Supplemental Material to the article
"The new polytype of NbS_3, a quasi-one-dimensional conductor with a high-temperature charge density wave"

An important common property of samples belonging to both phases is the existence of stacking faults (SFs) in them, that is, two-dimensional formations resulting from the shift of neighboring crystal blocks along the c axis by less than the lattice constant in this direction [7, 8, 9], or the appearance of new planes with Nb chains [2, 10]. Thus, the unit cells of NbS_3-II at the SFs contain extra or missing pairs of Nb chains. The density of SFs can affect the individual properties of the samples. Probably, CDW-2 forms on the SFs [4, 11], but this assumption requires verification.

The room temperature images of the bc surface in a scanning tunneling microscope [2, 10] reveal 4 chains per the lattice period along c, as well as two superstructures on these chains. SFs were also observed. As a rule, a unit cell crossed by a SF contains two extra Nb chains, that is, one extra chain in the projection onto the bc plane.

Recently we have observed SFs in TEM images on one of the NbS_3-II samples. Figure S1 shows the image in the bc plane. The trigonal prismatic columns are clearly visible. In the c direction, four columns of different types can be distinguished per the lattice period c, which is close to 18.3 Å [1]. The arrow marks an extra chain revealing a layer in the ab plane, that is, a SF.

The observation of a SF in a TEM clarifies its structure: since the TEM image is averaged over all the layers parallel to the bc plane, the observation of an extra chain means that SFs are planes parallel to the ab crystallographic plane, that is, to the van der Waals two-dimensional layers. Earlier we could not exclude that the SFs planes can go at an angle to the ab plane and, possibly, contain steps.

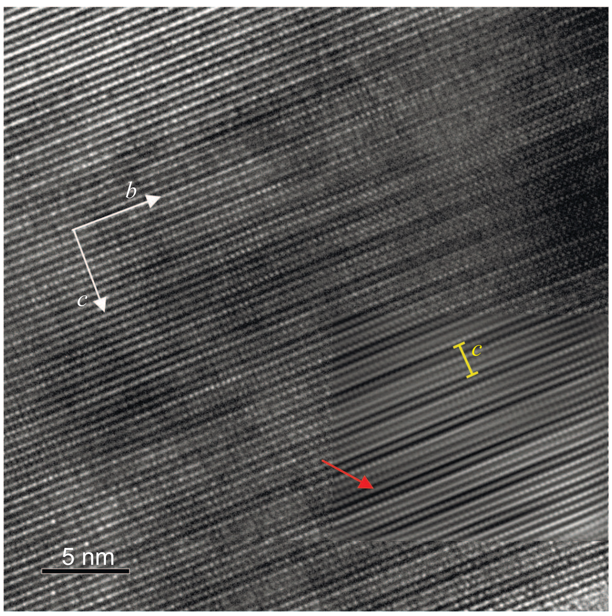

Fig. S1. A TEM image of a conventional NbS_3-II sample in the bc plane, obtained in JEM-2100. The fragment processed in the Digital Micrograph program is superimposed in the lower right part of the image. A SF is visible in this area: the red arrow shows the extra layer

The numerous SFs result in the high disorder of the structure in the bc plane complicating the acquisition of electron diffraction patterns in this orientation [2]. The diffraction pattern in the bc plane, corresponding to the image S1, is shown in Fig. S2. All reflections are elongated in the c^* direction, which reveals numerous period failures along the c axis.

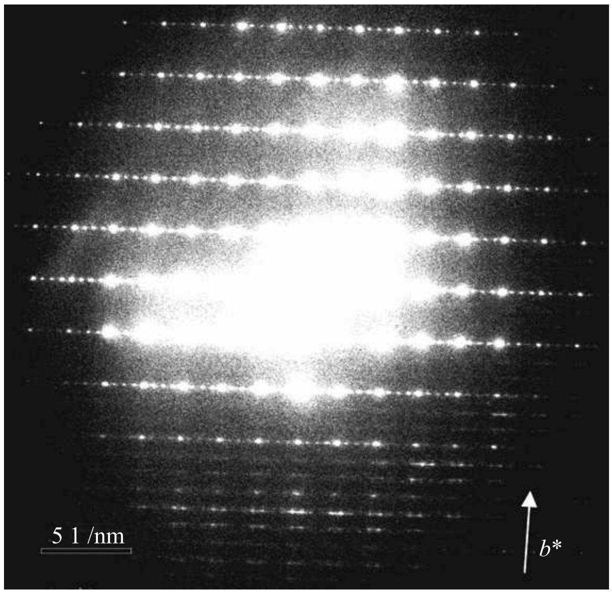

Fig. S2. The electron diffraction pattern obtained on a conventional NbS_3-II sample in the bc plane (see Fig. S1)

An important result is the observation of superstructure reflections in the bc plane (the [100] zone). As noted in [2], it is practically impossible to detect them in this zone. Interestingly, the satellites (also elongated along the c^* axis) are visible in the areas far from the center, in accord with the modulation model: satellites should be practically absent in the 0-Laue zone, that is, in the middle of the image.

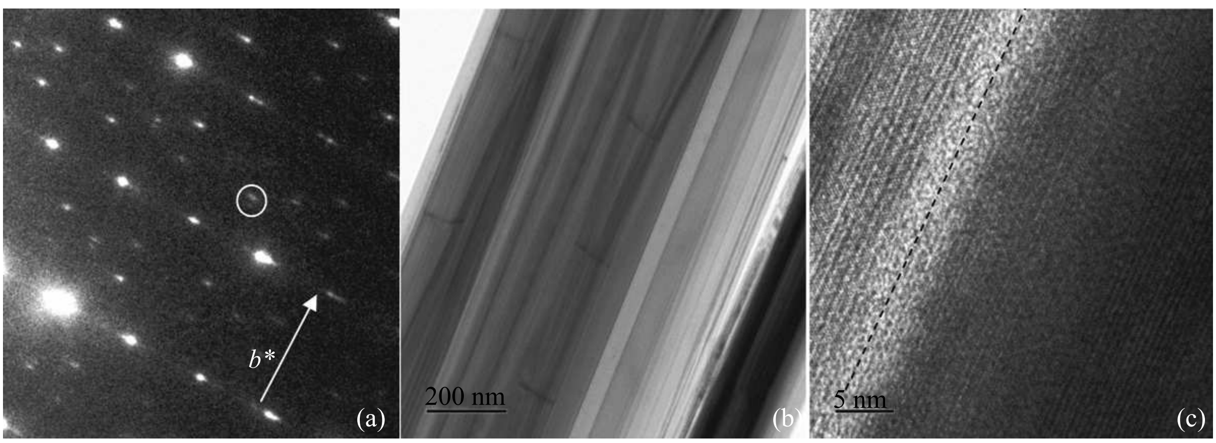

Fig. S3. A fragment of the diffraction pattern (a) and images (b), (c) of the NbS_3 whisker # 5 in TEM in a plane close to bc (positioned not exactly)

The electron diffraction pattern of the "mixed" sample, # 5, shows reflections corresponding to all the three superstructures: the central pairs $0.477b^*$, as well as the pairs of q_0 and q_1 (Fig. S3a). One of such pairs is marked with a white ring. A detailed TEM study showed the presence of a domain structure of the sample. Apparently, it consists of domains of normal and anomalous phases (Fig. S3b). The assumed domain wall at the atomic-scale magnification is shown by the dashed line in Fig. S3c. It is seen that the domains are separated with several disordered atomic layers. Such disordering at the boundary is most likely a feature of quasi-one-dimensional crystals with high growth anisotropy. For the usual and anomalous phases, the lattice constants along the b axis coincide, while they are different along the a and c axes, which can explain the formation of domain walls. This means that along the axis b the domains could grow in parallel.

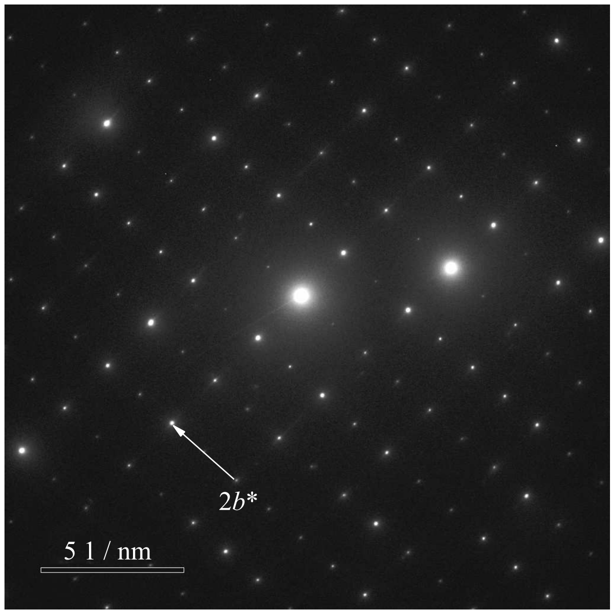

Fig. S4. Electron diffraction pattern in the ab plane of a NbS_3-I sample. The arrow marks the reciprocal-lattice vector without taking doubling into account, i.e., corresponding to the half-period, $b/2 = 3.3\,Å$