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Crystal Structure of $(NbSe_4)_3I$ and $(NbSe_4)_{10/3}I$ CDW Compounds at 14 K

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Both $(NbSe_4)_3I$ and $(NbSe_4)_{10/3}I$ compounds are interesting system possessing quasi one-dimensional linear chain character and exhibiting nonlinear transport properties with a second order phase transition. The compounds are built of $NbSe_4$ antiprisms, stacked along the tetragonal c axis into chains in a screw-like arrangement. Performed X-ray low temperature single crystal diffraction measurements allowed to solve, refine and analyze crystal structures of both compounds at 14 K. While $(NbSe_4)_{10/3}I$ compound undergoes structural phase transition to monoclinic phase, $(NbSe_4)_3I$ remains in tetragonal symmetry. Iodine atoms are responsible for the differences in $(NbSe_4)_{10/3}I$ and $(NbSe_4)_3I$ structures causing different spacing in the infinite $NbSe_4$ chains.

1. Introduction

$(NbSe_4)_3I$ and $(NbSe_4)_{10/3}I$ compounds possess one-dimensional character and belong to family of the $(MX_4)_nY$ quasi one-dimensional (1D) linear chain compounds with M = Nb or Ta, X = S, Se or Te, Y = Cl, Br or I, and $n = 1, 2, 3$, or 10/3 [1, 2] with interesting physical properties. Both studied compounds are a semimetal at the room temperature and at lower temperatures transform into a semiconductor [3]. Both compounds exhibit nonlinear transport properties with a second order phase transition observed at 274 K for $(NbSe_4)_3I$ [4] and at 285 K for $(NbSe_4)_{10/3}I$ [5]. The $(NbSe_4)_3I$ compound crystallizes in $P4/mnc$ space group, while $(NbSe_4)_{10/3}I$ crystallizes in $P4/mcc$. Nevertheless, the structures of both compounds at room temperature are closely related. The compounds are formed of $NbSe_4$ antiprisms, aligned into chains along the tetragonal c axis in a screw-like arrangement. The iodine atoms are positioned in two types of channels running along the $[00z]$ and along the $[\frac{1}{2}\frac{1}{2}z]$ directions. The Se–Se rectangles are rotated clockwise and anticlockwise along the c axis. The differences between these structures are largely a result of a different iodine ordering. In $(NbSe_4)_3I$, the unit cell is composed of stack of 6 $NbSe_4$ antiprisms, while the unit cell of $(NbSe_4)_{10/3}I$ contains stack of 10 $NbSe_4$ units. In both studied compounds relative strong diffuse scattering is observed at (h, k) planes in the form of concentric diffuse rings. Such observations were explained by a model based on a mismatch between the infinite $NbSe_4$ chains with random shifts along the c direction [6].

In order to compare crystal structures of studied compounds single crystal X-ray diffraction measurements were performed at liquid He temperatures.

2. Experimental

$(NbSe_4)_3I$ and $(NbSe_4)_{10/3}I$ have been studied using X-ray and electron diffraction. Single crystals of both compounds were grown from the elements in evacuated quartz tubes at 923 K. Good quality single crystals were selected under a stereoscopic microscope and then glued to quartz glass capillary. Temperature X-ray diffraction measurements were carried out using Super-Nova four-circle X-ray diffractometer (Cu K_α/Mo K_α microsource) with Atlas CCD camera from Agilent Technologies. In the X-ray measurements crystals were cooled by a gas stream of cold dry nitrogen or helium using Oxford Cryosystem Cryostream 700 and HeliJet cooling attachments respectively, both providing temperature stability of 0.1 K. Data reduction was carried out using CrysAllis^{PRO} [7] software. The structures were solved by means of direct methods and refined with the SHELXS97 and SHELXL97 programs [8].

High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) studies were performed on high resolution JEOL JEM3010 electron microscope working at 300 kV equipped with 2k × 2k Orius 833 SC200D Gatan CCD camera. HRTEM and SAED experiments were performed on gently crushed crystals in agate martyr and then deposited on Cu-grids covered with thin layer of amorphous carbon. Crushed crystals were dispersed in ultrasonic bath in methanol for 1 h in order to ensure good sample spread on the TEM grid.

3. Results and discussion

Due to the fact that crystallization conditions of the various compounds of the $(NbSe_4)_nI$ series are similar, multiple phases with essentially identical morphology were synthesized in the same batch. The actual compound could only be unambiguously distinguished on

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the basis of diffraction experiment. Two types of crystals were selected with unit cell parameters at room-temperature (RT) equal to $a = b = 9.4644(6)$ Å and $c = 31.9063(19)$ Å, $V = 2859.3(3)$ Å^3 and $a = b = 9.4904(2)$ Å and $c = 19.1264(8)$ Å, $V = 1722.67(8)$ Å^3, good corresponding with literature [1] to $(NbSe_4)_{10/3}I$ and $(NbSe_4)_3I$, respectively. Analysis of single crystal X-ray diffraction measurements, performed at room temperature (RT) confirmed that the structure of $(NbSe_4)_{10/3}I$ belongs to the $P4/mcc$ space group (no. 124), whereas the $(NbSe_4)_3I$ compound belongs to the space group $P4/mnc$ (no. 128). Furthermore, X-ray diffraction showed strong diffuse scattering in form of strong diffuse streaking perpendicular to the $c*$ direction for both compounds.
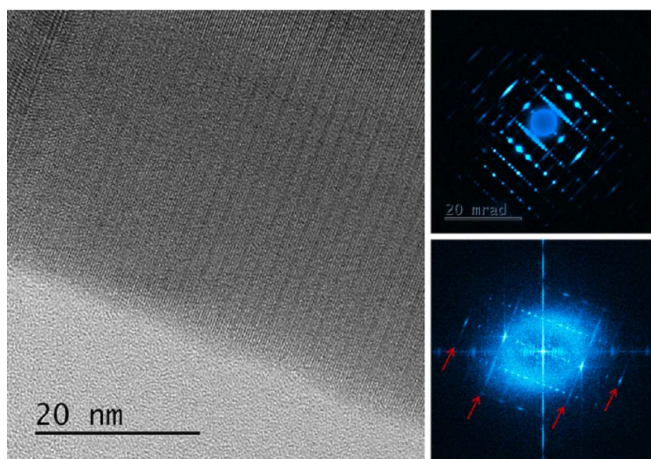

Fig. 1. The experimental HRTEM image of $(NbSe_4)_3I$, viewed along the [110] direction with the corresponding SAED and FFT patterns. The diffuse streaking perpendicular to the $c*$ direction is marked by arrows.

Performed transmission electron microscopy study also revealed structural mismatch (Fig. 1). Similar diffuse scattering features (strong diffuse streaking at $l = 6$) are visible on the selected area electron diffraction patterns. The Fourier transform calculated from the recorded high resolution transmission electron micrograph also shows corresponding diffuse scattering streaks. In the case of $(NbSe_4)_{10/3}I$ it has been shown [6] that the diffuse scattering at $l = 10n$ is associated with one-dimensional (1D) displacements of the $NbSe_4$ chains along the c axis.

Performed low temperature X-ray single crystal diffraction measurements at 14 K showed that $(NbSe_4)_3I$ compound still possesses tetragonal symmetry, but the symmetry is reduced from $P4/mnc$ (no. 128) above 274 K through $P\bar{4}2_1c$ (no. 114) at intermediate phase to the final $P\bar{4}$ space group (no. 81) at low temperature phase. The crystal structure is with good accordance with the one already published for this compound measured at 30 K [9]. Lattice parameter at 14 K were determined as follows to $a = b = 9.4203(1)$ Å and $c = 19.0655(3)$ Å, $V = 1691.91(4)$ Å^3.
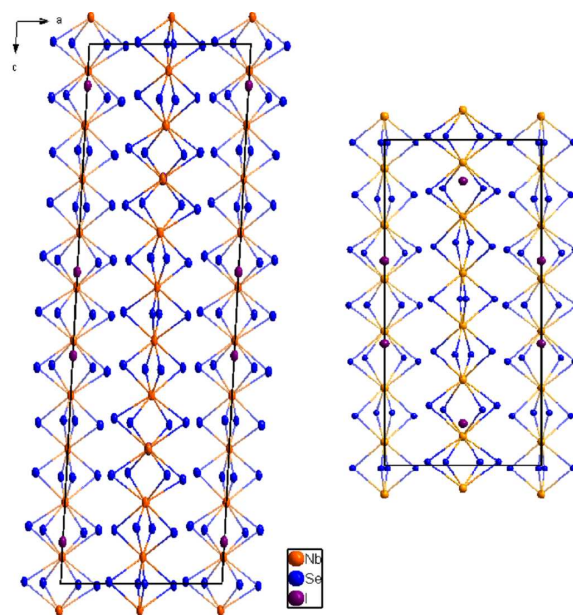

Fig. 2. Projection of the $(NbSe_4)_{10/3}I$ structure (left) and $(NbSe_4)_3I$ structure (right) along b direction both solved at 14 K.
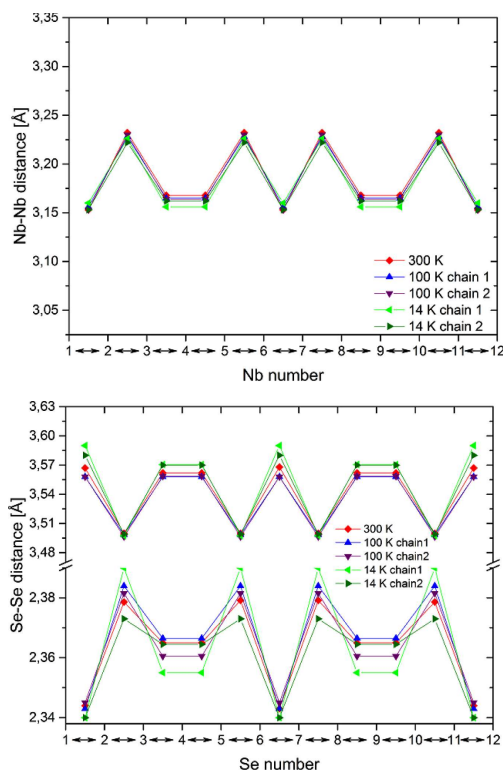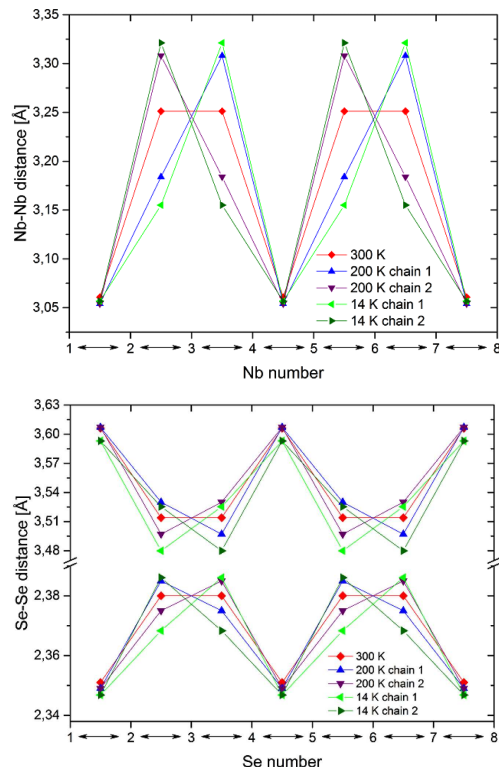
On the other hand, during cooling $(NbSe_4)_{10/3}I$ compound undergoes structural phase transition to monoclinic symmetry, which is accompanied with fourfold twinning. Performed low temperature X-ray single crystal diffraction measurements at 14 K showed that the space group $P2/c$ (no. 13) remains unchanged. The lattice parameters of the low temperature phase at 14 K were determined as follows to $a = 9.4375(2)$ Å, $b = 9.4250(2)$ Å, $c = 31.8440(6)$ Å, and $\beta = 93.041(2)°$, $V = 1691.91(4)$ Å^3. For both compounds diffuse scattering was not observed at 14 K. The detailed information regarding structure refinements are gathered in Table I.

The structure of $(NbSe_4)_{10/3}I$ is built of the Nb atoms assembled into Nb_2 and Nb_3 sections with variable Nb–Nb distances. Selenium atoms create cages correlating with the Nb groups (Fig. 2 and Fig. 3). The structures of the high temperature — tetragonal phase and low temperature — monoclinic phase are similar (Fig. 3), except for the slight deformations of the coordination polyhedra in the monoclinic phase. During cooling the deformation of the Se_4 rectangles takes place — they are slightly tilted and not any more perpendicular to the c-axis. The Nb–Nb distances do not change drastically and the structure conserves Nb_2 and Nb_3 assembles. Also the iodine atoms remain on the same positions in the unit cell occupying channels along c direction between $NbSe_4$ chains. Due to symmetry reduction in low temperature phase two adjacent $NbSe_4$ chains became symmetrically independent. Nevertheless, both chains do not differ strongly — the Nb–Nb distances and Nb arrangement remains nearly unchanged. The main differences is visible on the Se–Se rectangles that became more deformed.

TABLE I

Structure refinement details for $(NbSe_4)_3I$ and $(NbSe_4)_{10/3}I$ at 14 K.

Compound name	$(NbSe_4)_3I$	$(NbSe_4)_{10/3}I$
chemical formula	$I_2Nb_6Se_{24}$	$I_3Nb_{10}Se_{40}$
formula mass	2706.30	4468.20
crystal system	tetragonal	monoclinic
a [Å]	9.4203(1)	9.4375(2)
b [Å]	9.4203(1)	9.4250(2)
c [Å]	19.0655(3)	31.8440(6)
α [°]	90	90
β [°]	90	93.041(2)
γ [°]	90	90
unit cell volume [Å]³	1691.91(4)	2828.49(10)
Temperature [K]	14	14
space group	$P\bar{4}$	$P2/c$
formula units per unit cell, Z	2	2
radiation type	$Mo_{K\alpha}$	$Cu_{K\alpha}$
absorption coefficient, μ [mm⁻¹]	29.609	58.342
no. of reflections measured	15679	4357
no. of independent reflections	9214	4357
final r_1 values $(i > 2\sigma(i))$	0.0528	0.1182
final $wR(F^2)$ values $(i > 2\sigma(i))$	0.1210	0.5083
final r_1 values (all data)	0.0729	0.1184
final $wR(F^2)$ values (all data)	0.1324	0.5200
goodness of fit on F^2	1.078	3.059

Fig. 4. $(NbSe_4)_3I$ — comparison of Nb–Nb (left) and Se–Se (right) distances at 300, 200, and 14 K indicating formation of the Nb_2–Nb–Nb–Nb_2 chains.

The structure of $(NbSe_4)_3I$ compound is built of the Nb atoms assembled into Nb_2–Nb–Nb–Nb_2 chains (Fig. 4). As in the related $(NbSe_4)_{10/3}I$ structure, selenium atom create rectangles bonding two adjacent niobium atoms. The intermediate and low temperatures structures differs from the high temperature one quite strongly. The high temperature space group is centrosymmetric, while the intermediate and low temperature one are noncentrosymmetric. First of all, the Nb_2–Nb–Nb–Nb_2 sequence is violated. One of the two separated niobium atom approaches the Nb_2 group and increases distance to the other single Nb atom. Assembly of niobium atoms changes into group of three Nb atoms with increased distance between neighbouring Nb_3 groups. The selenium atom also correlates with the Nb atoms increasing deformation of the Se rectangles. Two adjacent $NbSe_4$ chains are related by the $\bar{4}$ symmetry operator. Due to that sequence of Nb distances along c axis in two adjacent chains is reversed. The iodine atoms remain on the same positions in all phases occupying channels along c direction between $NbSe_4$ chains.

Fig. 3. $(NbSe_4)_{10/3}I$ — comparison of Nb–Nb (left) and Se–Se (right) distances at 300, 100, and 14 K indicating formation of the Nb_2–Nb_3 chains.

4. Conclusions

Structural analysis of the low temperature (at 14 K) phases of $(NbSe_4)_{10/3}I$ and $(NbSe_4)_3I$ compounds was performed. Both structures were refined for the first time at such low temperature. Measurements confirmed

that $(NbSe_4)_3I$ compound possesses $P\bar{4}$ space group. The structural analysis performed for the $(NbSe_4)_{10/3}I$ at helium temperatures showed that studied compound remains in $P2/c$ space group. For both compound diffuse scattering was not observed at 14 K.

The crystal structure of $(NbSe_4)_{10/3}I$ changes only slightly with the phase transition, whereas $(NbSe_4)_3I$ structure exhibits more significant differences. Especially the Nb atom group and the adjacent $NbSe_4$ chains are reversed in different manner.

Iodine atoms are responsible for the differences in $(NbSe_4)_{10/3}I$ and $(NbSe_4)_3I$ structures. The main features of both structures are familiar but the most significant differences are the amount of I atoms causing different spacing in the infinite $NbSe_4$ chains. At room temperature in both structures iodine atoms exhibit disorder along c direction, whereas at 14 K iodine atoms are localized.

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