Misfit phase \((\text{BiSe})_{1.10}\text{NbSe}_2\) as the origin of superconductivity in niobium-doped bismuth selenide

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Topological superconductivity is of great contemporary interest and has been proposed in doped \(\text{Bi}_2\text{Se}_3\), in which electron-donating atoms such as Cu, Sr or Nb have been intercalated into the \(\text{Bi}_2\text{Se}_3\) structure. For \(\text{Nb}_{x}\text{Bi}_2\text{Se}_3\), with \(T_c \sim 3\) K, it is assumed in the literature that Nb is inserted in the van der Waals gap. However, in this work an alternative origin for the superconductivity in Nb-doped \(\text{Bi}_2\text{Se}_3\) is established. In contrast to previous reports, it is deduced that Nb intercalation in \(\text{Bi}_2\text{Se}_3\) does not take place. Instead, the superconducting behaviour in samples of nominal composition \(\text{Nb}_{x}\text{Bi}_2\text{Se}_3\) results from the \((\text{BiSe})_{1.10}\text{NbSe}_2\) misfit phase that is present in the sample as an impurity phase for small \(x\) (\(0.01 \leq x \leq 0.10\)) and as a main phase for large \(x\) (\(x = 0.50\)). The structure of this misfit phase is studied in detail using a combination of X-ray diffraction and transmission electron microscopy techniques.

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Recently there has been significant interest in layered topological insulators such as the chalcogenides Bi$_2$Se$_3$ and Bi$_2$Te$_3$\(^{-6}\). Topological insulators are phases of matter in which the bulk material is semiconducting, but the surface contains electrons that are chiral, massless and conduct electricity as though they were metals. Of particular interest is topological superconductivity, which features the existence of gapless surface states at the surface of a fully gapped semiconductor. Because of their unique electronic structure, topological superconductors are proposed to have great potential in fault-tolerant topological quantum computing\(^7\). Layered materials often allow for intercalation and/or deintercalation as a way of tuning the chemistry and physics. It has been shown, for example, that intercalation of copper into Bi$_2$Se$_3$ is possible and gives rise to superconductivity up to 3.8 K\(^8,9\). Moreover, superconductivity (with \(T_c \approx 5.5\) K) was observed when Bi$_2$Te$_3$ was reacted with Pd to form Pd$_x$Bi$_2$Te$_3$ with \(x = 0.15, 0.3, 0.5\) and 1\(^{10}\). Other reported superconducting intercalates are described by the chemical formulae Sr$_x$Bi$_2$Se$_3$ (\(T_c \approx 2.5\) K, \(T_c \approx 2.9\) K\(^{10}\)) and Nb$_x$Bi$_2$Se$_3$ (\(T_c \approx 3\) K\(^{11-13}\)), where \(x\) generally ranges from 0.05 and 0.25. Note that these M$_x$Bi$_2$Se$_3$ (M = Cu, Sr, Nb) phases are synthesised at elevated temperatures above a stoichiometric ratio of the elements, Bi and Se. This is in contrast to the work by Koski et al., where zerovalent metals are intercalated, at around ambient temperature, into Bi$_2$Se$_3$ post synthesis, and complex superstructures as a result of the ordering of the intercalated atoms are obtained\(^{14}\).

The chemical nature of these superconducting phases and the location of the intercalated metals in the chalcogenide structure is not trivial. For Cu$_x$Bi$_2$Se$_3$, synthesised at high temperatures from the elements, Cu is reckoned to be inserted in the van der Waals gap between the Bi$_2$Se$_3$ quintuple layers\(^{8,15}\), as confirmed by the significant increase in the \(c\)-axis lattice parameter from \(c = 28.666\) (1 Å) for Bi$_2$Se$_3$ to \(c = 28.736(1)\) Å for Cu$_{0.12}$Bi$_2$Se$_3$\(^8\). A comparable expansion of the unit cell volume is observed by Koski et al.\(^{14}\) using intercalation techniques. On the other hand, for phases described with the formula Sr$_x$Bi$_2$Se$_3$, there is no clear consensus on the structure. Competing studies state or assume variously that Sr is inserted in the van der Waals gap\(^{10}\) or within the quintuple layers themselves\(^{16}\). For Nb$_x$Bi$_2$Se$_3$, it was concluded from apparent small shifts in peak positions in powder diffraction measurements that the \(c\)-axis length expanded slightly leading to the assumption that Nb is inserted in the van der Waals gap of Bi$_2$Se$_3$ and the compound has a similar structure to Cu$_x$Bi$_2$Se$_3$\(^{12,17}\). The minimal change in lattice parameters implies a highly distorted coordination environment for Nb\(^{17}\). Several papers on Nb$_x$Bi$_2$Se$_3$ describe a range of detailed examinations of the superconducting properties, but in many of these works presented on Nb$_x$Bi$_2$Se$_3$ samples, the extent of the bulk characterisation of the samples is limited. Kobayashi et al.\(^{11}\) synthesised Nb$_x$Bi$_2$Se$_3$ with varying \(x\) and did examine the samples using bulk powder diffraction measurements. These showed, in addition to a phase with the Bi$_2$Se$_3$ structure, an impurity phase to which they assigned the formula BiNbSe$_3$\(^{18}\) and a second impurity, BiSe. These impurities increased in fraction with increasing \(x\) and indeed they showed that the phase fraction of the proposed Nb$_x$Bi$_2$Se$_3$ phase with the Bi$_2$Se$_3$ structure reaches zero (within the uncertainty) at \(x = 0.50\). Work by Wang et al.\(^{19}\) and recent work by Cho et al.\(^{20}\) also show that Nb$_x$Bi$_2$Se$_3$ samples are multiphase in the bulk. Nevertheless, all these reports assign the superconductivity evident in these samples to a Nb-doped Bi$_2$Se$_3$-type phase.

Here we show evidence for an alternative explanation for the observed superconductivity in Nb-doped Bi$_2$Se$_3$ samples of overall composition Nb$_x$Bi$_2$Se$_3$. We show that conventional high-temperature synthesis of samples with the composition Nb$_x$Bi$_2$Se$_3$ (0 \(\leq x \leq 0.50\)) results in a mixture of three phases: Bi$_2$Se$_3$, BiSe and the layered misfit compound (BiSe)$_{1.10}$NbSe$_2$. This so-called misfit compound is a layered composite (i.e. an intergrowth) compound made up of two (or more) interpenetrating sublattices of different chemical composition\(^{21}\). For (BiSe)$_{1.10}$NbSe$_2$, the two sublattices of composition BiSe and NbSe$_2$ occur with a ratio of 1:10:1 and have different intralayer lattice constants, which do not match, hence the term misfit, and the corresponding misfit ratio is evident in the formula. In this paper and particularly in the supporting information we describe the structure in detail and show how (BiSe)$_{1.10}$NbSe$_2$ compares with related misfit layered chalcogenides. This misfit phase corresponds to the peaks previously assigned to the BiNbSe$_3$ impurity\(^{18}\) (which is of fairly similar composition) by Kobayashi et al.\(^{11}\) and by Cho et al.\(^{20}\). We observe that the amount of the phase present with the Bi$_2$Se$_3$ structure (assumed to be the superconducting phase Nb$_x$Bi$_2$Se$_3$ in the literature\(^{11,12,17,19,20,22}\), including very recent literature\(^{19,20,21,23}\)) in the samples decreases with increasing Nb content in the synthesis mixture and completely vanishes for \(x = 0.50\) while the superconducting volume fraction of the sample is directly proportional to the Nb content of the sample. In addition we do not observe, with synchrotron resolution, a measurable \(c\)-axis expansion of the Bi$_2$Se$_3$-structure phase upon Nb doping, suggesting that it is pure and undoped Bi$_2$Se$_3$. Moreover, our energy-dispersive X-ray spectroscopy (EDX) measurements reveal no crystallites with elemental composition Nb$_x$Bi$_2$Se$_3$. Therefore, in contrast to previous reports, we deduce that Nb doping in Bi$_2$Se$_3$ does not take place and the superconducting behaviour in samples of composition Nb$_x$Bi$_2$Se$_3$ is actually caused by the misfit phase (BiSe)$_{1.10}$NbSe$_2$ that is present in the sample as an impurity phase for small \(x\) and as a main phase for large \(x\).

### Results and discussion

#### Composition dependence of structures and superconducting properties

Figure 1a shows the synchrotron powder diffraction pattern of a sample of composition Nb$_{20}$Bi$_2$Se$_3$, which is a typical diffraction pattern of these Nb$_x$Bi$_2$Se$_3$ samples. It is clear that this Nb$_{20}$Bi$_2$Se$_3$ sample consists of three phases as indicated by the fit and coloured markers: a phase with the Bi$_2$Se$_3$ structure, the misfit phase (BiSe)$_{1.10}$NbSe$_2$, and BiSe. The fit for the Bi$_2$Se$_3$ structure phase resulted in lattice parameters of \(a = 4.1390(8)\) Å and \(c = 28.6298(10)\) Å which are equal within one estimated standard deviation in the refinement to those of pure Bi$_2$Se$_3$ (\(a = 4.1393(11)\) Å and \(c = 28.6304(9)\) Å) which we measured with synchrotron radiation under the same conditions, from which we conclude that there is no evidence for Nb intercalation. Figure 1c–e shows representative scanning electron microscopy (SEM) energy-dispersive X-ray spectroscopy (EDX) maps of the sample. Figure 1b shows crystallites with different elemental composition corresponding to either (BiSe)$_{1.10}$NbSe$_2$ with a Nb:Bi ratio close to 1:1 or Nb-free Bi and Se phases, i.e. no crystallites with a composition close to Nb$_x$Bi$_2$Se$_3$ are observed for this sample with \(x = 0.2\) in the reaction mixture. The chemical composition of the misfit phase was determined by SEM-EDX as Bi/Se/Nb: 22(1)/59(1)/19(1) (Fig. 1) and additionally by scanning transmission electron microscopy (STEM) EDX measurements as Bi/Se/Nb: 21.4(2)/60.5(8)/18.1(7) (Supplementary Fig. S10), which are in agreement within the experimental uncertainty. Moreover, Nb is only found in combination with Bi and Se in a ratio corresponding to (BiSe)$_{1.10}$NbSe$_2$, no other Nb-containing phase such as NbSe$_2$ is observed.

In Fig. 2a, we show the superconducting properties of samples made with compositions Nb$_x$Bi$_2$Se$_3$. The critical temperature \(T_c\) of roughly 3.2 K is in agreement with previous reports of superconductivity in samples of these nominal compositions\(^{11-13}\). Moreover, the superconducting volume fraction is directly
proportional to $x$. We state the susceptibility per gram of material due to the fact that the Nb$_{20.20}$Bi$_2$Se$_3$ sample is a mixture of three phases and the ratios of these phases differ for different $x$. Figure 2b shows the first two characteristic peaks of the diffraction pattern: the 003 peak of the Bi$_2$Se$_3$-structure phase and the 002 peak of (BiSe)$_{1.10}$NbSe$_2$. The intensity of the Bi$_2$Se$_3$-structure 003 peak is reduced upon increasing $x$ and for $x = 0.50$ there is no evidence for a Bi$_2$Se$_3$-structure phase present in the sample. Moreover, as quantified above, we do not observe any evidence, with synchrotron resolution, for a measurable peak shift and hence a $c$-axis expansion within one estimated standard deviation of this Bi$_2$Se$_3$-structure phase present in the samples upon Nb doping (see Fig. 2c) suggesting that it is undoped Bi$_2$Se$_3$. This is in contrast to the variations stated in literature reports. However, these reports either do not refine the lattice parameters from the whole pattern$^{11}$, or do not present any uncertainties on the refined values$^{19}$, or do not make a comparison using the same measurement conditions with a pure Bi$_2$Se$_3$ phase$^{20}$. Wang et al.$^{19}$
report a slight expansion in \(c\) on Nb doping, but do not report the estimated standard deviation and Cho et al.\(^{20}\) report a \(c\) lattice parameter of 28.4633(7) Å, which is much smaller than what we and Wang et al.\(^{19}\) find for pure BiSe\(_3\). Our previous work on Li\(_{1-x}\)Fe\(_{1+y}\)As samples showed that trends in lattice parameters arising from very small compositional changes could only be monitored by synchrotron radiation.\(^{17}\) Our observation of no \(c\)-axis expansion within one estimated standard deviation with synchrotron resolution is strong evidence that no intercalation of Nb into BiSe\(_2\) took place. This argument, in combination with the fact that the superconducting volume fraction increases with \(x\) while the amount of the BiSe\(_2\)-structure phase decreases with \(x\), proves that the superconductivity does not arise from a BiSe\(_2\)-structure phase. Thus, the superconductivity does not arise from the assumed intercalate Nb\(_x\)Bi\(_2\)Se\(_3\) phase with Nb intercalated between or within BiSe\(_2\) slabs or substituted for one of the other elements. Particularly compelling is that the superconducting volume fraction is highest when there is no BiSe\(_2\)-structure phase present within the detection limits of the synchrotron powder diffraction experiment. In addition, the intensity of the 002 peak of (BiSe)\(_{1.10}\)NbSe\(_2\) is directly proportional to the superconducting volume fraction (Fig. 2d). For small \(x\), (BiSe)\(_{1.10}\)NbSe\(_2\) can be considered a small superconducting impurity and for larger \(x\), the (BiSe)\(_{1.10}\)NbSe\(_2\) phase dominates. Note that Fig. 2a shows that there appears to be a slight variation in \(T_c\) (between 3.0 and 3.2 K) among samples prepared under similar conditions with various Nb contents. As will be highlighted below, (BiSe)\(_{1.10}\)NbSe\(_2\) is subject to small variations in \(T_c\) depending on synthesis technique, and can contain various stacking faults.

As shown in Fig. 1, BiSe is also present in Nb\(_x\)Bi\(_2\)Se\(_3\) samples in addition to BiSe\(_2\) and (BiSe)\(_{1.10}\)NbSe\(_2\). As can be seen in Fig. 2b, when \(x\) reaches 0.5, Nb\(_{0.50}\)Bi\(_2\)Se\(_3\) contains no phase with the structure of BiSe\(_2\) and therefore solely consists of the misfit phase (BiSe)\(_{1.10}\)NbSe\(_2\) and BiSe according to the equation:

\[
\text{Nb}_{0.50}\text{Bi}_2\text{Se}_3 = 0.5 \text{Nb} + 2 \text{Bi} + 3 \text{Se} = 0.5\text{(BiSe)}_{1.10}\text{NbSe}_2 + 1.45 \text{BiSe}
\]

Our investigation of the relationship between the superconducting volume fraction and the ratio of (BiSe)\(_{1.10}\)NbSe\(_2\) and BiSe in Nb\(_{0.50}\)Bi\(_2\)Se\(_3\) reveals that the superconducting volume fraction increases with the (BiSe)\(_{1.10}\)NbSe\(_2\)/BiSe ratio, confirming that the misfit phase is responsible for the superconducting properties in samples of composition Nb\(_x\)Bi\(_2\)Se\(_3\) and BiSe is not. A full description of this investigation is given in Supplementary Section 1 and Supplementary Fig. S5.

Figure 3 shows the magnetometry data for the sample of composition Nb\(_{0.50}\)Bi\(_2\)Se\(_3\) in comparison with the superconducting properties of its two constituents, i.e. BiSe and the misfit phase (BiSe)\(_{1.10}\)NbSe\(_2\) synthesised in pure form (see ‘Methods’ section). The pure BiSe sample is not superconducting while the pure misfit phase is superconducting with a similar \(T_c\) as that reported for the mixed-phase sample of composition Nb\(_{0.50}\)Bi\(_2\)Se\(_3\) on synthesis method in ref. 17. The most recent of these papers by Cho et al.\(^{20}\) performed bulk analysis on a sample of nominal composition Nb\(_{0.25}\)Bi\(_2\)Se\(_3\) in response to the published referee report. According to the published powder diffraction pattern, that analysis showed that the sample used was a similar multiphase mixture to those which we report here, and there is also consistency with the work of Kobayashi et al.\(^{11}\). Thus, all the published works which show bulk analysis of Nb\(_x\)Bi\(_2\)Se\(_3\) samples show multiphase behaviour, and the published works on single crystals mentioned above have studied single crystals that were selected from these multiphase batches.

As shown in Supplementary Fig. S3, we found a small variation in \(T_c\) of (BiSe)\(_{1.10}\)NbSe\(_2\) depending on the synthesis technique. Herein, we show the magnetometry data of naturally cooled (i.e. at the rate of the furnace when switched off) and ice/water quenched pure misfit samples as obtained by the vapour transport method.\(^{35}\) The naturally cooled sample has a \(T_c\) ~ 2.3 K which is in good agreement with previous reports on the superconducting properties of the misfit phase.\(^{36}\) The ice/water quenched sample has a significantly higher \(T_c\) that is comparable to the ice/water quenched samples of Nb\(_{0.50}\)Bi\(_2\)Se\(_3\) shown in Fig. 2a. We do not observe any notable difference in the X-ray patterns between the samples. The (BiSe)\(_{1.10}\)NbSe\(_2\) data in Fig. 3 is obtained by annealing the ice/water quenched sample at 640 °C for a couple of days. We hypothesise that the small changes in properties are caused by either minute compositional changes...
Single-crystal X-ray diffraction. Restricting the amount of structural information available from powder diffraction data, the crystal consists of two separate translationally symmetric subsystems. Due to their mutual interaction, the elements using a vapour transport synthesis method, the structure drawn with anisotropic displacement ellipsoids is shown in Supplementary Fig. S7. The average crystal structure of (BiSe)\(_{1.10}\)NbSe\(_2\) has recently been reported.

Structural analysis of (BiSe)\(_{1.10}\)NbSe\(_2\). (BiSe)\(_{1.10}\)NbSe\(_2\) has been synthesised and studied previously, but complete structure solution by single-crystal X-ray diffraction was hampered, apparently by disorder in the BiSe sublattice along the stacking direction. To probe the structure of the misfit phase (BiSe)\(_{1.10}\)NbSe\(_2\), in more detail we synthesized it phase pure from the elements using a vapour transport synthesis method. Powder diffraction data (Fig. 4a) are in agreement with those of Zhou et al. Single-crystal X-ray diffraction measurements performed on the I19 beamline at Diamond Light Source (UK) show severely streaked reflections parallel to c (Supplementary Fig. S6), confirming a type of disorder intrinsic to this phase and restricting the amount of structural information available from single-crystal X-ray diffraction. Refinement of composite structures from powder diffraction data, gives less detailed models than those obtained from single-crystal X-ray diffraction as there is no reliable method to determine a modulation vector from powder data. Therefore, as the starting point for refining the crystal structure from synchrotron powder X-ray data, we performed transmission electron microscopy and combined its results with the previously published model for (BiSe)\(_{1.09}\)TaSe\(_2\), which is very similar to (BiSe)\(_{1.10}\)NbSe\(_2\). A detailed description of the modelling of the average crystal structure of (BiSe)\(_{1.10}\)NbSe\(_2\) (summarised in Fig. 4b, c) from synchrotron powder data and electron diffraction data is given in Supplementary Section 2 and Supplementary Figs. S8 and S9. In this description, the crystal consists of two separate translationally symmetric subsystems. Due to their mutual interaction, the subsystems will in reality be modulated.

In order to gain more insight into the local structure of (BiSe)\(_{1.10}\)NbSe\(_2\) and how it differs from that of the Ta analogue, and to explain the origin of the streaking in the single-crystal diffraction patterns, we performed high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) imaging. Figure 5a, b shows representative HAADF-STEM images acquired along the [100] direction. They clearly show a layered structure with alternating BiSe and NbSe\(_2\) blocks. The thickness of the blocks and their [100] orientation were constant in the whole area of investigation. The synthesis technique used here leads to a more uniform structure than the layer-by-layer vapour deposition employed by Mitchson et al. The structure of (BiSe)\(_{1.10}\)NbSe\(_2\), refined (Fig. 4a) using the (BiSe)\(_{1.09}\)TaSe\(_2\) model as a starting point, is overlaid on the images. The image in Fig. 5a perfectly matches the refined structure from Fig. 4b, c and all NbSe\(_2\) layers have the same orientation (as indicated by the red triangles). The presence of the two orientations can be seen from the shifts of Nb and Se atomic columns in Fig. 5b and as depicted in the figure legend. The two types of NbSe\(_2\) layers with opposing orientations of the NbSe\(_6\) columns in Fig. 5b and as depicted in the figure legend.
triangular prisms can perfectly alternate along the stacking direction (Fig. 5b) or occur in a random manner (Fig. 5c), obtaining the character of stacking faults. The corresponding electron diffraction pattern acquired from a large area is shown in Fig. 5d. It can be indexed with the cell parameters $b = 6.0 \text{ Å}$, $c = 24.0 \text{ Å}$, in agreement with the refinement parameters in Supplementary Tables S1 and S2, but shows elongated reflections 0kl when $l$ is odd, which is in agreement with the occurrence of these stacking faults and explains the streaked reflections observed for single-crystal X-ray diffraction in Supplementary Fig. S6 and as described in reference 35 which accounts for the difficulty in refining the structure from single-crystal data, and is a difference between (BiSe)$_{1.10}$NbSe$_2$ and the Ta analogue. Further explanation of how these stacking faults observed by STEM relate to the powder pattern as shown in Fig. 4a is given in the Supplementary Section 3, Supplementary Figs. S10 to S12 and Supplementary Table S3.

Concluding remarks. In conclusion, there are several reports in the literature of derivatives of the important narrow band gap semiconductor Bi$_2$Se$_3$ which show superconductivity. A notable contemporary example is the case of samples with the proposed formula Nb$_x$Bi$_{2-x}$Se$_3$. In this work, we show that there is no evidence for the chemically surprising formation of phases in which Nb is intercalated between the Bi$_2$Se$_3$ quintuple layer slabs or otherwise inserted or substituted into the Bi$_2$Se$_3$ structure. We conclude from analysis of high-resolution powder diffraction data, transmission electron microscopy and magnetometry measurements on samples of overall composition Nb$_x$Bi$_{2-x}$Se$_3$ ($0 \leq x \leq 0.50$) that pure Nb$_x$Bi$_{2-x}$Se$_3$ phases with the Bi$_2$Se$_3$ structure are not attainable using high-temperature synthetic methods, and that the superconductivity in these compositions arises from the misfit phase (BiSe)$_{1.10}$NbSe$_2$ which is a composite of NbSe$_2$ and Bi$_2$Se$_3$. This evident inhomogeneity of samples of nominal composition Nb$_x$Bi$_{2-x}$Se$_3$ might also explain why in one report it was noted that not all of the samples were of high enough quality to show a large superconducting volume fraction$^{15}$. Furthermore, the upper critical field data are reportedly dominated by two-fold symmetry, in contradiction to the three-fold symmetry of the Bi$_2$Se$_3$ structure which led to the proposal of a nematic state$^{22}$. We suggest that it should be checked whether the orthorhombic two-fold symmetry of the superconducting misfit phase (BiSe)$_{1.10}$NbSe$_2$ can account for the upper critical field response.

Methods

Synthesis. Polycrystalline samples of composition Nb$_x$Bi$_{2-x}$Se$_3$ ($x = 0.01, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50$) were synthesized by mixing together stoichiometric ratios of high-purity Bi pieces (Sigma-Aldrich; 99.999%), Se powder (Alfa Aesar; 99.999%) and Nb powder (Alfa Aesar; 99.99%), and heating them in an evacuated sealed silica tube to 850 °C at 30 °C h$^{-1}$. After holding the temperature for 1 week, the samples were cooled slowly to 610 °C at 3 °C h$^{-1}$ and finally quenched into ice/water, which is in agreement with various reports on the synthesis of Nb$_x$Bi$_{2-x}$Se$_3$.$^{12,15}$, in order to compare the results. The very slow cooling between 850 and 610 °C was performed in order to allow crystals to grow from the melt$^{11,12,15}$. Ice/water quenching was performed as this was done in the previous reports$^{11,12,15}$ with which we sought comparison, and it was found to be crucial for obtaining superconductivity in Sr$_x$Bi$_{2-x}$Se$_3$.$^{16}$ To verify the need for ice/water quenching, we synthesized single crystals of (BiSe)$_{1.10}$NbSe$_2$ by a vapour transport method with and without ice/water quenching as detailed below. Polycrystalline Bi$_2$Se$_3$ was synthesized by mixing together stoichiometric ratios of the Bi pieces and Se powder described above, following a previously reported synthesis method.$^{45}$ The elements were heated in an evacuated sealed silica tube to 850 °C at 2 °C min$^{-1}$. After holding the temperature for 1 week, the samples were quenched into ice/water, ground into a fine powder and annealed at 550 °C in order to increase crystallinity for roughly 2 months followed by quenching in ice/water. Single crystals of the layered misfit compound (BiSe)$_{1.10}$NbSe$_2$ were synthesized through a previously reported vapour transport method.$^{35}$ A stoichiometric ground mixture of the elements described above was placed in one end of an evacuated sealed silica tube and this end of the tube was placed in a tube furnace at 700 °C with the other end maintained at 640 °C. Around 10 mg of (NH$_4$)$_2$PbCl$_6$ per 500 mg of the total mass of the precursors was used as a transport agent. (NH$_4$)$_2$PbCl$_6$ was prepared by a modified synthesis method.$^{46}$ from a stoichiometric mixture of PbO$_2$ and NH$_4$ in ice-cold HCl. After around 10 days, the tube was ice/water quenched and the crystals were extracted from the cold end of the tube. Small crystals with sizes up to 0.5 mm were obtained. Naturally cooled samples without ice/water quenching (i.e. cooled at the rate of the tube furnace when switched off) were also prepared and the structures and properties of the obtained crystals were compared.

X-ray diffraction. Powder X-ray diffraction (XRD) measurements were performed on both laboratory XRD equipment (Bruker D8 Advance, Cu Ka radiation) and on the I11 beamline at the Diamond Light Source (UK). At I11, diffractograms were measured upon exposure of the monochromatic 15.0 keV ($\lambda = 0.8265(5)$ or 0.82640(8) Å calibrated using a Si standard) X-ray beam and collected using a Mythen position-sensitive detector. Single-crystal XRD measurements were performed on the I19 beamline at Diamond Light Source (UK). Data analysis was performed with TOPAS-Academic V5$^{47}$ and Jana2006.$^{48}$

Electron microscopy. Scanning electron microscopy (SEM) measurements were performed using a FEI Quantum FEG 650 operating in low vacuum mode with an accelerator voltage of 20 kV and a spot size of 3.5. Electron diffraction patterns were acquired on a Thermo Fisher Tecnai transmission electron microscope (TEM) operated at 200 kV. High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images and energy-dispersive X-ray spectroscopy (EDX) maps were acquired using a Thermo Fisher Titan 80-300 “cubed” microscope operated at 300 kV. Specimens for the TEM study were prepared in two ways: (1) the material was dispersed in ethanol for 1 h using an ultrasonic bath, with regular breaks to allow the water in the bath to cool. Then, a few drops of the suspension were deposited onto a copper TEM grid covered by a holey carbon layer. (2) The cross-section and plane-view lamellae were prepared from individual crystals using focused ion beam (FIB) milling. During the preparation process, Pt and carbon protective layers were deposited on top of the film. The specimens were prepared in air. TEM images obtained for the specimens prepared by the different methods were consistent. For the compositional analysis by STEM-EDX, Bi-M, Nb-L and Se-K lines were used.

Magnetometry measurements. Magnetic susceptibility measurements were conducted using a Quantum Design MPMS3 superconducting quantum interference device (SQUID) magnetometer. Gelatin capsules were used to contain accurately-weighed powder samples of about 20–30 mg in mass. Measurements were performed on warming in a d.c. field of 10 Oe in the temperature range 1.8–10 K after firstly cooling in zero applied field (ZFC) and then after cooling in the applied field of 10 Oe (FC).

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

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Author contributions
M.E.K. and S.J.C. synthesised the compounds, performed the diffraction and magnetometry experiments, and performed the structural refinement. M.B. and J.H. performed the TEM and HAADF-STEM measurements and corresponding analysis. M.E.K. wrote the paper involving all authors.

Competing interests
The authors declare no competing interests.

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