

Nb–Nb Interactions Define the Charge Density Wave Structure of 2H-NbSe₂

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S Supporting Information

ABSTRACT: 2H-NbSe₂ is a canonical Charge-Density-Wave (CDW) layered material the structural details of which remained elusive. We report the detailed structure of 2H-NbSe₂ below the CDW transition using a (3 + 2)-dimensional crystallographic approach on single crystal X-ray diffraction data collected at 15 K. Intensities of main reflections as well as CDW satellites of first order were measured. Quantitative information about the magnitude of the structural distortions and clustering of Nb atoms were extracted from the refined model. The Nb–Nb distances were found to distort between 3.4102(8) and 3.4928(8) Å in the CDW phase from the average undistorted distance of 3.4583(4) Å.

The understanding of electronic instabilities in low-dimensional correlated electron systems is of fundamental importance in condensed matter. Superconductivity and Density Waves are competing orders that derive from such instabilities.¹ Spontaneous formation of periodic lattice distortions and Charge Density Waves (CDW) can be thermodynamically favorable under certain conditions in low-dimensional metals where the wave vector is generally known to depend on the nesting properties of the Fermi surface.^{2–4} The symmetry breaking that follows the suggested phonon–electron coupling occurs usually at low temperature at the so-called Peierls phase transition temperature T_{CDW} .

CDW distortions have been observed in many low-dimensional compounds, such as transition metal chalcogenides and several of them, e.g., PbTe₂,⁵ 2H-TaS₂,⁶ 2H-TaSe₂,⁶ and 2H-NbSe₂,⁷ are known to be superconducting. Consequently, 2H-NbSe₂ became the canonical CDW material and is one of the most intensively studied to date.^{8–14} The superconducting transition temperature (T_c) is around 7 K and the CDW Peierls transition is around 33 K.^{12,15,16} The availability of large high-quality single crystals made NbSe₂ the first material to be studied by Scanning Tunneling Microscopy (STM) for observing vortex distributions.¹⁷ Currently, NbSe₂ is a reference material in the STM community for such investigations. Neutron diffraction measurement, electron diffraction,¹⁸ and STM revealed the presence of a complex CDW modulation with three \mathbf{q} -vectors around the main reflections of the hexagonal lattice at $\mathbf{q}_1 = \pm 1/3a^*$, $\mathbf{q}_2 = \pm 1/3b^*$, and $\mathbf{q}_3 = \pm (1/3a^* - 1/3b^*)$. A huge number of physical measurements and chemical modifications have been applied to NbSe₂ and other isostructural transition metal dichalcogenides in order to

study the CDW behavior.^{19–21} The interplay of CDW instability with superconductivity in NbSe₂ is not fully understood^{10,11,13,14} mainly because its CDW structure is unknown and the vast majority of reports is based on the superconducting state. The present work solves the long-standing question of the precise atomic structure of the CDW state.

The fact that the CDW instability has a logarithmic singularity at $q = 2k_f$ and therefore it is fragile has led to the question of whether the actual CDWs observed in quasi-2D materials are indeed a result of the Peierls instability.^{22,23} Thus, the exact mechanism of CDW formation in two-dimensional metals is still under extensive discussion.^{9–11,13,14} Electronic structure calculations at the DFT level have shown that the bare susceptibility does not have any sharp peak at the experimentally observed CDW wave vector, $\mathbf{q}_{\text{CDW}} = (2\pi/3, 2\pi/3)$, but at best a broad and shallow peak in the real part, while the imaginary part which directly represents the Fermi surface nesting does not peak at \mathbf{q}_{CDW} at all.^{22–25} The lack of nesting properties suggested that momentum dependence of the electron phonon interaction plays a crucial role in driving CDW instabilities.^{22–24} Neutron^{12,26} and X-ray scattering phonon-dispersion experiments^{27,28} give indirect confirmation where a softening was detected in only one of the low energy modes close to \mathbf{q}_{CDW} . Only recently the CDW gap at the Fermi level was experimentally observed by high resolution Angle Resolved Photoemission Spectroscopic (ARPES) studies on single crystals of NbSe₂.²⁹ Theoretical calculations of the electronic structure of NbSe₂ suggested that full Nb d-bands close to the Fermi level are responsible for the CDW instability which is not a Fermi surface effect.²³ Furthermore, NbSe₂ was suggested to be a two-band superconductor supported by several experiments^{30–33} but an alternative single-band scenario with the involvement of an anisotropic s-wave could also interpret the results.^{34–36} These are some of the issues highlighting the challenge in understanding the CDW and superconductivity states and their interplay in 2D systems. Compounding these challenges is the lack of information of the structural details of CDW below T_{CDW} .³⁷ Here we present for the first time the detailed structural picture of the CDW of 2H-NbSe₂ derived from a (3 + 2)-dimensional crystallographic analysis of X-ray diffraction data obtained at 15 K on a single crystal.

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NbSe₂ is a layered compound and it consists of trigonal prismatic Nb atoms surrounded by six Se atoms and it can crystallize into several polymorphs depending on the number of NbSe₂ layers and their packing in the unit cell.³⁸ In the most stable room temperature form, two NbSe₂ layers separated by a van der Waals gap are packed in a hexagonal unit cell (*P*₆₃/*mmc*) to form the so-called 2H-NbSe₂, Figure 1A. The Nb

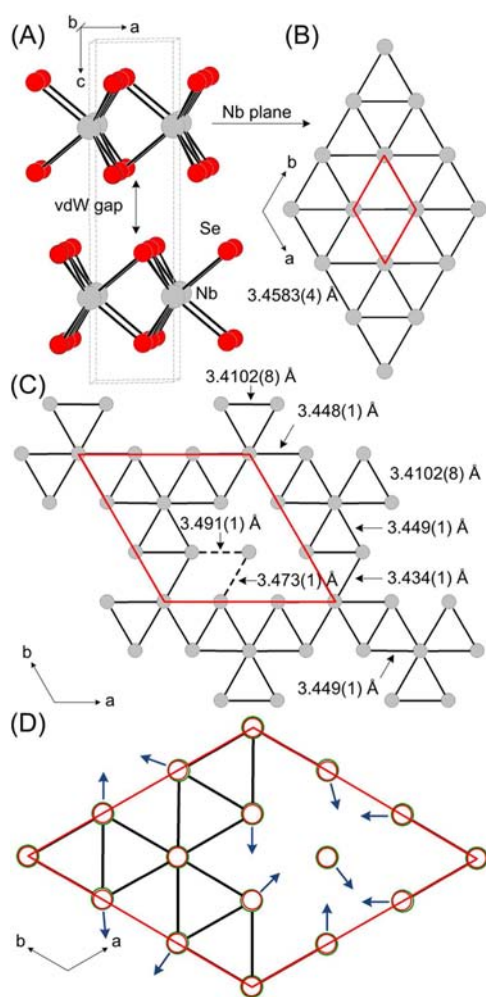


Figure 1. (A) Average structure of 2H-NbSe₂. NbSe₂ layers are separated by a van der Waals (vdW) gap as indicated in the figure by a double arrow. (B) Hexagonal plane of Nb atoms in the 2H-NbSe₂ average structure. The unit cell is marked with red solid lines. (C) CDW structure. Plane of Nb atoms only obtained by the crystallographic refinement at 15 K. The 3 × 3 commensurate supercell along the hexagonal plane is marked with red solid lines. The threshold of Nb–Nb connection was set equal to the *a*-parameter of the 2H-NbSe₂ average cell at 15 K. The formation of Nb clusters is apparent. (D) Superposition of the Nb atoms in the 3 × 3 commensurate CDW supercell (red inner circles) and the undistorted subcell (green outer circles) illustrating the displacement of the Nb atoms in the hexagonal plane. Direction of displacement due to the CDW wave is marked with blue arrow.

plane that plays a key role to the CDW formation as suggested by theory is perfectly hexagonal with a Nb–Nb separation equal to the *a*-parameter of the hexagonal unit, Figure 2B. Most of the physical characterization and interest has been focused on the 2H-NbSe₂ form since it possesses a superconducting and a CDW state at low temperature. We confirm that the structural distortions are associated with the Nb–Nb distances in the

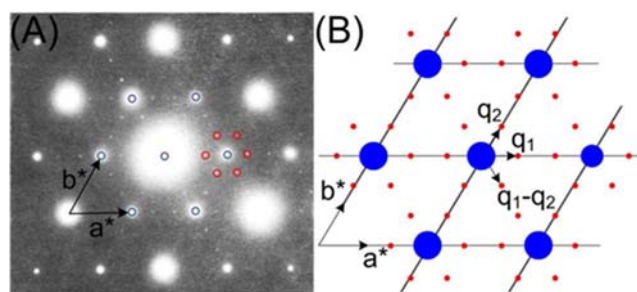


Figure 2. (A) Electron diffraction pattern of 2H-NbSe₂ at 17 K along the *c**-axis. Reprinted with permission from ref 18. Copyright 1975 Elsevier. Main (average structure) reflections are marked with blue circles and supercell CDW reflections around the main reflections are marked with red circles. (B) Calculated diffraction pattern of the refined structure based on the observed intensities from the X-ray data. Main reflections are shown in blue and satellite reflections in red. The three *q*-vectors *q*₁, *q*₂, and *q*₁ – *q*₂ are also indicated. The calculated diffraction is in agreement with the previously reported electron diffraction data.

hexagonal plane (which is in agreement with previous theoretical work) and create clusters of Nb atoms, Figure 1C.

The CDW structure of 2H-NbSe₂ at 15 K adopts the superspace group *P*₆₃/*m*(*α*00)(0/*β*0).³⁹ Generally, in superspace crystallography the position of the atoms is described with a combination of static waves using the atoms in the undistorted unit cell (subcell) as a reference. Consequently, the number of parameters required to describe a modulated system is much smaller than the number of parameters used in a classical 3-dimensional refinement since only the parameters for the atoms in the subcell and their corresponding wave(s) is used. Therefore, we used the multidimensional formalism to solve the complex structural problem of the CDW phase of 2H-NbSe₂. Two independent commensurate *q*-vectors were used for the data integration with *q*₁ = 1/3*a** and *q*₂ = 1/3*b**. The remaining of the satellite reflections could be indexed by the vector produced from the subtraction of *q*₁ and *q*₂, namely, *q*₃ = *q*₁ – *q*₂. Therefore, a (3 + 2)-dimensional approach was applied. The calculated diffraction pattern of our supercell (Figure 2B) matches with the reported¹⁸ electron diffraction pattern of 2H-NbSe₂ at 17 K, Figure 2A. A total of 5401 independent reflections were collected with 685 main and 4716 satellites (*q*₁, *q*₂, and *q*₃) of first order. The final agreement factors converged to the excellent values of around 5.4% for all observed reflections (*I* > 3σ(*I*)) and around 9.3% (wR) for all reflections. All atoms are displaced from their average (undistorted) position due to the CDW distortions. In more details, the average Nb–Se distance of 2.609(2) Å is distributed between lengths of a minimum of 2.598(2) Å and maximum 2.627(2) Å. The Nb–Nb distances that are defined by the length of the hexagonal cell constant *a* in the subcell distort from 3.4102(8) to 3.4928(8) Å. The CDW modulation breaks the perfect hexagonal arrangement of the Nb atoms into clusters as shown in Figure 1C. In the 3 × 3 commensurate cell, almost half of the Nb–Nb pairs are longer than the unit cell constant of 3.4583(4) Å. The distribution of the separation of Se atoms along the hexagonal layers from 3.4583(7) Å in the subcell becomes wider with a minimum Se–Se separation of 3.4490(7) Å and maximum of 3.4671(7) Å. Interestingly, the structural modulations and clustering of the transition metal atoms found in NbSe₂ are very different than those seen in the isoelectronic 1T-TaS₂⁴⁰ and isostructural 2H-TaS₂⁴¹ suggest-

ing that electronic structure and Fermi surface alone may not be the reason for the observed distortions. Interestingly, hyperfine investigations on 2H-TaSe₂ have been interpreted with a similar clustering of the Ta atoms.⁴²

The effect of the modulation on the distances between Nb and Se atoms and their displacements is illustrated in the plots of Figure 3. All curves in Figure 3 have been drawn for $u = 0$

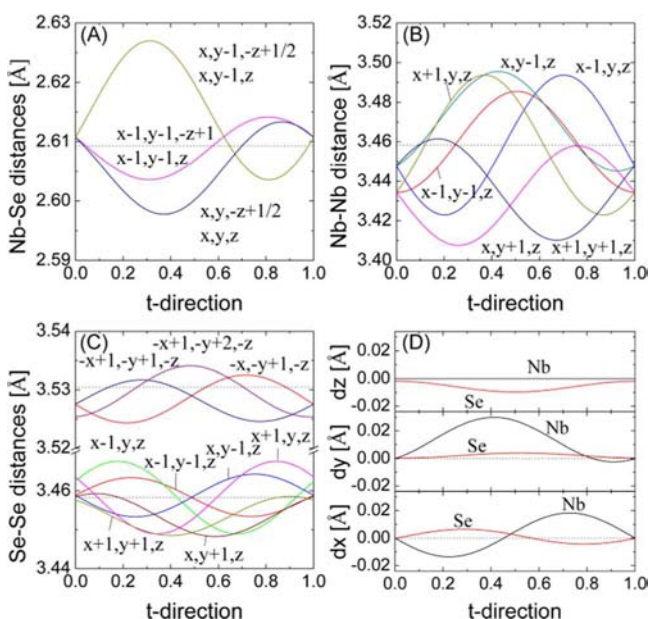


Figure 3. (A) Modulation curves of the Nb–Se distances (Å) found in the CDW crystallographic model as a function of t -coordinate for $u = 0$ (see text for details). Symmetry operators of the atoms in the unit cell are labeled next to each curve. (B) Modulation curves of the Nb–Nb distances as a function of t -coordinate for $u = 0$. (C) Modulation curves of the Se–Se distances as a function of t -coordinate for $u = 0$ and (D) Displacement parameters (Å) along the a -axis (dx), b -axis (dy), and c -axis (dz) of all atoms in the asymmetric unit cell as a function of t -coordinate for $u = 0$.

where u is defined in a similar fashion as the t -coordinate for the fifth dimension (see Supporting Information for more details). Therefore, the values in these plots do not show necessarily the total minimum or maximum displacements but they give a good representation of the trend of the distortion along the \mathbf{q} -vector. The majority of nearest neighbor Nb–Se distances in the trigonal prisms vary in the range of 2.610 ± 0.012 Å indicating a very weak distortion of the first coordination sphere of Nb, Figure 3A. The separation of the Nb–Nb atoms on the contrary is significantly affected with a distribution of 3.458 ± 0.042 Å, Figure 3B. The Se–Se distances along the hexagonal layer range around 3.458 ± 0.012 Å that is a difference of the same magnitude than the Nb–Se separation, Figure 3C. The distances between the Se atoms separated by the vdW gap fall in the range of 3.531 ± 0.005 Å, Figure 3C. The analysis of the atomic displacements (Figure 3D) suggests that the distortions of the Nb atoms are located in the hexagonal plane without a deviation from a planar arrangement. In the case of the Se atoms, the deviations from the average undistorted position are comparable for all three directions in real space and much weaker than those found for Nb. The structure of CDW in NbSe₂ elucidated here explains why the electron phonon coupling¹⁴ is large. The entire CDW is an extended metal bonded network. The Se atoms are not

involved. The driving force for this arises from the d^1 electronic configuration of Nb atoms and attempts to create a diamagnetic ground state. Thus, the previously observed extended phonon collapse¹⁴ in X-ray inelastic scattering experiments has its origin in the movement of Nb atoms from the ideal positions to participate in Nb–Nb bonding.

Despite the vast amount of experimental work on the CDW of NbSe₂, contradictions and controversy continue about the role of Fermi surface nesting in driving the distortions. At the same time, different theoretical models have supported the experimental results with interpretations ranging from nesting of the Fermi surface¹⁶ or saddle points^{4,43} to the nesting being irrelevant to the CDW.²³ Nevertheless, a clear answer to this problem does not exist since a proper structural model of the distorted state was missing. The detailed structure of the CDW in NbSe₂ reported here provides critical information on the exact nature of the CDW instability in this system. It is the Nb network that defines the CDW instability whereas the Se atoms act as spectators. These insights open a path for more informed theoretical treatments and better data interpretation as well as new lines of experimentation and deeper understanding. The new results may shed more light on the issue of how the CDW competes with the superconducting ground state that is present at lower temperature. The Nb–Nb interactions in the CDW of NbSe₂ are to be contrasted with the non-metal Te–Te interactions in the CDW structures of the RETe3 materials which are non superconducting.⁴⁴ In the latter superconductivity can be induced via the application of pressure.

■ ASSOCIATED CONTENT

📄 Supporting Information

Details about the refinement of the modulated structure and CIF. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Grüner, G. *Density Waves in Solids*; Addison-Wesley: Reading, PA, 1994.
- (2) Chan, S. K.; Heine, V. J. *Phys. F: Met. Phys.* **1973**, *3*, 795.
- (3) Peierls, R. E. *Quantum Theory of Solids*; Clarendon: Oxford, 1955.
- (4) Rice, T. M.; Scott, G. K. *Phys. Rev. Lett.* **1975**, *35*, 120.
- (5) Revolinsky, E.; Lautenschlager, E. P.; Armitage, C. H. *Solid State Commun.* **1963**, *1*, 59.
- (6) Wilson, J. A.; Yoffe, A. D. *Adv. Phys.* **1969**, *18*, 193.
- (7) Matthias, B. T.; Geballe, T. H.; Compton, V. B. *Rev. Mod. Phys.* **1963**, *35*, 1.

- (8) Bhattacharya, S.; Higgins, M. J. *Phys. Rev. Lett.* **1993**, *70*, 2617.
- (9) Eichberger, M.; Schafer, H.; Krumova, M.; Beyer, M.; Demsar, J.; Berger, H.; Moriena, G.; Sciaini, G.; Müller, R. J. D. *Nature* **2010**, *468*, 799.
- (10) Menon, G. I.; Ravikumar, G.; Higgins, M. J.; Bhattacharya, S. *Phys. Rev. B* **2012**, *85*, 064515.
- (11) Mohan, S.; Sinha, J.; Banerjee, S. S.; Sood, A. K.; Ramakrishnan, S.; Grover, A. K. *Phys. Rev. Lett.* **2009**, *103*, 167001.
- (12) Moncton, D. E.; Axe, J. D.; Disalvo, F. J. *Phys. Rev. Lett.* **1975**, *34*, 734.
- (13) van Wezel, J.; Schuster, R.; König, A.; Knupfer, M.; van den Brink, J.; Berger, H.; Büchner, B. *Phys. Rev. Lett.* **2011**, *107*, 176404.
- (14) Weber, F.; Rosenkranz, S.; Castellani, J. P.; Osborn, R.; Hott, R.; Heid, R.; Bohnen, K. P.; Egami, T.; Said, A. H.; Reznik, D. *Phys. Rev. Lett.* **2011**, *107*, 107403.
- (15) Harper, J. M. E.; Geballe, T. H.; Disalvo, F. J. *Phys. Lett. A* **1975**, *54*, 27.
- (16) Wilson, J. A.; Disalvo, F. J.; Mahajan, S. *Adv. Phys.* **1975**, *24*, 117.
- (17) Hess, H. F.; Robinson, R. B.; Dynes, R. C.; Valles, J. M.; Waszczak, J. V. *Phys. Rev. Lett.* **1989**, *62*, 214.
- (18) Williams, P. M.; Scruby, C. B.; Tatlock, G. J. *Solid State Commun.* **1975**, *17*, 1197.
- (19) Chen, C. H.; Gibson, J. M.; Fleming, R. M. *Phys. Rev. B* **1982**, *26*, 184.
- (20) Fleming, R. M.; Moncton, D. E.; McWhan, D. B.; Disalvo, F. J. *Phys. Rev. Lett.* **1980**, *45*, 576.
- (21) McMillan, W. L. *Phys. Rev. B* **1977**, *16*, 643.
- (22) Doran, N. J.; Ricco, B.; Schreiber, M.; Titterton, D.; Wexler, G. J. *Phys. C: Solid State Phys.* **1978**, *11*, 699.
- (23) Johannes, M. D.; Mazin, I. I.; Howells, C. A. *Phys. Rev. B* **2006**, *73*, 205102.
- (24) Johannes, M. D.; Mazin, I. I. *Phys. Rev. B* **2008**, *77*, 165135.
- (25) Whangbo, M. H.; Canadell, E. J. *Am. Chem. Soc.* **1992**, *114*, 9587.
- (26) Moncton, D. E.; Axe, J. D.; Disalvo, F. J. *Phys. Rev. B* **1977**, *16*, 801.
- (27) Murphy, B. M.; Müller, M.; Stettner, J.; Requardt, H.; Serrano, J.; Krisch, M.; Press, W. J. *Phys.: Condens. Matter* **2008**, *20*, 224001.
- (28) Murphy, B. M.; Requardt, H.; Stettner, J.; Serrano, J.; Krisch, M.; Müller, M.; Press, W. *Phys. Rev. Lett.* **2005**, *95*, 256104.
- (29) Borisenko, S. V.; Kordyuk, A. A.; Zabolotnyy, V. B.; Inosov, D. S.; Evtushinsky, D.; Buchner, B.; Yaresko, A. N.; Varykhalov, A.; Follath, R.; Eberhardt, W.; Patthey, L.; Berger, H. *Phys. Rev. Lett.* **2009**, *102*, 166402.
- (30) Boaknin, E.; Tanatar, M. A.; Paglione, J.; Hawthorn, D.; Ronning, F.; Hill, R. W.; Sutherland, M.; Taillefer, L.; Sonier, J.; Hayden, S. M.; Brill, J. W. *Phys. Rev. Lett.* **2003**, *90*, 117003.
- (31) Rodrigo, J. G.; Vieira, S. *Physica C* **2004**, *404*, 306.
- (32) Yokoya, T.; Kiss, T.; Chainani, A.; Shin, S.; Nohara, M.; Takagi, H. *Science* **2001**, *294*, 2518.
- (33) Zehetmayer, M.; Weber, H. W. *Phys. Rev. B* **2010**, *82*, 014524.
- (34) Fletcher, J. D.; Carrington, A.; Diener, P.; Rodiere, P.; Brison, J. P.; Prozorov, R.; Olheiser, T.; Giannetta, R. W. *Phys. Rev. Lett.* **2007**, *98*, 057003.
- (35) Hossain, M. D.; Salman, Z.; Wang, D.; Chow, K. H.; Kreitzman, S.; Keeler, T. A.; Levy, C. D. P.; MacFarlane, W. A.; Miller, R. I.; Morris, G. D.; Parolin, T. J.; Pearson, M.; Saadaoui, H.; Kiefl, R. F. *Phys. Rev. B* **2009**, *79*, 144518.
- (36) Huang, C. L.; Lin, J. Y.; Chang, Y. T.; Sun, C. P.; Shen, H. Y.; Chou, C. C.; Berger, H.; Lee, T. K.; Yang, H. D. *Phys. Rev. B* **2007**, *76*, 212504.
- (37) The most undisputed fact on the distorted structure of 2H-NbSe₂ is the presence of wave vectors at around $1/3a^*b^*$. The authors in Marezio, M.; Dernier, P. D.; Menth, A.; Hull, G. W. *J. Solid State Chem.* **1972**, *4* (3), 425–429 reported the structure solution of a two fold supercell. Most probably this is not the right phase related to the CDW distortion of 2H-NbSe₂.
- (38) Kadijk, F.; Jelinek, F. *J. Less-Common Met.* **1971**, *23*, 437.
- (39) Single crystals of 2H-NbSe₂ were grown by the chemical vapor transport technique. Pure elements of Nb (0.634 g) and Se (1.077 g) were loaded with a 1:2 ratio into a fused silica tube (13 mm in diameter and around 24 cm in length) together with a small amount of I₂ (0.048 g). The tube was flame sealed under vacuum ($<10^{-4}$ mbar) and placed in a dual zone furnace with a hot zone at 950 °C and a cold zone at 750 °C. The temperature was ramped in 1 d and the tube was soaked for 2 d at the target temperature. After 1 day of cooling time, single crystals of different sizes were formed on the cold side of the tube. Nonstoichiometric in the form of Nb_{1+x}Se₂ has been reported where the extra Nb atoms intercalate in the van der Waals gaps between the layers. We have verified the stoichiometric ratio in our 2H-NbSe₂ samples by measuring the superconducting transition (~ 7.2 K) using magnetic susceptibility. See Supporting Information for more details. Additionally, the 1:2 ratio is also supported by our single crystal refinement where no additional electron density in the van der Waals gap was found. A well diffracting hexagonal single crystal of approximate dimensions $20 \times 20 \times 1 \mu\text{m}^3$ was used for the X-ray diffraction experiment. The use of a high intensity synchrotron radiation source was necessary to collect the intensity of the extremely weak CDW-generated supercell reflections. Therefore, the data collection was performed at the 15-ChemMatCARS beamline of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). The small single crystal was glued at the end of a fine glass tip and mounted on the goniometer. A Bruker APEX II CCD detector was used and a wavelength of 0.41328 Å was chosen. A homemade open flow LHe cryostat was used to collect intensity data at 15 K. Two data sets were collected at 15 K because of the relative limited dynamic range of the CCD detector in order to collect intense enough reflections for both the main (subcell) and satellite reflections arising from CDW. A $360^\circ \varphi$ -scan with a step of 1° and exposure time of 0.5 s was used to collect intensity data of the subcell. A $360^\circ \varphi$ -scan with a step of 2° and exposure time of 14 s was used to collect intensity data of the satellite reflections. Data were integrated with a triclinic cell (SAINT; Bruker Bruker AXS, Inc., Madison, WI, 2007), scaled by using the intensities of common reflections present in both data sets, and merged into a single set by using Jana2006 (Petricek, V.; Dusek, M.; Palatinus, L. Jana2006: The crystallographic computing system; Institute of Physics: Praha, Czech Republic, 2006). Analytical absorption correction was performed by an integration method within Jana2006 with the aid of X-Shape2 (Stoe X-Shape2 within the X-Area package Darmstadt, Germany, 2010).
- (40) Spijkerman, A.; de Boer, J. L.; Meetsma, A.; Wiegers, G. A.; van Smaalen, S. *Phys. Rev. B* **1997**, *56*, 13757.
- (41) Wilson, J. A. J. *Phys. F: Met. Phys.* **1985**, *15*, 591.
- (42) Butz, T.; Saibene, S.; Lerf, A. J. *Phys. C: Solid State Phys.* **1986**, *19*, 2675.
- (43) Straub, T.; Finteis, T.; Claessen, R.; Steiner, P.; Hufner, S.; Blaha, P.; Oglesby, C. S.; Bucher, E. *Phys. Rev. Lett.* **1999**, *82*, 4504.
- (44) (a) Malliakas, C.; Billinge, S. J. L.; Kim, H. J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2005**, *127*, 6510. (b) Malliakas, C. D.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2006**, *128*, 12612. (c) Malliakas, C. D.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2007**, *129*, 10675. (d) Malliakas, C. D.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2009**, *131*, 6896. (e) Tomic, A.; Rak, Z.; Veazey, J. P.; Malliakas, C. D.; Mahanti, S. D.; Kanatzidis, M. G.; Tessmer, S. H. *Phys. Rev. B* **2009**, *79*, 085422.