, we will consider the link between the crystal and electronic structures of this material in order to understand the origin and mechanism of these CDW instabilities. The unit cell of NbS₃-II contains eight chains of Nb atoms trigonally coordinated with S atoms running along the *b*-direction (Figure 1d). There are four different types of NbS₃ chains which in order to simplify the discussion have been highlighted with different colors in Figure 1d (to help the comparison with experimental results, these colors are the same as those in the recent structural determination of the average structure¹⁹). The purple and yellow chains are paired in the respective dimer units, whereas the red and orange chains form mixed red-orange pairs. The purple, yellow, and orange chains contain one short S–S triangular side, compatible with an S–S bond (2.208, 2.241, and 2.040 Å in the experimental structure, i.e., the purple, yellow, and orange S–S bonds shown in Figure 1d, respectively). However, in the red chains, such a distance is too long (2.582 Å) to be associated with an S–S bond. We remind that because of the displacement of adjacent chains by half the repeat vector along the chain direction, every transition-metal atom is eight-coordinated (a triangular prism formed by six S atoms of its own chain with two additional S atoms of the neighboring chains capping two rectangular faces), thus leading to (*bc*) NbS₃ layers. There are several S...S contacts, both intra-layer (some being as short as 2.562, 2.752, 2.954 Å,...) and inter-layer (3.269, 3.422, 3.475 Å,...), shorter than twice the van der Waals radii of sulfur (i.e., 3.6 Å), thus conferring some 3D character to the whole system.

Since for electron counting purposes the isolated S atoms must be considered as S²⁻ and those involved in S–S bonds as (S₂)²⁻, the purple, yellow, and orange chains can be described as [Nb(S²⁻) (S₂²⁻)] and the red chains as [Nb(S²⁻)₃]. Thus, using the simplified notation for the chains defined in Figure 1d, NbS₃-II can be electronically described as 2 × [Nb_I(S²⁻) (S₂²⁻) + Nb_{II}(S²⁻)₃ + Nb_{III}(S²⁻) (S₂²⁻) + Nb_{IV}(S²⁻) (S₂²⁻)]. This leaves just four electrons to fill the low-lying bands of eight NbS₃ chains. Since the Nb atoms of chains II are formally d^0 , the four electrons will fill the low-lying bands of chains I, III, and IV. For a transition-metal atom in a trigonal prismatic coordination, there are three low-lying d orbitals. However, as it has been described in detail elsewhere,^{9,17,39} because of the actual eightfold coordination, two of these orbitals are pushed to high energies and only the Nb d_z^2 orbitals, with z in the direction of the chains, remain low in energy. Consequently, there are just four electrons to fill the six low-lying bands of NbS₃-II which, on the basis of these qualitative ideas, should be based on the d_z^2 -type orbitals of the Nb atoms in chains I, III, and IV. This leads to a set of six one-third-filled d_z^2 -type bands.

The band structure around the Fermi level calculated using the experimental crystal structure and the PBE functional is shown in Figure 2a (to facilitate the comparison with some previous works, we use the labeling of special points in the BZ shown in Figure S1 of the Supporting Information) together

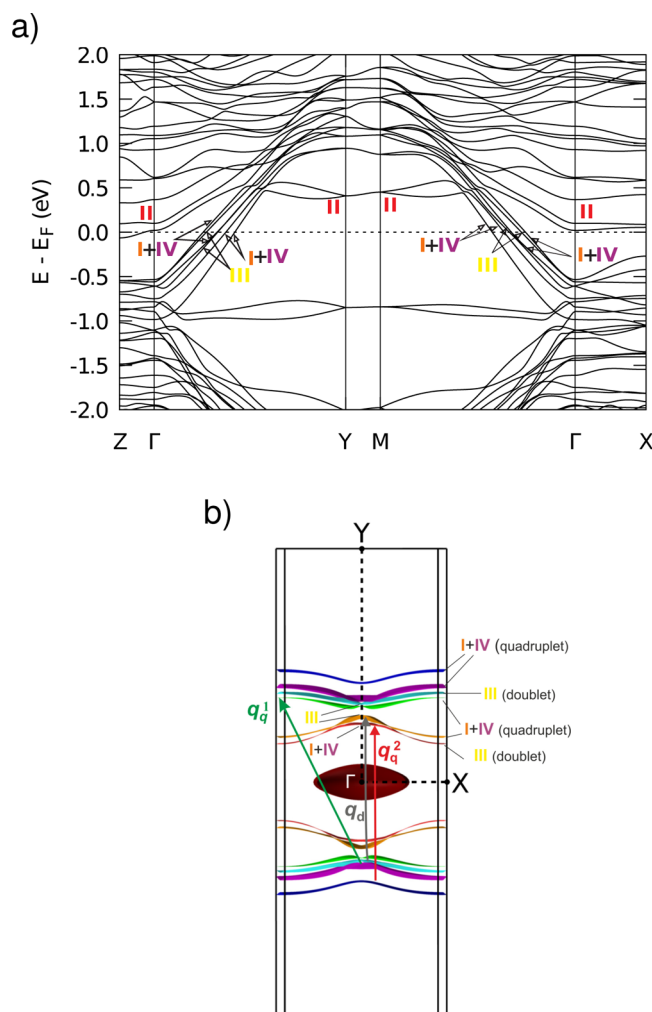


Figure 2. (a) Band structure of NbS₃-II calculated using the experimental crystal structure and the PBE functional. $\Gamma = (0, 0, 0)$, $X = (1/2, 0, 0)$, $Y = (0, 1/2, 0)$, $M = (0, 1/2, 1/2)$, and $Z = (0, 0, 1/2)$ in units of the monoclinic reciprocal lattice vectors. The chains associated with the different partially filled bands near the Fermi level are labeled with the corresponding roman numbers (see also Figure S3 in the Supporting Information). (b) Fermi surface calculated for NbS₃-II. The different colors are only a help to the view and are unrelated to the colors associated with the different chains. The doublet (chains III) or quadruplet (chains I + IV) character of the FS sheets is shown. Three nesting vectors relevant for the discussion are shown.

with a fatband analysis of the bands in Figure S3 of the Supporting Information (all along this work, we use a local system of axes to describe the orbitals centered at the Nb atom under discussion with the z -axis along the trigonal prismatic chains and the x -axis along the inter-chain direction within the layers). The bands calculated using the PBE functional for the optimized structure lead to the same conclusions (see the discussion below and Figure S2 in the Supporting Information). In agreement with the qualitative analysis, there are six dispersive and partially filled bands with an average filling of one-third which should confer metallic properties to this polymorph. As expected, these bands are strongly based on the Nb d_z^2 -type orbitals. Two of the six dispersive partially filled bands, the third and fifth bands at the Fermi level when going from Y to Γ , noted III (yellow) in Figure 2a, are located almost exclusively on the yellow Nb_{III}S₆ chains (see Figure S3a of the Supporting Information). The other four bands, noted I

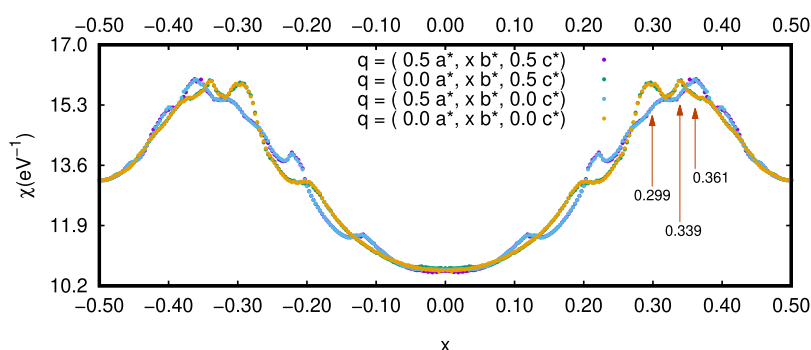


Figure 3. Four scans of the Lindhard response function calculated for NbS₃ at 5 K. Note that for a given value of the a^* component, the scans corresponding to the $0c^*$ and $0.5c^*$ components practically superpose so that only two scans are actually visible.

(orange) + IV (purple) in Figure 2a, have mixed character of the orange (Nb_IS₆) and purple (Nb_{IV}S₆) chains (see Figure S3 of the Supporting Information). Although along some lines of the BZ one of the two types of chains may appear to predominate, this is not the case because the predominant chain character varies along the BZ and the mixing is strong. The interaction between the purple and orange chains is mediated by an S...S contact linking directly the two S–S bonds of the respective chains which is considerably shorter than twice the van der Waals radius of sulfur (3.012 vs 3.60 Å). Thus, from an electronic viewpoint, the two purple and two orange chains should be collectively considered as a quadruplet. In short, at the Fermi level, two bands are strongly localized on the tilted pair of yellow chains and the remaining four in the quadruplet of purple and orange chains. The bands based on the red Nb_{II}S₆ chains, that is, the bands noted II (red) in Figure 2a, on the contrary, are above the Fermi level for most of the Brillouin zone (Figure S3b of the Supporting Information). One of the two bands of this type cuts the Fermi level only around the Z-point, leading to a small closed pocket in the Fermi surface. Consequently, despite their weak contribution to the metallic character, the red Nb_{II}S₆ chains should not be primarily affected by the formation of CDWs in the system. Although one should properly distinguish between oxidation states and atomic populations, note that in agreement with the formal oxidation states, the calculated Mulliken gross atomic populations of Nb atoms in chains without short S...S bonds are smaller (~4.6) than those of the Nb atoms in chains with a short S...S bond (~4.7–4.8) for all polymorphs considered in this work.

The two bands based on the tilted yellow chains are not degenerate around the Fermi level, in contrast with the situation in NbSe₃.^{7–9} In addition, the separation between the full set of dispersive, partially filled bands is larger here than in NbSe₃.⁹ Both facts evidence strong inter-chain interactions, in fact stronger than in the selenium-based NbSe₃, particularly when taking into account that sulfur atoms have less diffuse p orbitals. For instance, the inter-chain interactions in sulfur-based m -TaS₃ are clearly weaker than in NbSe₃ according to similar DFT calculations.⁹ However, the inter-chain interactions occur essentially through the inter-layer a -direction since the dispersion associated with these bands is very small along the c^* -direction (see Γ –Z in Figure 2a) but quite significant along the a^* -direction (see Γ –X in Figure 2a). Such inter-layer inter-chain interactions are quite significant for the yellow type III chains (see the Γ –X direction in Figure S3a of the Supporting Information). The chains of the quadruplet also interact, even if a bit less, mostly due to inter-layer contacts of the purple type IV chains (see the Γ –X direction in Figure S3c of the Supporting

Information). The dispersion along the inter-chain intra-layer c -direction is hampered by two structural features: (i) the long S...S distance (2.582 Å; dotted red line in Figure 1d) in the red chains which increases the energy of the Nb d_z^2 orbitals of the red chains, thus decoupling the quadruplet and doublet Nb d_z^2 -based bands, and (ii) the tilting of the yellow chains which leads to unfavorable S...S interactions between the orange and yellow chains.

Nature of the Fermi Surface. The calculated Fermi surface is shown in Figure 2b. As expected, there are six pairs of sheets associated with (i) the quadruplet of purple and orange chains and (ii) the doublet of yellow chains, with an additional closed pocket related to the red chains. Note that this closed pocket is not centered at the Γ -point as could be suggested by the view in Figure 2b but at the Z-point of the BZ (see Figure S4 in the Supporting Information). The six pairs of sheets are somewhat warped along the a^* -direction, whereas there is no warping at all along the c^* -direction because of the nature of the inter-chain contacts discussed in the previous subsection. The warping of these sheets is intermediate between those calculated with the same computational settings for the related NbSe₃ and m -TaS₃ phases.⁹ Since there are some avoided crossings between the FS sheets, we have included some labels to indicate the nature of the chains associated with the different sheets in order to facilitate the discussion. Note that the pair of FS sheets closer to Γ , one of the sheets being associated with the pair of yellow chains and the other with the quadruplet, interchanges character along a^* because of a very weakly avoided crossing as a result of the slightly larger inter-chain inter-layer interactions of the yellow chains. However, the fact that the crossing is very weakly avoided makes it clear that there is a substantial decoupling of the quadruplet and yellow chains as far as the electronic structure around the Fermi level is concerned.

The sheets of the FS in Figure 2b exhibit several nesting vectors, q . In order to see if some of them may be relevant to understand the origin of the CDWs in NbS₃-II, we have calculated the Lindhard response function (eq 1 in the Supporting Information). Four different scans of the $(0a^*, q, 0c^*)$, $(0a^*, q, 0.5c^*)$, $(0.5a^*, q, 0c^*)$, $(0.5a^*, q, 0.5c^*)$ Lindhard response at 5 K are shown in Figure 3. For a given value of the a^* component, the scans corresponding to the $0c^*$ and $0.5c^*$ components practically superpose so that only two of the scans are actually visible in the figure. Although these scans are quite noisy because of the occurrence of many inter-chain nestings which would be irrelevant under inclusion of the $|<i, k| \exp(iqr)|j, k + q>|^2$ matrix elements in the numerator of the Lindhard response function,⁴⁰ there are three well-defined maxima with b^* components matching very well the experimental ones.

These maxima of the response occur for the a^*/b^* components 0.5/0.361, 0/0.299, and 0/0.339, respectively. The first maximum corresponds to the vector nesting two quadruplet-based sheets, q_q^1 in Figure 2b. If the very weakly avoided crossing between the pair of warped sheets near to Γ is disregarded, the second maximum corresponds to the vector nesting pairs of doublet-based sheets, q_d in Figure 2b. Finally, the third maximum corresponds to the vector nesting the two remaining quadruplet-based sheets, q_q^2 in Figure 2b. Consequently, two intra-quadruplet nesting vectors, q_q^1 and q_q^2 , and one intra-doublet one, q_d , can destroy most of the Fermi surface of NbS₃-II upon the onset of the corresponding CDWs.

Origin of the CDW. NbS₃-II has been reported to exist in two different subphases, the so-called low-ohmic and high-ohmic phases with different conductivities and most likely with slightly different stoichiometries (i.e., some sulfur vacancies in the more conducting low-ohmic phase).^{41,42} The first subphase is prepared at 670–700 °C and the second one at 715–740 °C. At around 800 K, the high-ohmic phase converts into the low-ohmic one.²⁴ Both subphases exhibit two high-temperature CDWs at $T_{p0} \approx 450$ –475 K and $T_{p1} = 360$ K.^{23,24,43,44} The transition at T_{p1} is clearly detected in transport and structural studies.^{23,24,44} The associated $q_1 = (0.5a^*, 0.298b^*, 0)$ satellites^{23,43} decrease noticeably above 350 K,²³ and at higher temperatures, only the $q_0 = (0.5a^*, 0.352b^*, 0)$ satellites remain detectable up to around 450 K.²³ The low-ohmic phase exhibits a third CDW at $T_{p2} = 150$ K which is clearly detected in the resistivity curves.²⁴ However, X-ray and electron diffraction experiments were unsuccessful in providing evidence of structural changes. Remarkably, it has been reported that nonlinear conduction due to the sliding of the CDW occurs for the three CDWs.^{23,42}

The DFT calculation clearly points out the possibility of three different FS instabilities that would successively destroy most of the six FS sheets. The experimental wave vector of the highest temperature CDW, $q_0 = (0.5a^*, 0.352b^*, 0)$, is in nice agreement with one of the calculated FS nesting vectors, $q_q^1 = (0.5a^*, 0.361b^*, 0)$. We thus suggest that the 450–475 K CDW originates from a Fermi surface instability associated with the quadruplets of purple and orange chains. Note that although the number of charge carriers associated with the chains of the quadruplet must have decreased considerably as a consequence of this CDW, the quadruplet still sustains a metallic character for temperatures below this transition because of the two remaining pairs of quadruplet-based FS sheets.

After this transition, four of the six nested pairs of FS sheets still remain, and thus, the possibility for the occurrence of two more CDWs persists. The two instabilities are associated with either the yellow doublets or the quadruplets. The perfect match between the intra-chain components of the experimental modulation wave-vector ($0.298b^*$) and the calculated q_d nesting vector of Figure 2b ($0.299b^*$) strongly suggests that the second CDW originates from the doublet of yellow chains and more particularly from the niobium atoms of these chains. The $1/2a^*$ component in the experimental modulation is most likely a consequence of the already existing doubling of the periodicity along the inter-layer direction as a consequence of the higher-temperature CDW. Our results and proposal disagree with the discussion of Zupanič et al.¹⁹ which, in the process of putting forward different models for the CDW structural modulations, argued that only the sulfur atoms were affected by such modulations, leaving the niobium atoms in their equilibrium positions. In addition, the displacements of the sulfur atoms

were confined into the (010) planes (i.e., perpendicular to the chains). Based on well-known experimental facts for compounds of this family, we have real concerns about the appropriateness of these structural features. First, NbS₃-I, the well-known semi-conducting structure with doubled periodicity along the chains exhibits a strong Nb–Nb...Nb–Nb alternation along the chain direction.²⁰ Second, the transition-metal atoms in the CDW-modulated structures of NbSe₃ and *m*-TaS₃ are those more strongly affected by the modulation^{11,13,14,16,45} and their displacement is mostly in the chain direction. Third, a large number of physical measurements (nuclear magnetic resonance, X-ray scattering, etc.; see a review in ref 4) on the latter systems can only be understood on the basis of strong and dominant displacements of the transition-metal atoms. In addition, most of these data have been conveniently rationalized on the basis of DFT calculations similar to those reported here.^{7–9,46} We thus firmly suggest that the second CDW occurring near room temperature is associated with niobium displacements along the chain direction of the doublet of yellow chains.

After the second CDW transition, two pairs of nested FS sheets associated with the quadruplets still remain. Thus, we are tempted to associate the third CDW with the q_q^2 nesting which will destroy these quadruplet-based sheets. Note that the structural modulation associated with the first CDW must have already modified the structure of the quadruplets in a non-negligible way (but only in a minor way those of the yellow doublets which are protected from these changes by the red chains). This fact must provide a substantial hindrance for the development of this structural modulation which most likely will be of a small amplitude and thus difficult to detect except on transport measurements, as found in the experimental studies.

Note that the only aspect of the electronic structure that may depend on the details of the computational method used is the existence/absence of the closed pockets around Z. The occurrence of these pockets may subtly depend on slight structural differences (compare, for instance, Figures 2a and S2 on the Supporting Information obtained with the same functional and slightly different geometries showing a small variation of the pocket size) or even on the functional. This is a well-known fact on which we commented before for NbSe₃.^{8,9} The same ambiguity also occurs on the experimental side (see the experimental results for NbSe₃ quoted in refs 7 and 8, which have been attributed to an electron doping of some samples due to a slight non-stoichiometry). In the present case, closed pockets around Z for strictly stoichiometric samples should occur according to the PBE functional, although their real size may depend upon fine structural details. However, this ambiguity is not relevant in the present context since because the nesting of the Fermi surfaces is not perfect, other small closed pockets will occur at low temperature after the three CDWs develop. Additional calculations show that the disappearance of the pockets does not affect in any significant way the response function (i.e., only a minute change on the b^* -component of the nesting vector of the order of the precision of the calculations).

In short, we propose that the two q_0 and q_1 high-temperature transitions affect the chains of the quadruplet and doublet, respectively. Because of the different nature of these fragments, there is a charge transfer from the doublet to the quadruplet which results with CDWs with different b^* -components. These two b^* wave vector components practically add to the commensurate value of $2/3$. Consequently, the third and still non-structurally characterized CDW modulation, which will

destroy most of the remaining carriers of the quadruplets, should have a nearly commensurate component of $1/3$ along the chain.

“NbSe₃”-Type Polymorph: Changing the Filling of the Nb d_z^2 Bands. Kikkawa and co-workers²⁶ reported the preparation of a high-pressure form of NbS₃, NbS₃-HP, with cell constants (monoclinic $P2_1/m$, $a = 9.68$ Å, $b = 3.37$ Å, $c = 14.83$ Å, $\beta = 109.9^\circ$) very similar to those of NbSe₃ (monoclinic $P2_1/m$, $a = 10.009$ Å, $b = 3.4855$ Å, $c = 15.641$ Å, $\beta = 109.49^\circ$ ¹¹). However, their sintered powder pellets exhibited a semi-conducting behavior similar to that of NbS₃-I in contrast with the metallic character found for NbSe₃. In another work,²⁸ NbS₃ crystals obtained after annealing nearly stoichiometric samples were considered to correspond to sulfur-rich NbS₃ with compositions between NbS_{3.5} and NbS₄. These crystals, although having a semiconducting behavior and apparently the same crystal structure as NbS₃-I, exhibited two resistivity anomalies as for NbSe₃^{11,13} and isostructural m -TaS₃.¹⁶ Indeed, these transitions occur at temperatures around 235 and 140 K,²⁸ which are extremely similar to those of m -TaS₃, 235 and 160 K.¹⁶ Unfortunately, for all of these NbS₃ samples, only very limited structural information could be obtained: the space group and lattice parameters for the high-pressure samples and some indications about the periodicity along the chains (b -cell parameter) for the sulfur-rich samples, so that it has not been possible to clarify their structure and transport properties.

One of the seven polymorphs that we have located is isostructural with NbSe₃ and m -TaS₃ (see the “NbSe₃”-type polymorph in Table 1). The lattice parameters of this optimized structure are very close to those reported by Kikkawa and co-workers,²⁶ and the optimized structure (Table SI in the Supporting Information) exhibits all structural details characterizing the NbSe₃ and m -TaS₃ crystal structures (see Figure 1a): (i) three different types of trigonal prismatic chains, (ii) a doublet of tilted chains (type III chains), (iii) two chains with one of the triangular S–S sides compatible with a S–S bond (chain I: 2.151 Å, chain III: 2.101 Å) and one chain where it is not (chain II: 2.705 Å). As shown in Table 1, the relative stability of this polymorph with respect to NbS₃-I is computed to be practically the same as that of NbS₃-II so that we can deduce that it is very likely that this polymorph may actually exist and it is possible that the NbS₃-HP phase is actually this “NbSe₃”-type polymorph.

The calculated band structure around the Fermi level for this polymorph is shown in Figure 4a. In this figure, the size of the green, red, and blue circles is proportional to the Nb_I, Nb_{II}, and Nb_{III} character of the corresponding bands. We use the labeling shown in Figure 1a for the chains, which also parallels that used for NbS₃-II, that is, the tilted doublet is made of type III chains, the chains with the long S...S triangular side are type II chains, and the doublet of chains corresponding to the quadruplet in NbS₃-II is made of type I chains. As was the case for the NbS₃-II polymorph, the bands based on the Nb_{II}S₃ chains lie above the Fermi level and thus should not be primarily affected by the onset of the CDW modulations. The Nb_{III}S₃ and Nb_IS₃ chains lead to the two inner (blue) and outer (green) partially filled bands, respectively. According to the stoichiometry and the same electron counting scheme used above, the average filling of these four bands is $1/4$, instead of $1/3$ in NbS₃-II, and the polymorph should exhibit metallic properties. In all respects, the main features of this band structure are very similar to those of NbS₃-II, except for a slightly weaker interaction between the tilted chain III doublets and those of the non-tilted chain I. Note that as it happens for m -TaS₃,⁹ the type II chain bands do not

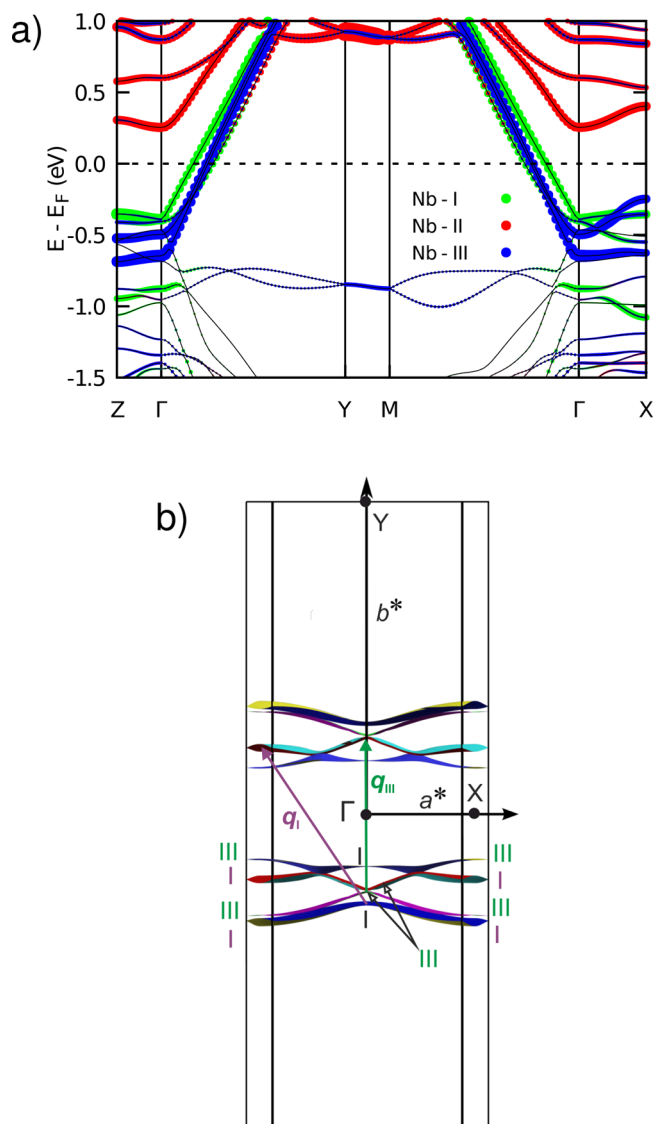


Figure 4. (a) Band structure for “NbSe₃”-type NbS₃ calculated using the optimized crystal structure and the PBE functional. $\Gamma = (0, 0, 0)$, $X = (1/2, 0, 0)$, $Y = (0, 1/2, 0)$, $M = (0, 1/2, 1/2)$, and $Z = (0, 0, 1/2)$ in units of the monoclinic reciprocal lattice vectors. The sizes of the green, red, and blue dots are proportional to the Nb_I, Nb_{II}, and Nb_{III} character, respectively (see Figure 1). (b) Calculated Fermi surface. The different colors are only a help to the view and are unrelated to the chain-type character of the different FS sheets. The chain I or chain III character of the FS sheets is shown. Two nesting vectors relevant for the discussion are shown.

cross the Fermi level so that no closed pockets appear to occur in the MS₃ ($M = \text{Nb, Ta}$) monoclinic phases with this structure.

The calculated Fermi surface is shown in Figure 4b, where the chain character on which the four different FS sheets are based is also given. Note the very weakly avoided crossing between the two inner pairs of sheets. The larger warping of the sheets based on the tilted type III chains is due to the short inter-layer S...S contacts. Not surprisingly, the analysis of the Fermi surface and Lindhard response function goes along the same lines as in our previous work for m -TaS₃⁹ to which we refer for further details. We find two nesting vectors $q_{\text{III}} = (0a^*, 0.247b^*, 0c^*)$ and $q_{\text{I}} = (0.5a^*, 0.250 - 0.251b^*, 0.5c^*)$ (see Figure 4b) associated with structural modulations affecting type I and type III chains, respectively, which would destroy the four sheets of the FS.

Thus, we predict the occurrence of two resistivity anomalies for this polymorph, as is the case for *m*-TaS₃¹⁶ and NbSe₃.^{11,13} Based on the absence of closed pockets and the kind of warping of the FS sheets, this polymorph should most likely exhibit a semiconducting behavior after the two CDW transitions.

We remind that (i) the lattice parameters of the samples prepared by Kikkawa and co-workers²⁶ are very similar to the ones we obtain (see Table 1), and (ii) the so-called sulfur-rich crystals of NbS₃ obtained after annealing nearly stoichiometric crystals,²⁸ even if being semiconducting, exhibited two resistivity anomalies at 235 and 140 K. These transition temperatures are very similar to those of *m*-TaS₃, which, as mentioned above, exhibits a FS extremely similar to that computed for “NbSe₃”-type NbS₃. Thus, we believe that the so-called sulfur-rich NbS₃ phase may contain a mixture of both polymorphs, semiconducting NbS₃-I and “NbSe₃”-type NbS₃. In addition, we suggest that the high-pressure NbS₃ prepared by Kikkawa and co-workers²⁶ is most likely to actually be the “NbSe₃”-type polymorph. The reason for the observed semiconducting behavior for the sintered powder pellets is probably due to a transformation from the “NbSe₃”-type polymorph to the more stable semiconducting NbS₃-I one occurring during the sintering process. Taking into account all these considerations, we suggest that it may be worthwhile to revisit the high-pressure synthesis of NbS₃.

The NbS₃-II and “NbSe₃”-type polymorphs are just two members of a family of MX₃ (M = Nb, Ta; X = S, Se) layered solids containing both a tilted doublet and an *n*-plet (*n* = 2, 4,...) of regular chains (i.e., containing a short X–X distance), connected by two separated chains without any short S–S contact. These phases will contain *n* + 2 partially dispersive bands and have a total of *n* electrons to fill them so that the average occupation will be *n*/(2*n* + 4) and could thus exhibit one CDW associated with the tilted doublets and several (from 1 to *n*/2) CDWs associated with the *n*-plets.

Polymorph with the Same Number of Isosceles and Equilateral-Type Chains. TaSe₃ is the only known group V transition-metal trichalcogenide exhibiting the layered crystal structure of Figure 1c which contains only two different types of chains. The different ratio between chains with a broken (equilateral-like, type II) and unbroken (isosceles-like, type I) X–X short triangular side with respect to the previously examined polymorphs changes the formal average *d*-electron count and, consequently, the filling of the lower transition-metal-based bands, a feature that drastically influences the transport properties. In contrast with the metallic members of this series, TaSe₃, which is really a semimetal, does not exhibit CDW instabilities and keeps the metallic conductivity until very low temperatures, entering into a superconducting state at around 2 K.^{47–49} However, the occurrence of a CDW state has been claimed to occur in TaSe₃ mesowires at 65 K.⁵⁰ A high breakdown current density^{36,51} and low-frequency electronic noise³⁵ in microwires have been recently reported for TaSe₃, suggesting potential applications in downscaled electronics. It has also been proposed that bulk TaSe₃ may be an appropriate system where the competition between superconducting and topological phases is studied.^{52,53} Recently, single-layer TaSe₃ nanoribbons on SiO₂/Si substrates have been obtained through a mechanical exfoliation procedure,³⁷ and a theoretical study³² has proposed that an interesting competition between metallic and semiconducting states can occur under the effect of strain.

“TaSe₃”-Type Polymorph. As shown in Table 1, the relative stability of the “TaSe₃”-type structure of NbS₃ (optimized

structure in Table SII of the Supporting Information) with respect to NbS₃-I is computed to be in between those of NbS₃-II and NbS₃-V, both of which are known. Thus, we believe that such a polymorph may also be actually prepared. The calculated band structure is shown in Figure 5a. The system is found to be

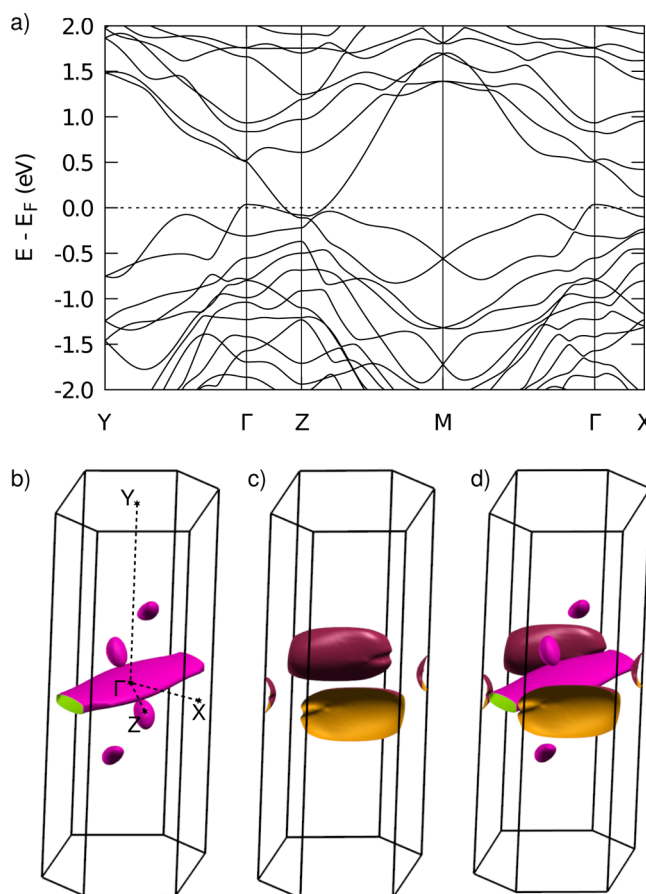


Figure 5. (a) Band structure for “TaSe₃”-type NbS₃ calculated using the optimized crystal structure and the PBE functional. $\Gamma = (0, 0, 0)$, $X = (1/2, 0, 0)$, $Y = (0, 1/2, 0)$, $M = (0, 1/2, 1/2)$, and $Z = (0, 0, 1/2)$ in units of the monoclinic reciprocal lattice vectors. (b–d) Calculated Fermi surface: (c) hole contribution, (d) electron contribution, and (d) full Fermi surface.

semimetallic, leading to the Fermi surface of Figure 5d containing hole (Figure 5b) and electron (Figure 5c) portions. The latter originates in a major way from Nb *d*_z² states of the regular chains I (see Figure 1c). The holes originate predominantly from S 3*p*_z states of the sulfur atoms of the open type II chains interacting directly with the Nb atoms of the regular type I chains (i.e., the S atoms marked with an asterisk in Figure 1c). Note that the two bands undergo a real crossing along the Γ –Z line, suggesting the possibility of topological effects as discussed for TaSe₃ itself.^{52,53} Let us note that the semimetallic overlap is kept after inclusion of spin–orbit coupling effects.

In fact, the electronic structure is even more interesting because of the occurrence of a third band which is filled but almost touches the Fermi level inside the BZ (see, for instance, the Γ –Y line in Figure 5a). As examined in detail elsewhere³² for the related case of TaSe₃ single layers, the bump of this band is very sensitive to strain along the (*a* + *c*) intra-layer direction. Under a small strain along such a direction, the bump can cross

the Fermi level, leading to pairs of additional pockets. Because of these two features, possible topological effects and strain-induced FS variations, both of which depend on subtle structural details, this polymorph could exhibit very challenging properties.

Finally, let us note that as for most semimetallic systems, the existence of a band overlap or a band gap may be a delicate question. Our PBE results are consistent with recent GGA-type DFT calculations for TaSe₃, either all-electron plane-wave-based⁵² or local orbital-based with pseudopotentials.³² Most details of the band structure are very similar, and the semimetallic overlap is a bit smaller in NbS₃, as should be expected for a sulfur-based compound. We thus believe that the calculated electronic structure of this polymorph is accurate enough.

Possible New Family of MX₃ Polymorphs. NbS₃ with this structure can be considered as a member of the family of the previously discussed polymorphs with $n = 1$ and no tilted chain doublet. Breaking (i.e., reducing) one S–S bond in the isosceles triangles creates inter-chain tension and leads to a rearrangement ending with a tilted chain doublet. However, the reasons behind such a rearrangement are more subtle than just avoiding unwanted S··S repulsions. In the parent TiS₃ structure (Figure 1b), all the S^{2−} atoms are stabilized by making Nb–S bonds with neighboring chains (i.e., the capping Nb–S bonds). The rearrangement leading to the tilted doublet does not only relieve the S··S inter-chain interactions but also facilitate that one of the two created S^{2−} can be stabilized by forming one of these capping Nb–S bonds with the Nb atom of one of the tilted chains. What the structure of TaSe₃ is telling us is that there is a second way to reach the same kind of stabilization without creating tilted chains just by pairing these open chains in a doublet. A layer of TaSe₃ can be seen as a succession of doublets of open and regular chains (however, note that the two types of doublets are slightly different). This simple structural view immediately opens the possibility for the existence of another family of MX₃ polymorphs in which one such double unit of open chains separates n -plets of regular chains. For the time being, TaSe₃ appears to be the lower ($n = 2$) and only known member of this family. The values reported in Table 1 suggest that the “TaSe₃”-type NbS₃ polymorph may be stable even if generation of a tilted doublet of regular chains appears to be somewhat more favorable than the creation of a doublet of open chains. It is also tempting to propose that a new family of MX₃ polymorphs may actually exist. Although the “TaSe₃”-type polymorph is predicted to be a semimetal, the higher members of this new series ($n = 4, 6, \dots$) will possess n partially dispersive bands and have a total of $n-2$ electrons to fill them so that the average band occupation will thus be $(n-2)/2n = 0.5 - (1/n)$. These phases should thus be metallic and could exhibit several (from 1 to n for $n = 4, 6, \dots$) CDWs associated with the n -plets.

Metallic (NbS₃-V and NbS₃-V') versus Semiconducting (NbS₃-I) Polymorphs: A Non-Conventional Peierls Distortion? For several decades, NbS₃-I was the only structurally well-characterized NbS₃ polymorph,²⁰ but recently, Balandin, Salguero, and co-workers²⁷ reported the crystal structure of two new polymorphs, NbS₃-IV and NbS₃-V. The latter is very interesting since it exhibits the same structure as NbS₃-I, with the same layer packing (ABCDE, see Figure S5 in the Supporting Information), but without Nb–Nb pairing, that is, with half the periodicity along the chain direction. This is the structure of TiS₃ (Figure 1b) which is formally seen as the structure of NbS₃ before the Peierls distortion. Thus, NbS₃ is one of the rare compounds which can be prepared with the

structure both before and after the Peierls distortion. The transport properties of this polymorph were not reported, although it should exhibit metallic behavior.

Polymorphs with a Non-Dimerized TiS₃-Type Structure. Non-dimerized structures were indeed considered in our search, and, as shown in Table 1, two different polymorphs of this type were located. One of them is the NbS₃-V polymorph reported by Balandin, Salguero, and co-workers.²⁷ The optimized structure is in excellent agreement with the reported crystal structure (Table 1). To our surprise, we located a second polymorph which is even a bit more stable. This polymorph is similar to NbS₃-V in the sense that it is non-dimerized along the chain direction, the unit cell contains a single layer, and the layers pack in an ABCDE mode (Figure S5 in the Supporting Information). Thus, we designate this polymorph as NbS₃-V'. However, an important difference between the two polymorphs occurs in the sulfur sublattice. While for NbS₃-V, as for NbS₃-I (and NbS₃-IV to be discussed in the next section), there is a large difference between the intra-chain S–S bond and the inter-chain S··S contact along the a -direction (i.e., **b** and **nb** in Figure 1b), 2.019 Å versus 2.931 or 2.050 Å versus 2.913 Å, in the experimental structures of NbS₃-V and NbS₃-I, respectively, they are considerably more similar, 2.227 versus 2.551 Å, in the optimized structure of NbS₃-V' (Table S-III in the Supporting Information). This is not an artifact of the computational approach since our calculations perfectly reproduce the mentioned strong difference occurring in the experimental structure of NbS₃-I and NbS₃-V (calculated values: 2.035 vs 2.937 Å for NbS₃-I and 2.055 vs 2.890 Å for NbS₃-V). Indeed, this kind of “long” bonds and “short” non-bonded contacts occur in other of the structures discussed. For instance, in the crystal structure of NbS₃-II, there are S–S bonds of 2.040, 2.186, and 2.208 Å as well as non-bonded contacts of 3.012, 2.752, and 2.582 Å. A similar situation can be found in selenides like NbSe₃ and TaSe₃, clearly witnessing the versatility of the chalcogen sublattice in these compounds which is one of the main reasons for the rich polymorphism.

Unusual Peierls Distortion: Interchain Interactions. The calculated band structure for NbS₃-V is shown in Figure 6a. According to the well-accepted view of the dimerized structure of NbS₃-I as the result of a Peierls distortion, we should expect a simple band structure with a half-filled and dispersive Nb d_z^2 -based band. However, this is not what can be seen in Figure 6a. Indeed, the simple description could be taken as grossly correct if we just look at the Γ –Y direction in Figure 6a (i.e., the chains' direction) where a pair of dispersive and not far from half-filled Nb d_z^2 bands associated with the two non-dimerized chains of the unit cell can be seen. However, if we look at other directions of the BZ (for instance, X–N), we can see that a second pair of bands that undergoes an avoided crossing with these Nb d_z^2 bands precisely around the Fermi level. This second pair of bands has a strong dispersion along the X– Γ direction (i.e., the inter-chain a^* -direction) and consequently introduces substantial intra-layer inter-chain interactions into the states around the Fermi level. This can be clearly seen in the calculated FS of Figure 6b. It results from the hybridization of two pairs of planes perpendicular to the direction of the chains (Γ –Y) and two closed cylinders with the ellipsoidal section approximately along the inter-layer c^* -direction and centered at the X-point.

The simple description of the Peierls distortion would require the absence of the two cylinders. Indeed, whatever structure is used for the calculations, the experimental or HSE06-optimized one (see the calculated band structure with the HSE06

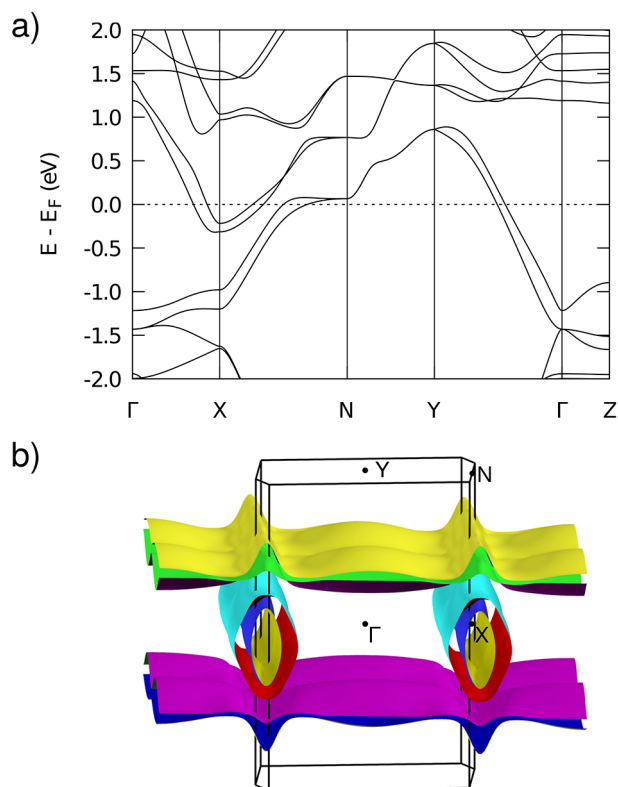


Figure 6. (a) Band structure for NbS₃-V calculated using the experimental crystal structure and the PBE functional. $\Gamma = (0, 0, 0)$, $X = (1/2, 0, 0)$, $Y = (0, 1/2, 0)$, $N = (1/2, 1/2, 0)$, and $Z = (0, 0, 1/2)$ in units of the monoclinic reciprocal lattice vectors. (b) Calculated Fermi surface.

optimized geometry in Figure S6 of the [Supporting Information](#)), these cylinders always occur in the FS. Thus, although nesting is obviously present in the FS, because of the occurrence of the cylinders, the nesting vector cannot have the commensurate $0.5b^*$ component required for a dimerization but an incommensurate value. In addition, even if such incommensurate structural modulation could occur, the polymorph would keep the metallic properties because of the existence of the cylinders as well as the additional pockets created by the modulation due to the corrugation (imperfect nesting) of the FS sheets. This new scenario with an incommensurate CDW modulation not far from dimerization is completely new within the MX₃ ($M = \text{Nb, Ta}$, $X = \text{S, Se}$) low-dimensional solids, and thus, it would be very interesting to study the transport properties of this new NbS₃-V polymorph in detail. It is worth pointing out that a theoretical study of the injection of carriers through electric field gating in single layers of TiS₃, where electrons are injected into the same type of band that we are discussing, indeed predicted the possibility of CDW-type anomalies.⁵⁴ Later, experimental work reported transport measurements suggesting CDW formation, although a more complete characterization is still needed.^{55–58}

The previous discussion makes clear that the origin of the pairing in NbS₃-I is not as simple as it is commonly believed. The reason is the existence of a second pair of bands undergoing an avoided crossing with the “expected” Nb d_{z^2} bands. This pair of bands originates from the Nb d_{xy} orbitals which are raised in energy because of the Nb–S capping interaction. These orbitals lead to a strongly dispersive band going down along the Γ –X

direction, that is, the intra-layer inter-chain direction. Consequently, the avoided crossing introduces inter-chain interactions into the Nb d_{z^2} bands. The main character of the Nb d_{xy} -based band at the Γ -point is sketched in [Figure 7](#). Around Γ , all

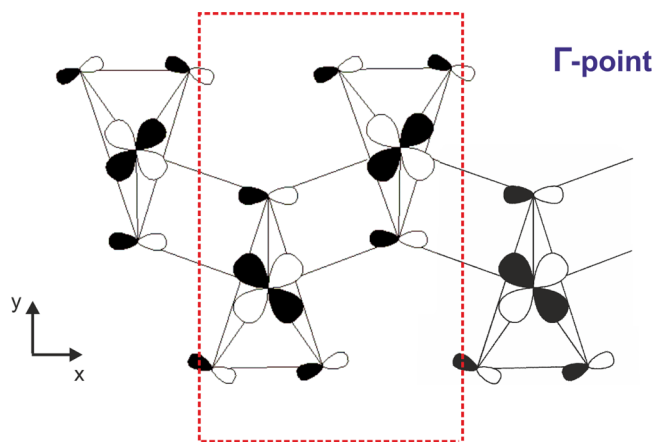


Figure 7. Nature of the band introducing inter-chain coupling into the Nb d_{z^2} pair of bands (Γ -point).

capping Nb–S interactions are antibonding. However, at the X-point, the sign of the crystal orbital changes on adjacent cells so that half of the Nb–S interactions become bonding (and half remain antibonding) so that the crystal orbital becomes globally Nb–S_{capping} non-bonding and hence, when going from Γ to X, the band is strongly lowered in energy, as seen in [Figure 6a](#). Note that this band contains substantial S p_x character which, around the X-point, is antibonding within the S–S bond but bonding in between S–S bonds. When going down along the Γ to X direction, this S–S contribution is considerably enhanced, providing an additional source of stabilization of the band around X. In other words, although in large parts of the BZ the half-filled band of NbS₃-V is dominated by the Nb d_{z^2} orbitals, the planes near the border of the BZ along the a^* -direction introduce substantial inter-chain interactions and, hence, the classical description of the origin of the dimerized structure of NbS₃-I is not really correct (see further discussion in the next section).

As noted above, the band introducing inter-chain interactions around the border of the BZ contains very substantial S p_x character which around the X-point is antibonding within the S–S bond but bonding in between S–S bonds. Consequently, changing the S–S distances within and between chains (**b** and **nb** in [Figure 1b](#)) as it actually happens in the NbS₃-V' polymorph will disturb the role of the inter-chain interactions in the band structure (Figure S7 in the [Supporting Information](#)), and the shape of the FS can be somewhat altered. The calculated FS for the NbS₃-V' polymorph is shown in [Figure 8](#). Because of a small shift in the pair of bands introducing inter-chain interactions, the FS now contains flat portions along both directions of the layer and different instabilities can be expected. Clearly, these “TiS₃”-type polymorphs can provide ground for very interesting physics.

Dimerized Polymorphs (NbS₃-I and NbS₃-IV). The well-known NbS₃-I polymorph²⁰ can be considered as the upper member of the NbS₃-II family with n very large and thus no partially filled bands. It is found to be a semiconductor with a strong Nb–Nb dimerization along the chains (3.037 and 3.693 Å). More recently, Balandin, Salguero, and co-workers²⁷

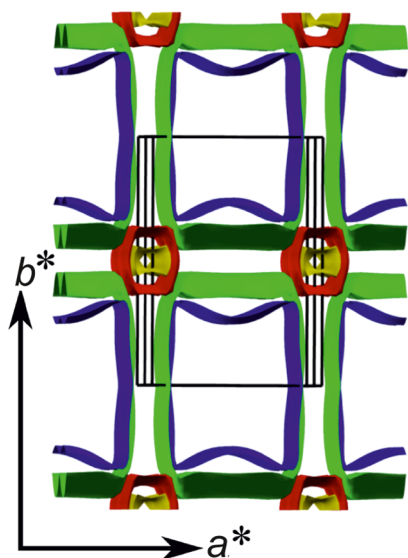


Figure 8. Calculated Fermi surface for the NbS₃-V' polymorph.

reported another polymorph, NbS₃-IV, with a very similar dimerization (3.045 and 3.709 Å) which exhibits somewhat different inter-layer interactions but a very similar volume per formula unit (see Table 1). The inter-layer stacking is of the ABCDE-type in NbS₃-I but AB in NbS₃-IV (see Figure S5 in the Supporting Information). Our optimized structures are in excellent agreement with the crystal structures (for instance, Nb–Nb distances of 3.028 and 3.719 Å for NbS₃-I). Both polymorphs are practically equally stable (Table 1) so that it cannot be excluded that inter-layer stacking disorder can occur in some samples.

As shown in Figure 6, for a relatively large part of the BZ, the classical description of the “TiS₃”-type structure of NbS₃, with a pair of half-filled Nb d_z^2 -type bands leading to planar sheets in the FS separated by $\sim 1/2b^*$, indeed holds. However, as we approach the border of the BZ along the a^* -direction (i.e., the intra-layer inter-chain direction), this picture is strongly perturbed because of the inter-chain interactions occurring for wave vectors in that part of the BZ. Thus, in order for the commensurate dimerization to occur, there must be some additional distortion that removes this inter-chain coupling from the FS (most likely some breathing of the S–Nb–S capping angle which will destabilize the Nb d_{xy} -based antibonding band). Only then, the classical picture of well-nested half-filled Nb d_z^2 bands holds and the dimerization may occur. In this sense, the Peierls distortion of these semiconducting NbS₃ polymorphs should be better qualified as a “Peierls-assisted” distortion.

The band structures calculated with the HSE06 hybrid functional for the NbS₃-I and NbS₃-IV phases are reported in Figures 9 and S8a of the Supporting Information, respectively. Both polymorphs are indirect band gap semiconductors with energy gaps of 0.91 (NbS₃-I) and 1.06 eV (NbS₃-IV). As usual for semiconductors, the calculated HSE06 band gaps are in excellent agreement with experimental values (0.83–1.1 eV for NbS₃-I^{2,59}). Let us note that the calculated band gap with the PBE functional²¹ is smaller than the HSE06 one, but the calculated band structure is practically the same, except for a nearly rigid shift of the conduction band (see, for instance, Figure S8a,b on the Supporting Information for the band structure of NbS₃-IV polymorph with the two functionals). The nature of the states at the top of the valence band and the bottom

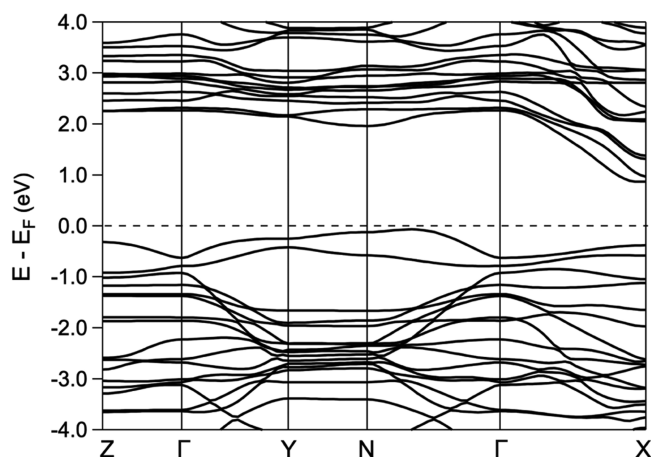


Figure 9. Band structure for NbS₃-I calculated using the experimental crystal structure and the HSE06 functional. $\Gamma = (0, 0, 0)$, $X = (1/2, 0, 0)$, $Y = (0, 1/2, 0)$, $N = (1/2, 1/2, 0)$, and $Z = (0, 0, 1/2)$ in units of the monoclinic reciprocal lattice vectors. The energy zero is the highest occupied energy level.

of the conduction band is based on the Nb–Nb bonding combination of the Nb d_z^2 orbitals (somewhat hybridized with the Nb s and p_z orbitals so as to accumulate a bit more of electron density along the short Nb–Nb distance) and the p_x and p_y orbitals of the capping S atoms, respectively. Note that the crystal structures of the NbS₃-I and NbS₃-IV polymorphs are given with different systems of axes: the chain axis is b in NbS₃-I but a in NbS₃-IV. Although the two band structures of Figures 9 and S8a in the Supporting Information could appear to be different, they are really almost identical when the different axes and the doubling of the bands for NbS₃-IV are taken into account. Consequently, no significant differences in their properties are expected for the two polymorphs (except for some phonon-related ones). As noted above, NbS₃-I, which is the more stable polymorph, also has the larger unit cell. However, the stability of this polymorph (as well as that of NbS₃-IV) is an electronic effect due to the opening of a band gap at the Fermi level and not a volumetric effect, as shown by the fact that there is no clear relationship between stability and size of the unit cell when the seven polymorphs are considered (see Table 1).

CONCLUDING REMARKS

When extra electrons are introduced into the very stable layered TiS₃-type structure by using a group V transition-metal atom, either (i) metal–metal bonding (i.e., commensurate or incommensurate CDW or Peierls distortions) or (ii) S–S bond reduction (i.e., the formation of equilateral trigonal prismatic chains) can occur. The ratio between the number of electrons used in the two processes will impose the shape of the trigonal prismatic-based layers and subtly change the d^x ($0 < x < 1$) electron count of the transition-metal atoms and consequently the electronic structure and properties of the solid. This is suggestive that some group V trichalcogenides should be prone to occur in several polymorphic forms with different properties and that the presently known systems may well be just the tip of the iceberg.

Based on both already existing experimental and new theoretical results, we have considered this aspect for NbS₃ and found that at least seven different polymorphs are possible. One is the well-known NbS₃-I, three correspond to the recently

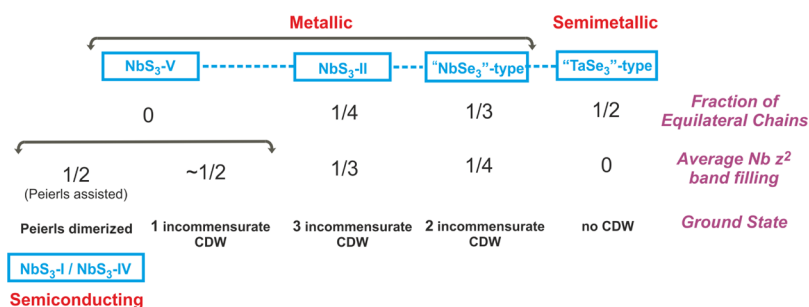


Figure 10. Summary of the different NbS₃ polymorphs discussed in this work (NbS₃-V' is a variety of NbS₃-V slightly differing in the sulfur sublattice).

characterized NbS₃-II, NbS₃-IV, and NbS₃-V phases, and the other remaining three are so-far non-reported polymorphs with the structures of NbSe₃, TiS₃, and TaSe₃. From the energetic point of view, the stability of these new polymorphs is compatible with those of the presently known ones. We have shown that this series of low-dimensional polymorphs should display a rich variety of physical behaviors (Figure 10). The well-known view of the dimerized structure of the semiconducting NbS₃-I polymorph as a typical example of a Peierls distortion is discussed and shown to be only partially correct because inter-chain interactions are stronger than naively expected. The NbS₃-V, NbS₃-II, and "NbSe₃"-type polymorphs are (or are predicted to be) metallic systems with incommensurate CDW instabilities associated with half-, third-, and quarter-filling of the Nb *d_{z²}* bands of the trigonal prismatic chains, respectively. This series of polymorphs thus provides a clear-cut illustration of the intimate link between structural and electronic features for a structurally related family of materials. Note that we have not considered an exhaustive list of possible polymorphs. Others can be conceived. For instance, we have pointed out a particularly appealing family based on the TaSe₃ structure. Our purpose here is to emphasize that the combined use of structural and electronic ideas can provide very useful hints in the search for these polymorphs.

It is worth noticing that several of the phases discussed here (and even their contrasting properties) may have been prepared in the past, although in an uncontrolled way that prevented their full characterization. A careful look at Table 1 in the work by Izumi et al.²⁸ with the present results in mind suggests that depending on the preparation conditions (temperature, sulfur pressure, annealing, etc.), at least four different products were found: (i) the semiconducting NbS₃-I polymorph, (ii) a mixture of semiconducting NbS₃-I and a metallic phase, most likely the "NbSe₃" type polymorph, (iii) a mixture of semiconducting NbS₃-I and a metallic (and superconducting) phase, most likely the NbS₃-V and/or NbS₃-V'-type polymorphs, and (iv) a metallic and superconducting phase, most likely the NbS₃-V and/or NbS₃-V'-type polymorphs. *T_c* of the superconducting phase is very similar to that of NbSe₃ (or *m*-TaS₃) under pressure when the CDW is suppressed.⁴ This observation thus strongly suggests that a chemical control of the phase diagram can most likely be attained. Also, in view of these comments, we urge investigation of the transport properties of the already prepared NbS₃-V phase and point out the importance of single-crystal structural determinations in unambiguously distinguishing the different polymorphs.

The very rich landscape of different structures and properties of these low-dimensional polymorphs should provide a strong stimulus for studying these materials as flakes with different numbers of layers as a basis for the development of new electronic and optoelectronic devices. Chemical doping by

preparation of M/M'S₃ alloys has been recently reported,^{60–62} thus bringing additional expectations for the very rich diversity of physical and chemical behavior of NbS₃ (and probably also the other M/X; M = Nb, Ta, X = S, Se) polymorphs.

EXPERIMENTAL SECTION

All calculations were carried out using first-principles DFT.^{63,64} The structural optimizations and evaluation of the relative energies of the different polymorphs were carried out using the *ab initio* CRYSTAL17 code.^{65–67} All other calculations were carried out using a numerical atomic orbitals DFT approach implemented in the SIESTA code.^{68–70} Full details about the computations are reported in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.1c01417>.

Details of the DFT calculations; labeling of the special points of the monoclinic Brillouin zone used in this work; band structure of NbS₃-II calculated using the HSE06-optimized structure and the PBE functional; fatband analysis of the band structure of NbS₃-II calculated using the experimental structure and the PBE functional; rotated view of the Fermi surface of NbS₃-II; comparison of the different stackings of the NbS₃ bilayers in polymorphs NbS₃-I and NbS₃-IV; band structure for NbS₃-V calculated using the HSE06-optimized structure and the PBE functional; band structure for NbS₃-V' calculated using the HSE06-optimized structure and the PBE functional; band structure of NbS₃-IV calculated using the experimental crystal structure and the HSE06 and PBE functionals; calculated crystal structure for the NbS₃ polymorph with the "NbSe₃"-type structure using the HSE06 hybrid functional; calculated crystal structure for the NbS₃ polymorph with the "TaSe₃"-type structure using the HSE06 hybrid functional; and calculated crystal structure for the NbS₃-V' polymorph using the HSE06 hybrid functional (PDF)

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Notes

The authors declare no competing financial interest.

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Bogdan Guster is currently a Postdoctoral Researcher under the supervision of Prof. Xavier Gonze at the Catholic University of Louvain. He obtained his Ph.D. degree in Physics at the Autonomous University of Barcelona in 2019 under the supervision of Pablo Ordejon, Enric Canadell, and Miguel Pruneda. His research is mainly focused on the manifestation of large polarons and charge density waves from a theoretical perspective as well as developing new functionalities at the ground state level in density functional theory codes.

Pere Alemany is a Full Professor in the Chemistry Department of the University of Barcelona, where he started his academic career in 1991 after a postdoctoral stay at Cornell University working in the group of Roald Hoffmann. He has published about 150 research articles, mainly on the electronic structure and bonding in solids and molecules, with special focus on electronic transport and magnetic exchange coupling in low-dimensional systems and the use of continuous symmetry measures to address stereochemical problems.

Jean-Paul Pouget is Emeritus Research Director of the Centre National de la Recherche Scientifique (CNRS). He got his Ph.D. from the University Paris-Sud (UPS) in 1974. He moved to the neutron scattering group of the Brookhaven National Laboratory (USA) for a postdoctoral year (1976–1977). Then he joined the Laboratoire de Physique des Solides of UPS to study structural instabilities in low-dimensional conductors. He was Representative (1995–1997) then Scientific Director (1997–2001) of the Physics and Mathematics Department of the CNRS and Director of the Laboratoire de Physique des Solides (2002–2009).

Enric Canadell was educated at the Universities of Barcelona and Autónoma de Madrid, conducted research at the Universities of Barcelona, Chicago, and Paris-Sud, and since 1996, is a Research Professor at Institut de Ciència de Materials de Barcelona (CSIC). He is mostly interested in the development of ideas to relate the structure and properties of solids in which field he has co-authored around four hundred papers and two books. He received an honorary Degree from Université de Rennes and is a member of Academia Europaea and the Royal Academy of Sciences and Arts of Barcelona.

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